Leaching of copper, chromium and arsenic from treated vineyard posts in Marlborough, New Zealand

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Abstract

There have been conflicting reports as to the extent that copper–chromium–arsenic (CCA) treatments leach from timber. In New Zealand, vineyards utilise CCA-treated posts at a rate of 579 posts per hectare. This represents a potential CCA burden on the soil of 12, 21, and 17 kg/ha, respectively, for the three elements. Given a replacement rate of 4\% per year, the use of CCA-treated posts may result in an accumulation of these elements in the soil, possibly leading to groundwater contamination. We undertook a general survey to determine the extent of CCA leaching from treated vineyard posts. Treated \textit{Pinus radiata} posts were sampled at six sites around the Marlborough region of New Zealand to represent a range of post ages and soil types. For each post, above- and belowground wood samples were taken. As well, the soil adjacent to the post was sampled at a 50 mm horizontal and 100 mm vertical distances from the post. The belowground wood samples of the posts had significantly lower CCA concentrations than the aboveground portions, which were not significantly different from new posts. This indicates leaching. Soils surrounding the posts had significantly higher CCA concentrations than control soils. Higher CCA concentrations were measured under the posts than laterally. Some 25\% of the samples exceeded 100 mg/kg As, the Australian National Environment Protection Council (ANEPC) guideline level for As in agricultural soil, and 10\% exceeded 100 mg/kg Cr, the ANEPC limit for chromium. At one site, we found a significant positive correlation between post age and CCA-leaching. The CCA issue could be eliminated by using alternative posts, such as steel, concrete, or untreated woods such as \textit{Eucalyptus} or beech. Alternatively, CCA-treated posts could, for example, be lacquered or otherwise protected, to reduce the rate of CCA leaching.

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1. Introduction

1.1. Leaching from copper–chromium–arsenic (CCA) treated timber

There is evidence from several studies that under certain conditions, copper–chromium–arsenic treatment (CCA) leaches out of treated timber into the soil and receiving water environments (Archer and Preston, 1994; Hingston et al., 2001; Stilwell and Graetz, 2001; Schultz et al., 2002; Chirenje et al., 2003; Zagury et al., 2003). Schultz et al. (2002) showed that after 5 to 6 years, 24% of the CCA treatment in stakes of southern yellow pine had leached into the surrounding soil. Zagury et al. (2003) found soil Cu, Cr and As concentrations adjacent to treated posts up to 1460, 287, and 410 mg/kg, respectively. After 85 months of exposure in a marine environment, some 50% of Cu had leached from pine timber in the study by Archer and Preston (1994).

1.2. Soil contamination resulting from CCA treated timber

In the United States of America, the use and disposal of CCA-treated timber has resulted in large amounts of As in many residential soils, as well as in landfills from disposal of treated wood (Bleiwas, 2000). According to the US Environmental Protection Agency (US EPA, 2002), “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.” Soil conditions, especially pH, organic matter, and clay content, and type play an important role in leaching of CCA out of the post and its subsequent movement through soil (Carey et al., 1996b; Hingston et al., 2001). Zagury et al. (2003) showed soil-contaminant levels were more strongly correlated with soil type rather than the age of pole. Crawford et al. (2002) found that the soil’s percent base saturation and pH were the most important factors controlling the rate of Cu loss from treated posts while the rate of As loss was a function of the soil’s Cu content, exchangeable K, and silt fraction.

Studies on treated posts have shown that soil CCA concentrations decreased rapidly with increasing distance from the post (Zagury et al., 2003), especially for Cu and Cr, whereas As is more mobile. Copper and Cr concentrations approached background levels 50 mm away radially, whereas As has been found 500 mm out from posts and to a depth of 1 m below (Zagury et al., 2003). Allinson et al. (2000) reported that once in soil, the Cu component of CCA is arrested by exchange with the soil, even in sandy soils. Nonetheless, an absence of CCA in the soil surrounding treated posts does not necessarily indicate that CCA is not coming out of the post. The absence of metals may be due to prior leaching. Henningsson and Carlsson (1984) demonstrated As mobility in a children’s sand pit. They found that some 20–25% of As had leached from the treated wood used in the sandpit’s construction, yet the sand adjacent to the wood contained just 4–6 mg/kg, close to background levels of As.

Nurmi (1990) found an average of 21% to 25% of the As that was originally in 10-year old treated power poles in Finland had leached out. The soil surrounding the posts contained up to 420 mg/kg As, with an average concentration of 180 mg/kg. However, Huffman and Morrell (2003) reported only negligible concentrations of CCA (<10 mg/kg As) in soils surrounding treated posts in Florida soils. They concluded “…most of the original As is fixed, bound to the wood and poses few risks to humans and the environment.” Lebow et al. (2004) pointed out the extent of conflicting reports on CCA leaching from treated timber. These differences were attributed to environmental variables.

1.3. Rate of CCA leaching from treated timber

During treatment, end-grain penetration of CCA is many times greater than lateral penetration. In reverse, this may greatly influence the leaching rate back out (Morgan and Purslow, 1973). Archer and Preston (1994) demonstrated this by showing that CCA leaching was 40 times greater out of the end of the post than the sides. This would indicate that the greatest concentrations should be found under the post. The release of CCA from the bottom of the post has less soil to pass through before reaching groundwater. Moreover, compared to surface soil, soils beneath the post contain less organic matter that would otherwise retard the passage of CCA. In some locales, the bottom of the post may even be periodically immersed in groundwater.
Furthermore, if the post is dipping intermittently into groundwater, then convective flow of water, the vehicle for CCA transport, between the wood and the soil could greatly increase any leaching (Hingston et al., 2001). Crawford et al. (2002) found, in their soils, that Cu loss from treated posts was equal or greater to As loss. However, in water, the rate of As loss was approximately twice that of Cu. In the aquatic environment, Cu is particularly toxic to organisms (Brooks, 1996) and may pose a greater environmental risk than As, even though the latter leaches from timber at a higher rate.

### 1.4. Environmental risks associated with CCA-contaminated soil

The leaching of CCA from treated posts into soil is of concern because, depending on its extent, it may reduce soil fertility, contaminate groundwater, and present a human health hazard if land use changes occur and new exposure pathways develop. If Cu, Cr, and As are released from treated posts, they may remain in the soil for a long time. All three elements are found naturally in New Zealand soils, usually at low concentrations. For example, As concentrations in natural soils seldom exceed 10 mg/kg (Adriano, 2001). The abundance of As in the Earth’s crust is only 1.8 mg/kg (Mason and Moore, 1982). Arsenic can also occur naturally at elevated levels in ground and surface waters in New Zealand (Aggett and Aspell, 1978).

Arsenic is a nonessential element. Chromium is an essential micronutrient for animals, while Cu is essential for both plants and animals (Salisbury and Ross, 1992). At elevated concentrations, all three elements are toxic (McLaren and Cameron, 1996).

Past and present pesticide use can contribute to Cu and As in horticultural soils (Merry et al., 1983; Peryea and Creger, 1994). Copper-based fungicides are used commonly on vineyards. Historically, As-based pesticides were used extensively to control insect pests on orchards and as a biocide in sheep dips, a practice that has left an estimated 50,000 locally contaminated sites throughout New Zealand (McBride et al., 1998; McLaren et al., 1998).

In soil, As is the most bio-available of the three elements. Unfortunately, it is also the most toxic to humans (Read, 2003). Nonetheless, Belluck et al. (2003) reported that there have been no cases of morbidity or mortality from exposure to either anthropogenic or natural elevated soil As levels. It is, however, a concern in groundwaters worldwide, especially in South East Asia, where it occurs naturally.

In general, the accumulation of As into the edible parts of most plants is low (O’Neill, 1995). Stem, leaf, and fruit tissue of grapes growing adjacent to CCA-treated posts was analysed by Levi et al. (1974). Levels of Cr and As were below the detection limit of 0.2 and 0.05 mg/kg, respectively. Copper levels were between 4.7 and 11.6 mg/kg, well within the normal range found in plant tissues. It would thus appear that the risk of grapes accumulating CCA from adjacent posts is low.

### 1.5. CCA treated posts in New Zealand vineyards

Bourne (2003) expressed concern over the possibility of CCA leaching from vineyard posts across the nearly 10,000 ha of vineyards throughout the Marlborough region, New Zealand. Most vineyard posts have received an “H4” treatment that protects the pine against decay when in contact with soil. This results in a wood concentration of Cu, Cr and As of 1730, 3040, 2710 mg/kg, 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 Cu, Cr and As loading of 12, 21, and 17 kg, respectively. Anecdotal evidence indicates that the posts are replaced at a rate of 4% per year, indicating that, if leaching from posts occurs, soil CCA contamination could 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, in aerobic conditions, dichromate [Cr(VI)] is rapidly reduced to Cr(III), which is less toxic and less mobile than any of the other components of CCA (Kerndorff and Schnitzer, 1980).

The aim of this study was to determine, through a general survey, the extent of any leaching from CCA-treated Pinus radiata posts in Marlborough vineyards. Particular emphasis was given to vineyards in the Rarangi region (site [6]) where the groundwater level periodically rises above the bottom of the
posts. Typically, these soils are sandy gravels with low organic matter content.

### 2. Materials and methods

Six sites were selected to represent a range of post ages and soil types from around the Marlborough region (Table 1). In November 2003, three classes of *Pinus radiata* posts (quarter round, half round, and full round) were sampled. All posts had been rammed into the ground to a depth of approximately 600 mm. At site (6), an area where shallow groundwater intermittently bathes the bottoms on the posts, 1 to 3-year-old posts were sampled to determine the rate of CCA leaching. Posts were levered out of the ground. Care was taken to cause minimal soil disturbance around each post. For each class of posts, three replicates were taken.

For each post, five soil samples of at least 200 g dry weight and two wood samples were taken (Fig. 1). Soil samples adjacent (0–10 mm) to the post, (A), and at 50–60 mm horizontal distance, (B), were collected by scraping soil from the side of the post-hole using a 440 mL steel can. Soil samples immediately beneath (0–10 mm) the post, (C) and 100–110 mm vertical distance (D), were collected using a soil auger. As a reference, soil from the inter-row, (E), was collected after the surface litter and any vegetation was removed. At site (6), an additional sample was taken between the rows to determine the effect that drip irrigation might have had on the metal concentrations. Subsequently, we found that there were no significant differences between the samples underneath the vines, and those taken from between the rows, so only the former are reported here.

Approximately 20 g (dry weight) samples of wood were removed from both the above- and belowground portions of the post using a chisel. For the half-round and quarter-round posts, wood was removed to 15 mm deep at the intersection between the flat face and the circumference. An additional six samples were taken from new posts at site (2) where they were stored in dry conditions awaiting installation.

### Table 1

<table>
<thead>
<tr>
<th>Site number</th>
<th>Soil type</th>
<th>pH</th>
<th>Year of post installation</th>
<th>Type of post</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Shallow and loamy silt loam</td>
<td>6.4</td>
<td>1988</td>
<td>Half rounds</td>
</tr>
<tr>
<td>2</td>
<td>Loamy and sandy alluvium</td>
<td>NA*</td>
<td>2001</td>
<td>Quarter rounds</td>
</tr>
<tr>
<td>3</td>
<td>Deep silt loam</td>
<td>6.2</td>
<td>1983</td>
<td>Full rounds</td>
</tr>
<tr>
<td>4</td>
<td>Clay loam</td>
<td>6.1</td>
<td>2002</td>
<td>Half rounds</td>
</tr>
<tr>
<td>5</td>
<td>Deep silt loam (poorly drained)</td>
<td>6.1</td>
<td>2001</td>
<td>Quarter rounds</td>
</tr>
<tr>
<td>6</td>
<td>Very shallow silt loam overlying</td>
<td>NA*</td>
<td>2000</td>
<td>Half rounds</td>
</tr>
</tbody>
</table>

For each location and post type, three replicates were chosen.

* Not available.

![Fig. 1. Locations of soil and wood samples taken from around each post.](image-url)
We therefore consider there to have been no CCA leaching from these posts.

The samples were analysed at a commercial laboratory (Hill Laboratories, Hamilton, New Zealand) for dry-weight determinations of Cu, Cr, and As using the US EPA method 200.2 (US EPA, 1994) for total recoverable metals. The digestion uses nitric and hydrochloric acids to dissolve sieved soil samples. It does not destroy the silica matrix nor does it fully extract strongly bound interstitially held metals. Digests were analysed using inductively coupled plasma emission spectroscopy (ICPES).

All statistical analyses were performed using Minitab (Minitab Inc., Pennsylvania State University). Means were compared using analysis-of-variance (ANOVA) technique, and significant differences were determined using Fisher’s Test with a 95% confidence interval.

3. Results and discussion

3.1. General overview of CCA leaching from vineyard posts in Marlborough

For all posts tested, the average CCA concentrations in the control soil and soils surrounding the treated posts are shown in Fig. 2 (I). The soils surrounding the posts had significantly higher CCA concentrations, (A to D), than the control soil (E). Soil directly beneath the posts (C) had the highest CCA concentration, followed by soil immediately adjacent (A). Soils at 50 mm from the side of the post (B) and at 100 mm beneath the post (D) were significantly lower than directly adjacent soils. They were all, however, still significantly higher than the controls. The average soil CCA concentrations in our study are consistent with the findings of Hingston et al. (2001), Chirenje et al. (2003) and Zagury et al. (2003).

Fig. 2 (II) shows the CCA concentrations in new posts, and the average of all the aboveground and belowground samples that were taken from posts of various ages. The belowground samples in the wood were significantly lower than the aboveground samples in the wood, and the new post levels. The change in wood concentrations in Fig. 2 (II) confirms that CCA is leaching out of vineyard posts. However, there were no significant differences between the new posts and the aboveground samples. Leaching from the aboveground portions appears minimal. This is in contrast to the findings of Cooper and Ung (1997), who reported significant leaching from the aboveground portions of utility poles. Here, the surface soils around the posts had an additional CCA burden due to rainwater dripage and runoff from the pole.

Soil samples from several sites contained more than 100 mg/kg As, which is the guideline value of the Australian National Environmental Protection Council (ANEPC), for agricultural soils. Across all sites, 25% of the samples were above the ANEPC guidelines for As, and 10% of the samples were above ANEPC guidelines for Cr (100 mg/kg). None of the Cu values exceeded ANEPC guidelines (1000 mg/kg). However, 33 samples were above 200 mg/kg, a level shown to cause plant toxicity in other studies (Thayalakumaran et al., 2003).

Zagury et al. (2003) showed that soil contaminant levels were more strongly correlated with soil type than pole age. They found that more leaching occurred in low-organic matter and low-clay content soils. Lebow et al. (2004) showed that the amount of CCA that leaches from vineyard posts is dependent on a range of environmental variables. The rate of CCA leaching is also dependent on the pole geometry as well as the treatment processes. All poles in this study had undergone a standard “H4” treatment, however, we were unable to determine the exact treatment process for each class of poles.

Therefore, when considering the relationship between one variable and CCA leaching, no significant correlation might be found from a general survey because of the confounding influence of other variables. In our regional study, across all sites tested, there was no significant correlation between post age and the CCA concentration in the surrounding soil. Nevertheless, a significant positive correlation was found between post age and soil CCA concentration on a single soil type, site (6) (Fig. 3). This seems to relate specifically to the conditions at site (6), which would merit closer scrutiny, possibly as a result of the shallow groundwater.

3.2. CCA leaching in shallow-groundwater areas

Fig. 3 (I–III) shows the CCA concentrations in soils surrounding posts at this site (6). The distribution
of CCA around the post here is similar to all the posts sampled elsewhere (Fig. 2 I), with the highest CCA concentrations occurring beneath the post. At site (6), three ages of posts were selected on the same soil type. The soil CCA concentrations show an increase with post age in the ground. This is consistent with the hypothesis that CCA is leaching out of the posts over time. It is interesting to note that at site (6) there is less lateral movement of CCA. At 50 mm away from the post, (B), the CCA levels are reduced, although still significantly greater than the controls (E). However, there is a larger vertical movement. At 100 mm beneath the posts, As levels are still approaching the ANEPC limit of 100 mg/kg.

Fig. 3 also shows a significant difference in the soil CCA concentrations between the posts installed in 2000 compared to those installed in 2001. This indicates that CCA leaching is still occurring some three years after installation.

Fig. 4 shows the CCA concentrations in the wood of the posts from vineyards at site (6). Here we calculate the recovery of CCA in the soil surrounding the posts at site (6) that were installed in 2000. If we assume that all posts had the same initial CCA concentration, then the apparent loss of CCA may be
Fig. 3. Soil As (I), Cr (II), and Cu (III) from vineyard posts at site (6), a shallow groundwater area. The locations of ‘A’ to ‘E’ are shown in Fig. 1. Bars represent the standard error of the mean ($n=3$). The dashed line is the ANEPC guideline for As in soil.
estimated as the difference between the posts installed in 2003, some 3 months before sampling, and those installed in 2000. The posts were half-rounds, weighing approximately 12 kg of dry-mass, of which 23% (2.8 kg) of the post was buried in the soil, so the concentration change of 511 mg/kg (Fig. 4).
implies that 1.43 g of As was lost from the wood.

From average concentrations measured in the soil around posts at site (6) that were installed in 2000 (Fig. 3I), we found concentrations of 76 mg/kg close to the post at (A), and 23 mg/kg at 50 mm horizontal distance (B). Below the post, at (C) and (D), the As concentrations were 177 and 92 mg/kg. We calculated the soil volume represented by sampling locations A–D to be 19.3 L. This was done by subtracting the volume of the buried portion of the post (15.1 L) from the volume represented by a cylinder with a radius of 125 mm and a depth of 70 mm (34.4 L). Considering a background of 3.6 mg/kg, measured at location (E), and a bulk density of 1.2, then mass balance reveals that we have recovered 1.323 g of As. This represents 93% of the “missing” As.

Applying the same calculations to Cr and Cu, we find recoveries of 30% and 80% in the same soil volume. The low recovery of Cr does not necessarily indicate that this element has leached more than As and Cu. The apparently “missing” Cr may have been due to soil heterogeneity or an incomplete extraction of Cr during the sample digestion procedure. Previous reports indicate that Cr (III) is the least mobile of the CCA components (Archer and Preston, 1994; Cooper and Ung, 1997; Zagury et al., 2003). Any leaching from the aboveground portions of the posts would increase levels of CCA in surface soils as well as alter the ratios of Cu, Cr, and As (Cooper and Ung, 1997). Cooper et al. (2001) showed how this disproportional effect could confound mass balance calculations. This effect may also have been present in our study.

3.3. Impacts from CCA leaching from treated posts in vineyards in the Marlborough region

The results from our general survey indicate that CCA leaches from treated posts over time. As the average post life is expected to be 25 years, and around 4% of the posts are replaced annually, the use of treated posts could lead to a gradual accumulation of CCA in the soil. Further, there could be movement of As away from the posts. CCA levels might eventually accumulate locally around the post to concentrations above threshold values. The rate of accumulation is, nonetheless, likely to be low.

For soils where groundwater does not come into contact with the posts, there seems a low environmental risk posed by the use of CCA treated timber. Previous studies (O’Neill, 1995) indicate that uptake of CCA into the grapes is unlikely.

The possibility of CCA reaching groundwater from treated posts at site (6) cannot be discounted. This study has shown that CCA-leaching from posts has occurred in a three-year period. Previous studies (Hingston et al., 2001) have shown that the contact of posts with groundwater greatly increases leaching. Further testing could include measuring CCA at various distances from the posts and the determination of the soil’s capacity to retard CCA movement.

There could be several low-cost means of reducing/eliminating CCA from new or replacement posts. Changing the ratios of Cu, Cr, and As in the treatment fluid or lowering the total amount of CCA that is impregnated into the posts may decrease the rate of CCA leaching. Lebow et al. (2004) found that wood with a lower CCA concentration might have greater leaching due to lower concentration of Cr that fixes the preservative in the wood. However, this effect was only relevant at low CCA concentrations in timbers intended for aboveground use.

Lacquering CCA-treated posts has been demonstrated as an inexpensive way of reducing CCA leaching from treated timber (Lebow and Evans, 1999). However, it is unclear how much of the lacquer will be removed when the post is rammed into the ground. Alternatively, soil amendments, such as lime or bentonite may immobilise any CCA that has leached out of the post.

Posts made from steel, or untreated timbers such as Eucalyptus or beech will clearly not leach CCA. However, galvanised steel posts may contribute Zn and Cu to the soil. Beder (2003) reports that if alternatives to CCA-treated timber were used more often, their price would probably fall.

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