Arsenic in the New Zealand environment

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Abstract

In New Zealand, elevated levels of arsenic in soils and waters occur as a result of geothermal activity, exacerbated by geothermal power exploitation, and the past and present use of arsenic-based pesticides. Some lakes and rivers in the Taupo Volcanic Zone have arsenic concentrations above the World Health Organisation’s (WHO) limit for arsenic in drinking water (0.01 mg/L). Aquatic plants from this region accumulate inordinate amounts of As, in some cases to more than 1000 mg/kg on a dry weight basis, the threshold for arsenic hyperaccumulation. At least one of these species, watercress (Rorippa nasturtium-aquaticum), is consumed by humans. Other aquatic plants may be periodically consumed by stock that have access to waterways. Ground and surface water used for irrigation may lead to accumulation of arsenic in agricultural soils.

Historical use of arsenic based pesticides in sheep-dips has resulted in an estimated 50,000 sites contaminated with arsenic and persistent organic pollutants such as dieldrin. Urbanisation of agricultural land has resulted in the belated discovery of arsenic-contaminated residential soils. As well, past pesticide practices in agriculture and horticulture employed arsenic-based compounds. Recent sampling of previously productive soils has uncovered high levels of arsenic in some soils.

Soils associated with the production and use of Copper-Chromium-Arsenic (CCA) treated timber also exhibit elevated arsenic concentrations. Wood-waste and timber-treatment sites often contain arsenic hot spots that present a risk to groundwater. The extensive use of CCA-treated posts in agricultural and horticultural systems might lead to the long-term arsenic contamination of New Zealand’s productive soils.

This paper discusses, using case studies, the extent of arsenic contamination in the New Zealand environment, as well as possible exposure pathways to humans, and options for remediation.

Sources of arsenic in the New Zealand environment

The toxic element arsenic is widespread in New Zealand’s aquatic and terrestrial environments. Elevated concentrations of arsenic in ecosystems result from both geogenic and anthropogenic sources. Arsenic is ubiquitous in all of the geothermal areas and waterways that fall within or pass-through the Taupo Volcanic Zone (TVZ), an area in the central North Island that stretches from Mt Ruapehu to White Island (Figure 1). On its way to the surface, super-heated geothermal water dissolves appreciable amounts of arsenic from the surrounding volcanic rock. Aggett and Aspell (1978) have reported that in some lakes and rivers of the TVZ, arsenic concentrations often exceed 0.01 mg/L, the recommended maximum concentration for arsenic in drinking water set by the World Health Organisation (WHO) and the New Zealand Drinking Water Standard (NZDWS). The arsenic loading in surface waters is exacerbated by the commercial exploitation of geothermal power (Axtmann 1975).

Arsenic levels in New Zealand’s longest river, the Waikato, seldom fall below the New Zealand drinking water standard of 0.01 mg/L (Robinson et al. 1995).
Human activity has also resulted in innumerable arsenic-contaminated sites. Arsenic is used as a timber preservative in a copper-chromium-arsenic (CCA) cocktail. Consequently many sites associated with the timber industry or where treated timber is used, are contaminated with arsenic. Timber treatment effluent is considered to be the major source of arsenic-contamination in aquatic and terrestrial environments (Bolan and Thiyagarajan 2001). Contaminated sites range from treatment sites to dump sites to children’s playgrounds where treated timber has been used for construction.

There is evidence from several studies that CCA leaches out of treated timber into surrounding soil (Stilwell and Graetz 2001; Schultz et al. 2002; Chirenje et al. 2003; Zagury et al. 2003) or water (Archer and Preston 1994; Hingston et al. 2001). Schultz et al. (2002) showed that after 5-6 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.

Arsenic is present in many pesticides, herbicides and fertilizers. Historically, extensive use of the horticultural pesticides, lead arsenate (PbAsO₄), calcium arsenate (CaAsO₄), magnesium arsenate (MgAsO₄), zinc arsenate (ZnAsO₄), zinc arsenite [Zn(AsO₂)₂] and Paris Green [Cu(CH₃COO)₂·3Cu(AsO₂)₂] in orchards has contributed to soil arsenic contamination (Merry et al. 1983; Peryea and Creger 1994). The use of sodium arsenite (NaAsO₂) to control aquatic weeds has also contributed to the arsenic burden of some New Zealand lakes (Tanner and Clayton 1990).

Soil arsenic contamination has also been reported due to the extensive use of arsenical pesticides in sheep and cattle dips to control ticks, fleas and lice (McBride et al. 1998; McLaren et al. 1998). While an effective means of controlling skin parasites, this practice resulted in an estimated 20,000 contaminated sites nationwide. Arsenic concentrations in the surface soil (0-10 cm) of historical sheep dip sites can range between 37-3542 mg/kg, with up to 2282 mg/kg occurring at 20-40 cm depth (McLaren et al. 1998).

Lesser sources of arsenic contamination in New Zealand originate from coal ash disposal, and the mining industry (Nriagu and Pacyna 1988; Eisler 2004). Arsenic trioxide (As₂O₃) is extensively used in the manufacturing of ceramic and glass, electronics, pigments and antifouling agents, cosmetics, fireworks and Cu-based alloys (Leonard 1991). Coal combustion not only releases gaseous arsenic into the atmosphere but also generates fly and bottom ash containing varied amounts of arsenic. Disposal of these materials often leads to arsenic- contamination of soil and water (Beretka and Nelson 1994).
Continuous application of fertilisers that contain trace levels of arsenic also results in arsenic-contamination of soil, thereby reaching the food chain through plant uptake (McLaughlin et al. 1996).

Uptake of arsenic by aquatic macrophytes

A survey of aquatic and terrestrial plant as well as waters and sediments from the Taupo Volcanic Zone (TVZ) and Waikato river was undertaken in April 2003. The average arsenic concentrations in the soils, sediments, waters, as well as aquatic and terrestrial plants collected from the TVZ are presented in Table 1. The geometric mean arsenic concentration in the water samples was over twice that of the New Zealand Drinking Water Standard (0.01 mg/L). There was a clear demarcation between terrestrial plants, that accumulated negligible concentrations of arsenic, and aquatic species that had arsenic concentrations many fold higher than the ambient waters whence they were taken.

Table 1. The geometric means and standard deviation ranges of the arsenic concentrations waters (mg/L), as well as soils, sediments, aquatic and terrestrial plants (mg/kg dry matter) from the TVZ.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>No. of samples</th>
<th>Geomean [As] and S.D. range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soils</td>
<td>4</td>
<td>50 (33 – 79)</td>
</tr>
<tr>
<td>Geothermal sediments</td>
<td>10</td>
<td>895 (135 – 1470)</td>
</tr>
<tr>
<td>Terrestrial plants</td>
<td>36</td>
<td>&lt;0.5 (30 samples) – 11</td>
</tr>
<tr>
<td>Waters</td>
<td>23</td>
<td>0.021 (0.005 – 0.078)</td>
</tr>
<tr>
<td>Aquatic plants</td>
<td>184</td>
<td>125 (12 – 1222)</td>
</tr>
</tbody>
</table>

Many species of aquatic plants had arsenic concentrations in excess of 1000 mg/kg on a dry matter basis, the threshold for hyperaccumulation (Brooks et al. 1977). By contrast, 83% of the terrestrial plants were below detection limits for arsenic (<0.5 mg/kg). All the aquatic plants tested accumulated arsenic to concentrations greater than 5 mg/kg on a dry matter basis, and none of the terrestrial plants tested had arsenic concentrations surpassing 11 mg/kg.

Sixteen different species of aquatic plants were tested, and all of them accumulated higher concentration of arsenic than the terrestrial plants. Algae (unidentified species) growing in the water of Tokaanu had the highest concentration of arsenic: between 1252 – 9632 mg/kg dry matter. Specimens of numerous other species were found to accumulate more than 1000 mg/kg arsenic. Most specimens of *Myriophyllum propinquum* (geo-mean 2101, s.d.-range 873 - 5056 mg/kg) were over the 1000 mg/kg threshold. There have been no previous reports of arsenic hyperaccumulation by this species.

Previous studies of aquatic plants from the TVZ (Liddle 1982; Robinson et al. 1995; Brooks and Robinson 1998) focused on four species: *Ceratophyllum demersum*, *Egeria densa*, *Lagarosiphon major* and *Rorippa nasturtium-aquaticum*. These previous studies reported average arsenic concentrations in *C. demersum*, *E. densa*, *L. major* and *R. nasturtium*, of 400, 500, 300, 400 mg/kg, respectively. Although sampled at different locations, the results in this study were in good agreement, being 284, 568, 127, and 369 mg/kg respectively. The most abundant species in terms of biomass in the Waikato River are *C. demersum*, *E. densa* and *L. major*. These species were also found to have the highest arsenic concentrations.

The present study also determined arsenic levels in several species that had not previously been analysed. It was found that *M. propinquum*, *E. canadensis* and a hot water alga from Tokaanu all accumulated arsenic to levels greater than 1000 mg/kg, the threshold for arsenic hyperaccumulation. Additionally, *Callitriche petrei*, *Lotus corniculatus*, *Lycopersicon europaeus*, *Mentha* spp., *Polygonium hydropiper*, *Potamogeton orchreatus*, and *Typha orientalis* all accumulated more than 100 mg/kg. Although not technically hyperaccumulators, arsenic hyperaccumulation by these species may be environmentally significant because they represent a food source for animals and, in the case of *Mentha* spp., for humans.

The accumulation of arsenic and other elements by aquatic macrophytes may facilitate the entry of this toxic element into the food chain. Plants are the primary producers of most food chains. Humans may be affected directly, if plants such as watercress and mint are consumed, or indirectly when humans consume species that have high arsenic levels due to contamination of the food-chain. Much of the Waikato River is surrounded by farmland and stock may occasionally have access to aquatic weeds that have been left on
the banks after a flood. A risk-assessment study is warranted to evaluate potential arsenic exposure pathways.

In a lake or river system, the amount of plant-bound arsenic at any one time may be a significant portion of the total amount of arsenic in the river. Therefore if, for example, drought or herbicides kill the plants, then there may be a large pulse of arsenic released into the water as the plants decay. The effect on humans of consuming arsenic-rich watercress is unclear. There have been no reports of arsenic poisoning in the region, despite regular consumption of watercress from contaminated areas by local people. Any arsenic toxicity from consuming watercress will depend on the amount eaten, the frequency, how the watercress is prepared, what it is consumed with, and the chemical form of arsenic in the plant. Inorganic arsenic is considerably more toxic than organic arsenic (Food Standards Aus/NZ 2002).

**Arsenic leaching from treated timber**

A general survey was undertaken to determine the extent of copper, chromium and arsenic leaching from treated posts used in some New Zealand vineyards. Twenty-seven vineyard posts were exhumed and soil and wood samples taken as shown in Figure 2.

![Figure 2. Locations of soil and wood samples taken from around each post](image)

Figure 3(I) shows the average CCA concentrations in the control soil, and soils surrounding the treated posts, for all the posts tested. 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 still significantly higher than the controls. The average soil CCA concentrations in our study are consistent with the findings of overseas studies (Hingston *et al.* 2001; Chirenje *et al.* 2003; Zagury *et al.* 2003).

Figure 3(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. Figure 2(II) confirms that CCA is leaching out of vineyard posts into the soil. However, there were no significant differences between the new posts and the aboveground samples. Leaching from the aboveground portions appears minimal.
The arsenic concentration in the soil samples collected from several sites was greater than the threshold level (100 mg/kg arsenic) set by the Australian National Environmental Protection Council (ANEPC), for agricultural soils. Across all sites, 25% of the samples were above the ANPEC guidelines for arsenic and 10% of the samples were above ANPEC guidelines for chromium (100 mg/kg). None of the copper values exceeded ANPEC guidelines (1000 mg/kg).

The amount of CCA that leaches from vineyard posts will be dependent on a range of variables such as soil type, climate, irrigation regime, and fertiliser regime. 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.

Zagury et al. (2003) showed that soil contaminant levels were more strongly correlated with soil type rather than pole age. They found that more leaching occurred in low-organic matter and low-clay content soils.

Overall, copper occurred at the greatest concentration in the soil, despite having the lowest concentration in the post. Arsenic was second, followed by chromium. This may be due to the relative binding strengths of the CCA in the timber. However, the higher soil copper concentration does not necessarily indicate that more copper is leaching out of the posts relative to the other CCA components. In soil, arsenic is the most soluble component of CCA (Read 2003). Therefore, a lower arsenic concentration adjacent to the post relative to the other elements may be the result of prior leaching.

The results from our general survey indicate that CCA does leach 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 will lead to a gradual accumulation of CCA in the soil and possible movement of arsenic away from the posts. CCA levels might eventually accumulate locally around the post to the point where they could have negative impacts. The rate of accumulation is likely to be low. Our survey focused on newer posts, and did not measure soil around posts that had been replaced. In the future, measurement of CCA in soils surrounding replacement posts, in older vineyards, would enhance our understanding of long-term CCA accumulation and leaching processes.

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.

**Remediation options**

The full extent and degree of arsenic contamination in the New Zealand environment has not yet been determined. Nevertheless, the current levels of arsenic in agricultural and aquatic systems have not resulted in any reported morbidity, mortality, or elevated arsenic levels in commercial produce. This may not always be the case. Continual use of arsenic-containing compounds can only increase the levels of arsenic in New Zealand’s environment. Urbanisation of agricultural land has resulted in the belated discovery of many arsenic-contaminated residential soils. Traditional remediation techniques such as landfilling and capping can be prohibitively expensive. A need exists therefore, to develop low-cost remediation options to prevent the entry of arsenic into the food chain.

In the case of CCA-treated timber, lacquers could be developed that not only prevent CCA leaching from the wood, but also reduce the adsorption of water, which would reduce deformation of the timber. Lacquering CCA-treated posts has been demonstrated as an inexpensive way of reducing CCA leaching from treated timber (Lebow and Evans 1999).

Arsenic-contaminated sites that are leaching this toxic element into receiving waters could be cleaned up or contained using phytoremediation. This technology uses plants to either stabilise arsenic in situ or extract it from the soil so that it can be stored in an area where it does not pose an environmental risk. This technology has been proven effective for mitigating leaching from a disused wood-waste pile (Robinson et al. 2003). Promising work is being conducted to use arsenic-accumulating ferns to extract arsenic from contaminated soil and placing the arsenic-rich biomass into a sealed landfill (Chen et al. 2002).

Chemical immobilisation of arsenic in contaminated sites may be achieved through adsorption/precipitation of arsenic through the addition of soil amendments (Bolan et al. 2004). Recently there has been interest in the immobilisation of arsenic using a range of inorganic compounds such as lime, phosphate fertilisers, alkaline waste materials, and organic compounds such as biosolids (Knox et al. 2000). Depending on the source, application of phosphate compounds can cause direct adsorption of arsenic onto these materials, promote arsenic complex formation, or induce desorption of arsenic through competition. This method is considered more economical and less disruptive than the conventional remediation option of soil removal (Naidu 2003).

**Conclusions**

Arsenic is being continually added to ecosystems in New Zealand, principally through geothermal activity and the production and use of CCA-treated timber. Clearly, nothing can be done to reduce the continual flow of arsenic from geothermal springs. However future geothermal power developments may further increase the amount of arsenic entering the aquatic biosphere. Irrigation schemes using water with elevated concentrations of arsenic may result in an increase in soil arsenic levels. Aquatic plants in the Taupo volcanic zone may provide an exposure pathway of arsenic to humans via both direct consumption, as in the case of watercress, or via animal products if stock are allowed access to rivers or lakes that contain arsenic-rich aquatic vegetation. Further research is needed to elucidate these possibilities.

Regarding the use of CCA timber treatment, there has been a great deal of emotive discussion both for and against its continued use. However, since no viable alternative for CCA treatment currently exists, future research should focus on innovative technologies that prevent arsenic from entering soils and...
surface or groundwater. There could be several low-cost means of reducing / eliminating CCA from new or replacement posts.

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 may be used to immobilise any CCA leachate.

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

References
Food Standards Australia New Zealand 2002: http://www.foodstandards.gov.au (FSANZ New Zealand, PO Box 10599 The Terrace, Wellington)


