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Arsenic Hyperaccumulators in the Taupo Volcanic Zone

The toxic element arsenic is widespread in New Zealand's aquatic and terrestrial environments. Arsenic is ubiquitous in all of the geothermal areas and waterways that fall within or pass-through the Taupo Volcanic Zone, 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. Arsenic levels in New Zealand's longest river, the Waikato, seldom fall below the New Zealand drinking water standard of 0.01 mg/L.

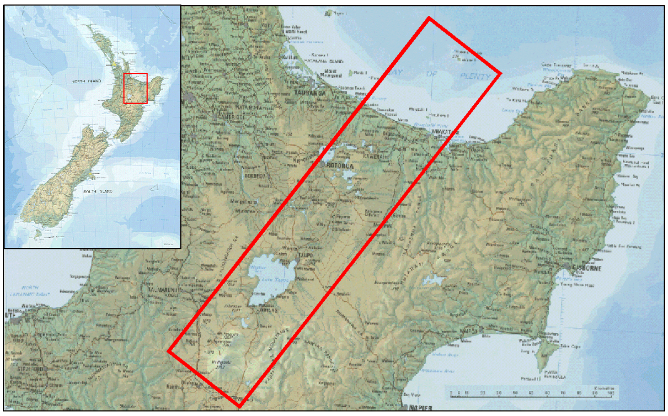

Figure 1. The Taupo Volcanic Zone, North Island, New Zealand

Human activity has also resulted in innumerable arsenic-contaminated sites. Arsenic is used as a timber preservative in a copper-chromium-arsenic cocktail. Consequently many sites associated with the timber industry or where treated timber is used, are contaminated with arsenic. These range from treatment sites to dump sites to children's playgrounds where treated timber has been used for construction. Historically, arsenic-based pesticides were used in sheep dips. While an effective means of controlling skin parasites, this practice resulted in an estimated 20,000 contaminated sites nationwide.

Worldwide, arsenic poisoning afflicts millions of people in India, Bangladesh and Mexico. In these countries, arsenic is present in well water due to leaching from arsenic-rich rocks. Poisoning results from drinking the water and by consuming vegetables that have been irrigated with it.

In 1999, Chinese and American scientists discovered that the Chinese Brake fern, *Pteris vittata* accumulated up to 20,000 mg/kg arsenic in its fronds. This was an extraordinary find because most plants have less than 10 mg/kg arsenic in their aerial portions, even when growing in arsenic-rich environments. Trials are being conducted in China and the USA on using this fast-growing fern for the phytoremediation of arsenic-contaminated sites. This operation would cleanse arsenic-contaminated soil by repeatedly cropping the fern until acceptable levels of arsenic were achieved. The plant material would be placed in a sealed landfill, where it does not pose a risk to the environment. Essentially, the ferns are used to move arsenic from where it is a problem, i.e. in a large volume of soil, to where it poses no risk to humans, i.e. as a small volume of arsenic-rich fronds stored in a sealed landfill. Phytoremediation could be a long-term and low-cost means of cleansing the innumerable arsenic-contaminated sites worldwide because it relies on simple plant cropping, a technology that has existed since civilisation began. Alternative means of arsenic-cleanup involve 'dig and dump' and soil capping, technologies that can be many times more expensive than phytoremediation.

In order to protect New Zealand's agricultural production sectors and wildlife reserves, strict bio-security laws proscribe the importation of many exotic species such as *Pteris vittata*. However, New Zealand has a very rich native fern flora, with many species occurring in arsenic-rich areas such as the Taupo Volcanic Zone. Could New Zealand have its own native arsenic accumulating fern? To investigate this possibility, Monica Marchetti, a graduate student from Switzerland, came to New Zealand to search for arsenic-accumulating plants (and then she left with the America's Cup!). Working with our plant-expert, Georgie Milne, Monica conducted a survey of the terrestrial and aquatic vegetation in the Taupo Volcanic Zone. Shade house experiments were set up in Palmerton North to investigate the potential of five native-fern species to accumulate arsenic from artificially spiked soils (Figure 2).

Figure 2. Monica Marchetti among native ferns growing in arsenic-spiked soils.

Unfortunately, the arsenic concentrations in nearly all terrestrial plants tested, including the ferns, were below detection limits (0.5 mg/kg), even when the ferns were grown in soil containing over 100 mg/kg arsenic.

This disappointment was, however, more than offset, when very high levels of arsenic (10 – 8000 mg/kg) were found in every single aquatic species tested. Previous reports had shown that watercress and a few weeds growing in the Waikato River accumulated arsenic. However, Monica's results indicated that due to some peculiarity of plant physiology in the aquatic environment, these plants accumulate and store high concentrations of this toxic element with no obvious detriment to their growth. Figure 3 shows the range of arsenic concentrations found in the plants tested.

Watercress grows in both aquatic and terrestrial environments, however, it only accumulates arsenic in the former. This implies that that watercress has no specialised mechanism for translocating arsenic to the above-ground tissues. It also raises the question as to whether arsenic is *ab*sorbed or *ad*sorbed. Arsenic may simply bind to the cell surfaces of aquatic plants, indicating that there is no specialised arsenic-uptake mechanism. However, in such a scenario, the plants would still need to have a tolerance mechanism for arsenic.

The arsenic levels in some of the aquatic plants qualify them as *hyperaccumulators*, i.e. they have greater than 1000 mg/kg arsenic on a dry matter basis. Some of these aquatic plants were rooted to sediments that contained 50 mg/kg arsenic, while others were free-floating. The high arsenic concentrations in the free-floating plants are even more extraordinary because the arsenic concentrations in the ambient water were less than 0.1 mg/L. Figure 4 shows the *bioaccumulation coefficients* for the aquatic plants. The bioaccumulation coefficient is defined here as the plant: water arsenic concentration quotient.

Strategic Change

"Can I call you back? We're in the middle of transitioning from tree-frog allergies to bioterrorism."

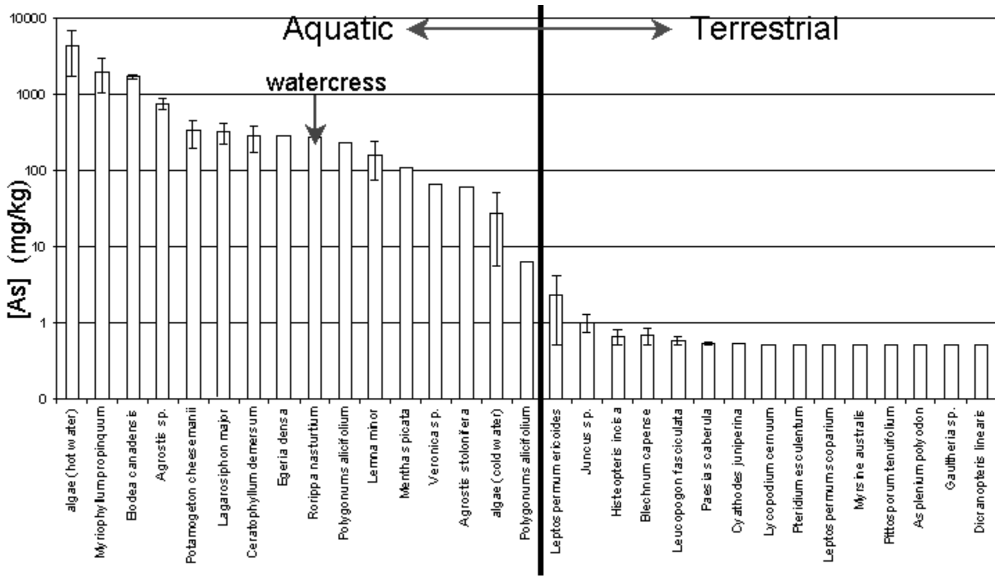

Figure 3. Arsenic accumulation by aquatic and terrestrial plants from the Taupo Volcanic Zone.

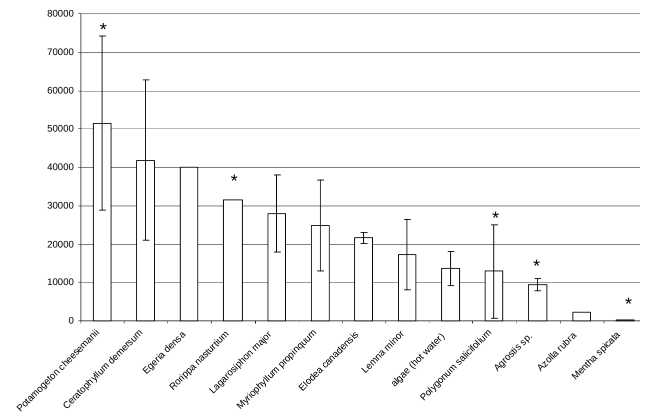

Figure 4. Bioaccumulation coefficients (plant/water concentration quotient) for the aquatic plants tested in this study. Asterisks denote plants that are rooted to sediments.

The high bioaccumulation coefficients of the aquatic plants tested may make them good candidates for the bioindication of arsenic contamination in aquatic systems. In this rôle, plants may provide a low-cost means of assessing drinking water quality, or the health of an ecosystem. Arsenic is difficult and expensive to measure at low concentrations; sophisticated techniques such as Hydride Generation Atomic Absorption Spectroscopy and Inductively Coupled Plasma Mass Spectroscopy are beyond the reach of villagers who live in developing countries. By contrast, concentrations greater than 100 mg/kg can be easily measured using a low-cost colorimetric test. Low-cost testing kits could, for example, be provided to determine the arsenic concentration in aquatic weeds that grow in water used for the village. If the test were positive then the water should not be used for drinking, cooking or irrigation. Even in developed countries, where expensive techniques are available, analyses of aquatic plants may provide information on very-low concentrations in the water at the ng/L (parts per trillion) level. This information could be useful for biogeochemical surveys.

The second reason for using aquatic plants as bioindicators is that they provide information on the history of arsenic in the water, rather than a 'snapshot' at the time of sampling. Arsenic levels in water can vary due to rainfall, evaporation, or sporadic contamination for example a chemical spill. Analysing aquatic plants may elucidate any historic arsenic contamination, even if current levels in water are within acceptable limits.

Ceratophyllum demersum (hornwort) is a ubiquitous weed in the Waikato River. Figure 5 shows the arsenic accumulation of *Ceratophyllum demersum* as a function of the ambient water concentration. There was a highly significant correlation (r^2=0.70, P<0.001) between the plant concentration and that of the ambient water, indicating that the arsenic concentration of the plants could be used to predict the arsenic concentration of the river water. Moreover, the plants with average arsenic concentration of 412 mg/kg, contained ten times the arsenic concentration of the sediments that, in turn, had over 1000 times the arsenic concentration of the ambient water.

Other factors, such as the pH, water temperature and nutrient availability will doubtless affect arsenic accumulation. Further work needs to be carried out on these effects to determine how well these bioindicators would perform under various scenarios. This study and earlier studies analysed whole specimens of *C. demersum* rather than stems and leaves. Leaves and stems could well have different arsenic concentrations and hence different bioaccumulation coefficients.

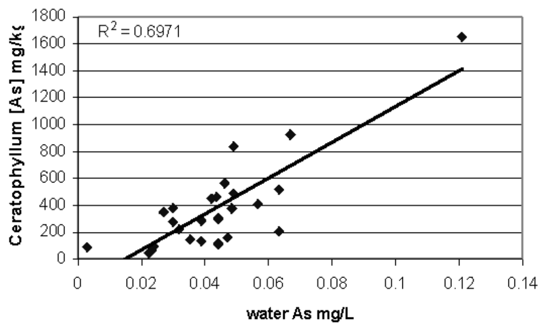

*Figure 5. The accumulation of arsenic by hornwort (*Ceratophyllum demersum*) as a function of arsenic concentration in ambient water from the Waikato River.*

The high bioaccumulation factor of aquatic plants may make them useful for the phytoremediation of arsenic contaminated drinking water. *Myriophyllum propinquum* was found to accumulate 2000 mg/kg arsenic on a dry matter basis, from water containing just 0.08 mg/L arsenic. Monica's experiments indicate that 1 kg of plant material (d.m) grown in a water containing 0.08 mg/L arsenic should contain 2000 mg of arsenic. Thus, *in theory*, 1 kg of plant material could halve the concentration in 25,000 L of water that had an initial concentration of 0.16 mg/L.

Aquatic plants could, therefore, provide a very efficient means for removing arsenic from drinking water. Plants would be grown in ponds containing contaminated water, then simply removed and placed in an area where they do not pose a risk to the environment, such as a sealed landfill. Very simple low-cost technology such as this could potentially save lives in developing countries that cannot afford expensive water purification systems.

Much work needs to be done, however, to determine the feasibility of aquatic arsenic phytoremediation. We analysed *Myriophyllum propinquum* growing in flowing water containing 0.08 mg/L arsenic. The bioaccumulation factor may be much less if it is grown in still water. The biomass production of these plants is unknown. The growth rate is critical in determining the time needed to remove arsenic from the water. Anecdotal evidence indicates that the biomass production is rapid, because these plants are weeds and choke waterways. Nevertheless, experiments need to be done to quantify the biomass production in various scenarios. Arsenic accumulation by *Myriophyllum propinquum* is doubtless affected by other environmental parameters such as water temperature and nutrient availability. It is conceivable that plant uptake could be improved by water amendments.

Even if these calculations overestimate the efficiency of phytoremediation by a factor of 100, and 1 kg of plant material could be used to treat only 250 L of drinking water, then phytoremediation could still be a cost-effective technology, when comparing it to other water treatment techniques such as distillation and reverse osmosis.

Arsenic accumulation by aquatic plants may facilitate the entry of this poisonous element into the food chain. Plants are the primary producers most food chains and are consumed by herbivores and omnivores. Humans may be affected directly, if plants such as watercress and mint are consumed, or indirectly when species 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. Fishing is also popular in the region. Presumably the fish eat plants and animals that have high arsenic concentrations.

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 pesticides kill the plants, then there may be a large pulse of arsenic released into the water as the plants decay. The desorption of arsenic by these plants has not been tested.

The aquatic plants analysed in this study have the capacity to take up and tolerate high concentrations of an element that is toxic to most organisms. The mechanisms of this uptake and tolerance are unknown, however, they may involve some genetically controlled enzymatic systems. The possibility exists, therefore, that these plants could be 'mined' for genetic material that could be used to induce terrestrial plants to accumulate arsenic. Further research needs to be done to determine if arsenic accumulation is genetically controlled or simply related to the normal metabolic processes of aquatic plants. Figure 6 shows the location where a geothermal alga thrives in water at 60 ^oC and accumulates over 1% arsenic on a dry matter basis. Could the genes from this algae be used to create new plants that hyperaccumulate arsenic?

Figure 6. The habitat of an arsenic-hyperaccumulating hot water alga.

There is a clear distinction between aquatic and terrestrial plants regarding their ability to accumulate arsenic. Obviously the reported terrestrial arsenic hyperaccumulators have specialised mechanisms that allow them to solubilise, take-up and store arsenic in a non-toxic form. Arsenic accumulation is widespread among aquatic plants, and this study identified three new arsenic hyperaccumulators. More species will undoubtedly be found as further surveying is conducted. The question as to how aquatic plants accumulate arsenic could be partially resolved by conducting microanalyses on the tissues to determine if arsenic is present inside the cells or simply bound to the cell walls.

Arsenic accumulation by aquatic plants may make them valuable tools for the bioindication and phytoremediation of arsenic. Additionally, the ecological impacts of arsenic accumulation are likely to be profound. Christophe Moni, a graduate student from Paris, has recently arrived to tackle these new challenges.

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