

Phytoremediation: using plants as biopumps to improve degraded environments

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Abstract

Plants pump large amounts of water, solutes, and organic matter as part of their normal physiological processes. This pumping action can be exploited to improve degraded environments by stabilising, removing, or breaking-down contaminants in the substrates. In addition, soil amendments such as fertilisers and microbes may also be added to enhance the efficacy of the operation. Basic plant physiology sets limits on the capacity of phytoremediation. However, combining this technology with the production of saleable products may render the extra time needed for clean-up relatively unimportant. Phytoremediation is still poorly developed, particularly the phytoextraction of heavy metals. Continual innovation will greatly expand the scope and efficacy of phytoremediation. The greatest potential use for this technology may be in developing countries that have the highest levels of environmental degradation, and scant funds for remediation. Phytoremediation could provide a low-cost and sustainable way to improve local economies. Here a case study is reported on the phytoremediation of a 3.6 ha sawdust pile that was leaching unacceptable amounts of boron (B) into local waterways. High water-use poplars were used to control leaching and potentially remove B from the site via phytoextraction. Selected trees that are coppiced before leaf-fall could be mulched and used to provide 'organic' B on nearby orchards that are deficient in this element.

Additional keywords: heavy metals, modelling, lysimeter, phytoextraction, phytomining, phytoremediation.

Introduction

Phytoremediation is the use of plants to improve degraded environments. This technology has been used for hundreds of years to treat human waste, reduce erosion, and protect water quality. Research focusing specifically on the phytoremediation of contaminated soils has only grown significantly in the last 25 years.

Pioneering work by the late Professor Robert Brooks at Massey University, Palmerston North, New Zealand popularised the study of plants that accumulate inordinate amounts of heavy metals. Chaney (1983) suggested that these so-called 'hyperaccumulator' plants (Brooks *et al.* 1977) could be used to remove heavy metals from contaminated soils. McGrath *et al.* (1993) and Baker *et al.* (1994) demonstrated that the Brassicaceous herb *Thlaspi caerulescens* could be used to extract Zn from contaminated soil. Since these benchmark studies, there has been a plethora of work using plants to phytoremediate contaminated soils. This work has expanded to include soils polluted with organic contaminants and excess plant nutrients as well as heavy metals. Dedicated phytoremediation companies have appeared around the world to service a global market that is estimated to be over US\$100 million/year currently (Glass 1999).

The general process of phytoremediation

In phytoremediation, plants are exploited as bio-pumps that use the sun's energy to remove water and contaminants from the soil to the above-ground portions, and return some of the products of photosynthesis back into the root-zone. Transpiration is the cornerstone of phytoremediation. By removing water from the substrate, plants help to reduce erosion, runoff, and leaching, thereby limiting the movement of contaminants off-site. Some soil contaminants are taken up in the transpiration stream, where they may be metabolised, volatilised, or stored. By drying out the soil profile, the plant roots may also create an aerobic environment where metal mobility is reduced and biological activity is enhanced. Plants stimulate microbiological activity in the root-zone by providing a carbon source from root exudates and decaying root material. It is well documented (Gudin and Syrratt 1975; Reilley *et al.* 1996) that soil microbiota enhance the degradation of some organic contaminants as part of their normal metabolism.

Categories and applications of phytoremediation

Phytoremediation can be broadly categorised by the way plants are being used. In *phytostabilisation* and *hydraulic control*, transpiration and root-growth are used to immobilise contaminants by reducing leaching, controlling erosion, creating an aerobic environment in the root-zone, and adding organic matter to the substrate that binds the contaminant. Root exudates may also play a role in phytostabilisation. Rugh *et al.* (1996) showed that genetically modified *Arabidopsis thaliana* could reduce toxic mercuric ions into relatively inert metallic mercury. Phytostabilisation involves the establishment of vegetation on the contaminated site that is left in perpetuity. Substrate amendments may be added and a succession of plant species may be used to establish the desired climax vegetation. Establishing a healthy substrate microflora, especially mycorrhizal symbionts, can greatly enhance phytostabilisation (Vosátka 2001). Phytostabilisation can be used to control erosion and leaching on metalliferous mine tailings (Vangronsveld *et al.* 1996). Establishing vegetation directly on the tailings reduces dust and leaching, enhances public appeal, and is more cost-effective than capping, which could require re-engineering of any tailings dam as well as a large earth-moving operation.

Some of the negative environmental effects of tip-sites, land effluent disposal, and intensive farming can be mitigated by using plants to prevent contaminants leaching to groundwater or local waterways (Dix *et al.* 1997). Phreatophytic trees, such as poplars and willows, are particularly suited to this role (Ferro *et al.* 1997).

Phytoremediation may be a solution to the 'dirty dairying' problem that is emerging in New Zealand as nitrates contaminate groundwater and streams after the irrigation of dairy shed effluent onto pasturelands (Roygard *et al.* 2001). Effluent, high in N, may be irrigated onto an area planted with high water-use, fast-growing, palatable species such as poplar and willow that can, in turn, be fed back to stock as fodder.

Deep-rooting, high water-use, evergreen trees can be used to lower a saline water table, thus reducing salt toxicity to crops, a technology that has been demonstrated to be effective on some Australian soils (Bell 1999).

Phytodegradation, *phytostimulation*, *phytodetoxification*, and *rhizodegradation* are terms used to describe the use of plants, in association with soil microbiota, to degrade contaminants in the root-zone. There are 3 possible ways that plants can lead to the degradation of contaminants: (1) uptake and metabolism; (2) direct action or plant root exudates; and (3) enhanced microbial activity in the root-zone through aeration, root

exudates, and the decomposition of dead root material. Ideally, soil contaminants should be degraded to carbon dioxide, water, and halide ions, if they are present in the original molecule. However, plants can be used to partially degrade some organic compounds to produce daughter products that are less harmful than the original contaminant. The effectiveness of phytodegradation is dependent on the type of contaminant present in the system. Plant roots have been shown to enhance the degradation of petroleum compounds, explosives such as trinitrotoluene (TNT) (Hannink *et al.* 2001), perchlorates (Nzengung *et al.* 1999; Susarla *et al.* 1999), pentachlorophenol (PCP) (Ferro *et al.* 1994), and some polycyclic aromatic hydrocarbons (PAHs) (Reilley *et al.* 1996). Other compounds, such as dichlorodiphenyltrichloroethane (DDT), are recalcitrant even in the presence of plant roots (Chaudhry *et al.* 2002).

Phytodegradation could be a low-cost way of cleaning up disused sheep and cattle dipping sites in Australasia. Here phreatophytic trees could be used to enhance the degradation of organochlorines such as dieldrin (Schnabel and White 2001), control leaching, and demarcate the area so that stock can be prevented from ingesting contaminated pasture or soil.

Soil amendments such as surfactants, fertilisers, and a carbon source may be added to enhance the bioavailability of the contaminant, plant growth, and microbiological activity, respectively. The soil may also be inoculated with a new strain of bacteria that is more effective in degrading the contaminant than the local microflora.

Gaining a better understanding of the root-zone processes that lead to contaminant degradation should elucidate better ways to render phytoremediation more effective than trial and error experiments involving various plant–microbe–amendment combinations.

Phytoextraction describes the use of plants to remove metals and other contaminants from soils. This technology, involves the repeated cropping of plants until the soils' contaminant concentrations have reached acceptable levels. After each cropping, the plant biomass is removed from the area and may be burned to reduce its volume, whereupon it can be stored in an appropriate area, such as a contained landfill, that does not pose a risk to the environment.

Phytoextraction relies on plants that translocate inordinate amounts of one or more contaminants into their above-ground biomass. Some plants, known as *hyperaccumulators* (Brooks *et al.* 1977), do this as part of their normal metabolic processes. Hyperaccumulation was originally used to describe plants that take up Ni to concentrations greater than 1000 mg/kg on a dry matter basis. This concentration is at least an order of magnitude greater than concentrations found in other plants growing in the same environment. At present, there are in total over 400 species of known hyperaccumulators for As, Cd, Mn, Na, Ni, Tl, and Zn.

The mass of metal that can be removed by a single crop sets a practical limit on the speed of any phytoextraction operation. While hyperaccumulator plants can achieve a high metal concentration in their biomass, their biomass production is usually inferior to non-hyperaccumulator plants.

For some common metals, such as Pb, there are no reliable reports of any hyperaccumulator species. A possible solution is the use of *induced hyperaccumulation*. Non-hyperaccumulator plants can be made to take up metals such as Pb, or even Au, by the addition of solubilising agents to the substrate (Huang and Cunningham 1996; Blaylock *et al.* 1997; Anderson *et al.* 1998). Such additions increase the mobility of the metal in the soil, allowing it to be taken up more easily by the plant. At the same time, however, there is the possibility that some of the metals might leach through the soil profile, possibly

entering groundwater (Lombi *et al.* 2001). Physical soil processes such as preferential flow may exacerbate metal leaching (Bundt *et al.* 2000), and these soil amendments may also persist in the environment creating additional and unforeseen problems. Environmental concerns may limit the use of induced hyperaccumulation to hydraulically isolated treatment sites where the connection to receiving waters has been 'broken'.

More promising work is being conducted where high biomass plants are being genetically altered to extract larger amounts of metal from soils (Rugh *et al.* 1998), or where the potential biomass of smaller varieties of hyperaccumulator plants is being improved (Ow *et al.* 1998). Dhankher *et al.* (2002) demonstrated that *Arabidopsis thaliana* could be engineered to accumulate arsenic by inserting 2 bacterial genes that imparted tolerance and the ability to translocate arsenic to the aerial portions. The soil's microbiota plays a crucial role in plant metal tolerance and uptake (Whiting *et al.* 2001), and can be manipulated to enhance plant uptake (Nie *et al.* 2002).

Lasat *et al.* (1997) discussed the use of plants to extract radioactive ^{137}Cs from contaminated soils. Radionuclides and other metals could be extracted from contaminated waters using plant-roots in a process called *rhizofiltration* (Dushenkov *et al.* 1995). Here, metals only need to be adsorbed by plant roots that can easily be removed from a hydroponic system.

To date, there are very few field demonstrations of the potential success of phytoextraction. Blaylock (2000) showed an impressive decrease in soil Pb concentration over 2 years at 2 sites in the United States using a combination of *Brassica juncea* and EDTA to induce accumulation. Unfortunately the mass balance of Pb was not reported. It is therefore uncertain just how much Pb the plants removed, and how much leached through the soil profile. It is well known that chelators such as EDTA can act as chemical ploughs, redistributing surface contamination down the soil profile, thereby causing an observed reduction in concentration near the soil surface but having little effect on the total amount of contaminant in the soil profile.

In Australasia, phytoextraction could be used to remove Cd from agricultural lands that have become contaminated through repeated applications of sewage sludge or Cd-rich phosphatic fertilisers (Robinson *et al.* 2000).

Phytovolatilisation is a form of phytoextraction where the extracted contaminants are transformed into volatile compounds rather than being stored in the plant tissues. Plant-microbial systems have been discovered that volatilise Hg, As, and Se (Brooks 1998). One obvious drawback of phytovolatilisation is that there is no control on the destination of the toxic heavy metals that are volatilised. In the case of Se, however, phytovolatilisation offers the possibility of redistributing this element from areas where Se toxicity exists to downwind areas where there is a selenium deficiency (Zayed *et al.* 2000).

Nicks and Chambers (1994) reported another possible role for hyperaccumulator plants: for economic gain in the mining industry. This operation, termed 'phytomining' includes the generation of revenue by extracting saleable heavy metals from otherwise sub-economic ore bodies (Robinson *et al.* 1997a, 1997b). No commercial phytomining operations have yet been conducted, although an American company, Viridian Environmental, has patents on the phytomining process (US Patent Nos 5711784 and 5944872).

Advantages and limitations of phytoremediation

Phytoremediation has several advantages over other remediation and metal extraction technologies. First and foremost is the low cost of phytoremediation, which is, in essence,

not dissimilar to normal agricultural cropping practices. Competing technologies, such as soil removal, capping, and *ex situ* cleansing, can cost around US\$ 1 million/ha, compared with an estimated \$60 000–100 000/ha for phytoremediation (Salt *et al.* 1995). Other benefits of phytoremediation include the ultimate fertility of the cleansed site, the high public appeal of 'green' technology, and the possibility of producing secondary products that offset the cost of the operation or even produce a small profit.

Huang *et al.* (1991) and Pulford *et al.* (1995) suggested that phytoremediation could be combined with conventional silviculture, as long as the growth of the trees was unimpeded by the soil contaminant. An elevated concentration of contaminants in the wood of the trees is unimportant for human health. Vegetation could also be combusted to produce electricity in a bio-energy operation (Nicks and Chambers 1994). If a metal hyperaccumulator is used, and the metal is of sufficient value, then the metal could be smelted from the plant-ash and resold. Plants that accumulate essential trace elements such as Zn, Co, and B may be used as an organic mineral supplement to crops, livestock, or even humans.

Basic plant physiology, nonetheless, limits the scope of phytoremediation. Only surface contamination can be removed or degraded, and the clean-up is restricted to areas that are amenable to plant growth. Most importantly, it may take a long time for site remediation to be effective. Phytoremediation can only be used if it meets environmental regulation during the operation as well as at its end point.

Plants may provide an exposure pathway for the soil contaminants to enter the food chain if the plants are consumed (Tibazarwa *et al.* 2001). This will be particularly relevant if plants that are genetically modified to accumulate heavy metals cross-pollinate with crop species. Care has to be taken to avoid such scenarios that could stifle innovation by adding fuel to the anti genetic engineering lobby (Watanabe 2001).

Implementing phytoremediation

Effective phytoremediation requires that the site first be assessed, the correct species planted, and a suitable crop management regime implemented. Soil amendments may need to be added to enhance plant growth and/or contaminant uptake or degradation.

Here, we present a case study where plants are being used to pump water and contaminants out of a 3.6-ha pile of timber-industry waste.

Case study

Site description

The Kopu sawdust pile is located at the base of the Coromandel Peninsula, North Island, New Zealand (37.2° S, 175.6° E). The pile has a surface area of 3.6 ha and an average depth of 15 m. Over a 30-year period, from 1966, sawdust and yard-scrappings from timber milling in the region were dumped on the pile. Land around the pile has been engineered so that no surface or ground water enters the pile, and all leachate resulting from rainfall is collected in a small holding pond at the foot of the pile. In the past, vegetation has failed to establish and evaporation from the surface of the pile has been negligible, even in the summer months. This is demonstrated by the presence of saturated material at depths as shallow as 20 mm.

Leachate resulting from the annual rainfall of 1135 mm, as measured at a nearby meteorological station at Thames, regularly caused the holding pond to overflow and enter a local stream. This overflow elevated boron (B) concentrations in the stream to levels that were in excess of 1.4 mg/L, the New Zealand Drinking Water Standard (NZDWS),

especially in the summer months when stream flow was low. In response to these breaches, the local environmental authority placed an order on the forestry company responsible for the site that the problem be remedied.

Phytoremediation of the sawdust pile

In July 2000, a 1-ha trial was established on the Kopu site using 10 poplar and willow clones as well as 2 species of *Eucalyptus*. Two *Populus deltoides* hybrid clones were then chosen as the best candidates for phytoremediation based on survival, biomass production, and B uptake. The following year, the remainder of the pile was planted to these 2 clones at a density of 7000 trees/ha. Fertilisers were periodically added to the trees and a pump was installed near the holding pond at the foot of the pile for irrigation during the summer months.

A concurrent lysimeter experiment was set up at HortResearch, Palmerston North, to derive a model that could be used to predict the uptake and leaching of water and contaminants at the Kopu site. Details of this experiment can be found in Robinson *et al.* (2002).



Fig. 1. Photographs of the Kopu sawdust pile taken at planting in July 2000 (top), and after 2 years growth in April 2002 (bottom).

Performance of phytoremediation at the Kopu site

Figure 1 shows tree growth on the Kopu pile over the first 2 years. Approximately 30% of the trees are 2 years old, and the remainder are only 1 year old. Figure 1 demonstrates clearly how phytoremediation helps the contaminated site become part of the landscape by transforming the bare pile into an actively growing 'green' plant cover. The estimated above-ground biomass production in the first and second years of the trial was 1.2 and 13.3

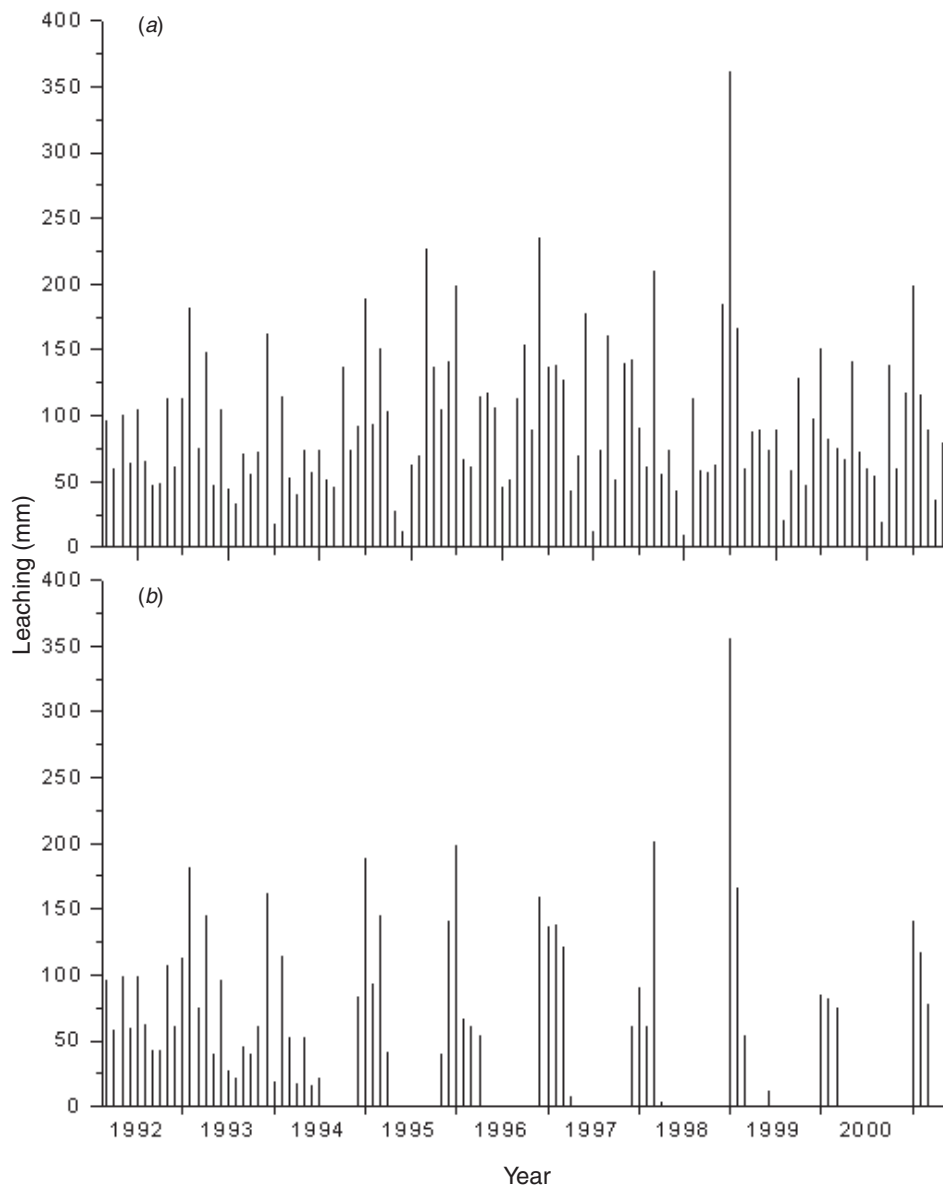


Fig. 2. Estimated monthly leaching (mm) from the Kopu sawdust pile (a) without trees, and (b) with trees. Meteorological data were used from the nearby town of Thames from 1991 to 2000. It was calculated that maximum transpiration would be achieved after 3 years.

t/ha dry matter, respectively. The average leaf area index of the 2-year-old trees was 2.6, which is well below the value of 6 reported by Heilman *et al.* (1996) for maximum photosynthesis and transpiration of poplar under high light conditions. We would not expect the water use of the trees to be maximised until the biomass exceeds 30 t/ha on a dry matter basis. This level of productivity should occur in the third or fourth years.

The monthly water balance of the pile was calculated using a computer model similar to that described in Green *et al.* (1999). The model uses daily weather data taken from a meteorological station at nearby Thames. Some parameters for the model (water use efficiency, crop coefficient) were derived from the lysimeter experiment. Field measurements at Kopu were used to estimate plant root distribution, and the leaf area index. The water retention curve for the sawdust was measured using a combination of Haines' apparatus and pressure plates. Disk permeameters were used *in situ* to derive the hydraulic conductivity close to saturation. Model calculations of leaching are shown in Fig. 2*a* and *b*, respectively. As expected for such a high rainfall site, the bare pile leaches a considerable amount of drainage water through all months of the year (Fig. 2*a*). The impact of trees is to substantially reduce the drainage of water during the summer months when the trees are fully leafed and transpiring at their maximum. The summer months are of greatest concern for contamination of the local waterways because stream flows are lower and there is less dilution of the contaminants. The reduced leaching that occurs during the winter months can be irrigated onto the trees in times of drought during the summer, or alternatively, released into a nearby stream at times of high flow when the risk of exceeding the NZDWS is minimal.

Table 1 shows some lysimeter results of the total concentrations of Cu, Cr, As, and B in the sawdust, as well as the average concentration in the leachates over the duration of the experiment. Boron was the only detectable contaminant in the leachate that exceeded the NZDWS. The level of As in the leachate was below detection limits (0.1 mg/L) but could still have exceeded the NZDWS for As (0.01 mg/L).

Poplar leaves contained Cu and Cr concentrations that were on average 6.6 and 4.9 mg/kg dry mass, respectively (Table 1). Arsenic concentrations were below detection limits (1 mg/kg). Results from the lysimeter experiment revealed that poplar have the capacity to accumulate significant amounts of B in their leaves (Fig. 3). This trait has previously been reported for poplar by Bañuelos *et al.* (1999). At the end of the growing season, the average leaf B concentration was nearly 700 mg/kg on a dry matter basis, over 28 times higher than the B concentration in the sawdust (40 mg/kg dry matter). The amount of B extracted by the poplar was predicted using the model developed by Robinson *et al.* (2003), which is based on the water use of the tree and the soluble concentration of B in the substrate. There was very good agreement

Table 1. Average metal concentrations in leachate (mg/L), sawdust (mg/kg dry mass), and leaves (mg/kg dry mass) from four lysimeters

Leachate concentrations represent the average of monthly values collected throughout the experiment. Values in parentheses are the standard error of the mean

Element	NZDWS ^A	Leachate	Sawdust (initial)	Leaves (final)
Cu	2	0.30 (0.07)	140 (25)	6.6 (1.7)
Cr	0.05	0.03 (0.01)	15 (0.8)	4.9 (1.2)
As	0.01	<0.1	6.3 (0.8)	<1
B	1.4	1.87 (0.10)	39.9 (2.7)	654 (109)

^ANew Zealand Drinking Water Standard (Drinking Water Standards for New Zealand 2000).

between the calculated and measured B concentration in the leaves of the lysimeter trees (Fig. 3). The B concentration in the leaves of the trees at the Kopu site has also been estimated using parameters from the lysimeter experiment. Figure 4 shows

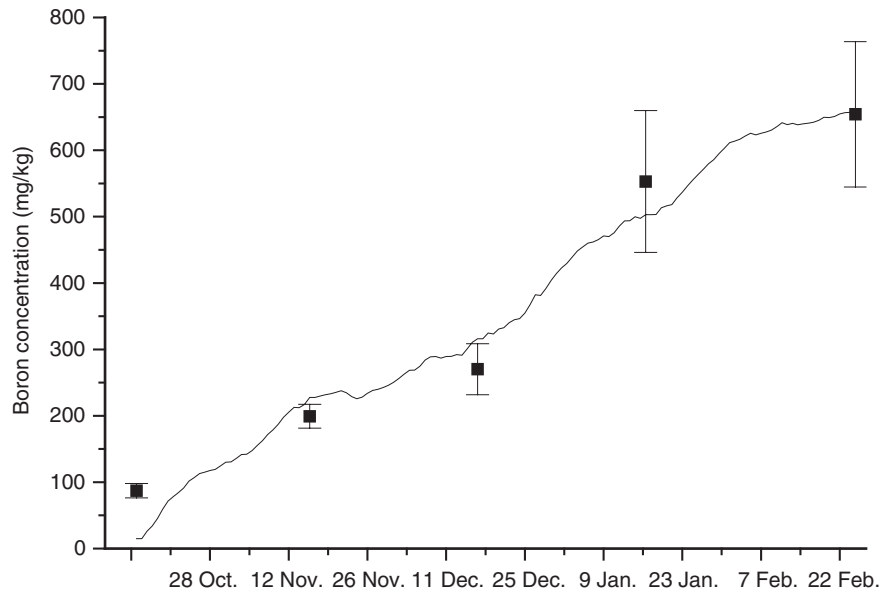


Fig. 3. The concentration (mg/kg dry mass) of B in poplar leaves from the lysimeter experiment during the 2001–02 season. Values are averages of four trees. Bars represent the standard error of the mean.

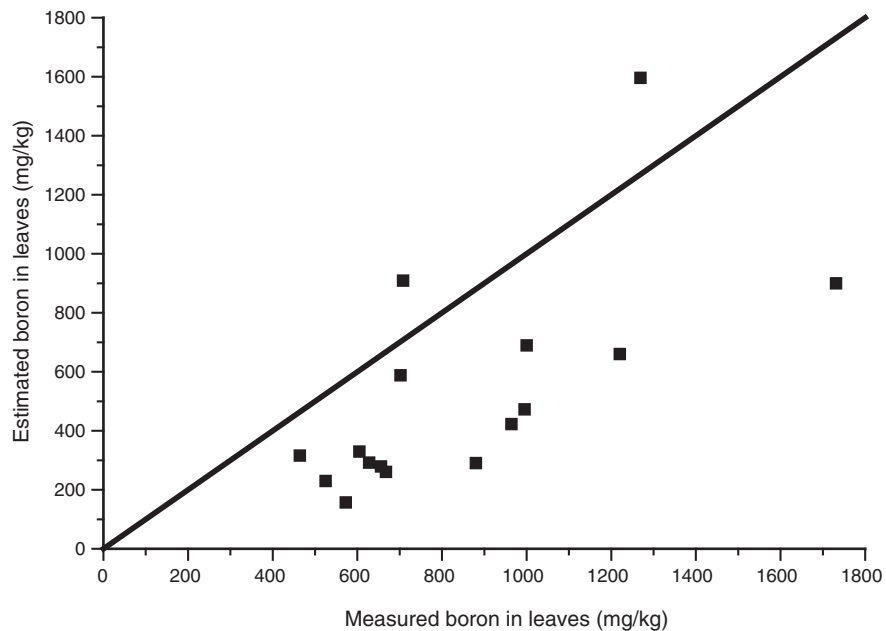


Fig. 4. Measured *v.* estimated B concentrations (mg/kg dry mass) in leaves from the trees growing on the Kopu sawdust pile at the end of the 2001–02 season. The solid line represents $y = x$.

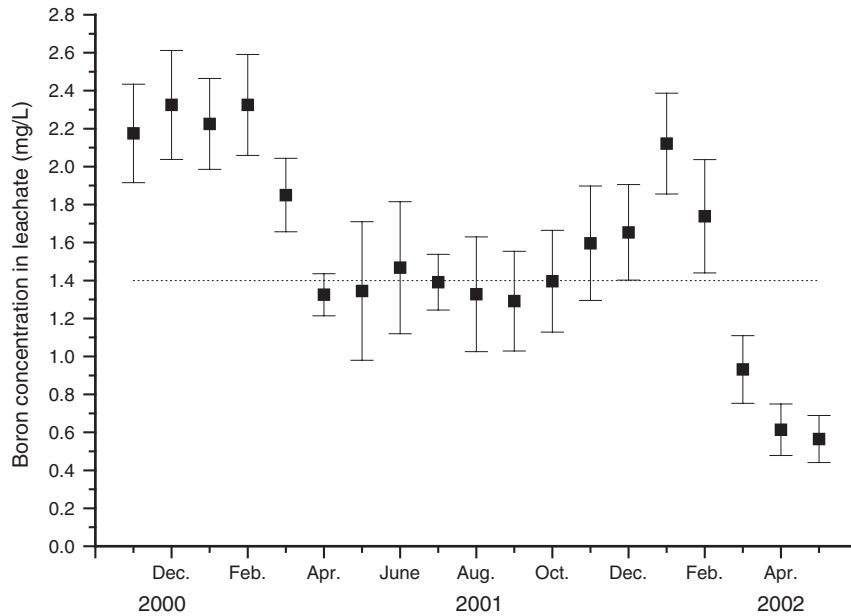


Fig. 5. Concentration (mg/L) of B in the drainage of the lysimeters from November 2000 until May 2002. Values are averages from 4 lysimeters. Bars represent the standard error of the mean.

estimated B concentration against the actual measured B concentration in the leaves. Once again, there was a reasonable correlation ($r = 0.74$, $P < 0.01$) between the estimated and measured values. Our simple model provides a robust description of the capacity of trees to dewater and decontaminate the site.

The results indicate that in addition to controlling leaching at the site, poplars may also be able to reduce the B loading by phytoextraction. Unless the trees are harvested, most of the B is returned to the sawdust via leaf-fall. Harvested material could, however, be used as an organic B supplement to trees in orchards that are B-deficient in other parts of the country. The concentrations of other heavy metals in the leaves (Table 1) are unlikely to cause further environmental problems.

The average B concentration in the drainage water from the lysimeters decreased progressively during the course of the experiment. After 2 years the B concentration dropped below the NZDWS (1.4 mg/L, Fig. 5). This decrease occurred late in the growing season when tree water uptake was at a maximum. There have been insufficient measurements on the leachate from the Kopu sawdust pile to determine if there has been a similar decrease in the field situation. Further measurements are planned over the next few years, and further modelling will be carried out to determine the success of phytoremediation at Kopu.

The cost of phytoremediation at Kopu is estimated to be NZ\$200 000, including a site maintenance plan over 5 years. Half of this total cost was taken up as site assessment, involving scientists' time to conduct the plant trial and chemical analysis. The alternative cost of capping the site was estimated by the local environmental authority to be over NZ\$1.2 million. Capping will also require ongoing maintenance to ensure its integrity.

Conclusions

Phytoremediation offers the possibility of a low-cost clean-up for a wide range of contaminated sites. The technology offers long-term solutions, but is constrained by basic plant physiology in the types of environmental degradation that can be ameliorated. Combining phytoremediation with the production of saleable products may circumvent phytoremediation's Achilles heel, which is the time needed for remediation.

The processes by which phytoremediation systems accumulate and degrade contaminants are still poorly understood, the implication being that the innovation may increase the scope and efficiency of this technology.

The greatest application of phytoremediation may be in developing countries, where this technology can provide a low-cost means of controlling environmental problems that would be rectified using high-cost technologies in the developed world. An example may be the treatment of municipal effluent using trees to prevent the contamination of groundwater and local waterways. The field trial at Kopu, supported by basic research being carried out via lysimeter experiments, is showing phytoremediation as a cost-effective and practical solution to reduce the problem of B leaching into local waterways. Our research involves observations, experimentation, and modelling to improve our understanding of the whole system. Further development of models, supported by apt experimentation and site characterisation, will enable us to make robust predictions of the efficacy for phytoremediation of contaminated sites.

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Manuscript received 15 October 2002, accepted 17 January 2003