

PHYTOREMEDIATION – A LONG-TERM SOLUTION FOR CONTAMINATED SITES

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ABSTRACT

Phytoremediation, the use of plants to remove, contain or render harmless, environmental contaminants. It is a latent idea gaining new exposure and success. There is documented use of phytoremediation as a strategy for the treatment of domestic wastewater in Germany during the 1700's. In more recent times, armed with new knowledge and understanding, phytoremediation has emerged as a solution for waste treatment and contaminant remediation in water and soil. This paper gives an overview of the mechanisms of phytoremediation. We will discuss phytoextraction of heavy metals and present results which demonstrate the efficacy of our poplar and willow clones. We will also discuss the long-term containment of contaminated sites under a vegetation canopy, and the quantitative tools that allow us to provide risk assessments of these sites. Preliminary results will also be presented on the degradation, under a phytoremediation regime, of dieldrin a persistent organic pollutant (POP) present at disused sheep dip sites. We also discuss the use of mosses as early colonisers to accelerate the re-vegetation of disturbed sites such as mine tailings and the implications for the indigenous re-vegetation of these challenging sites.

Phytoremediation can help support the health of New Zealand's unique environment. Our environment is an integrated part of our heritage, culture and quality of life. The development of management systems, and in turn, the commercial application of phytoremediation to degrade waste depends upon understanding waste and the dynamics of contaminated environments. With technologies such as phytoremediation the future is bright green.

KEY WORDS

Heavy metals, organic contaminants, re-vegetation, poplar, willow, moss

INTRODUCTION

Phytoremediation is a rapidly developing technology with potential to remediate soil and water that is contaminated with heavy metals, hydrocarbons, persistent organic pollutants (POPs), and excess plant nutrients. Taken in a broader sense (*phyto* = plant, *remediation* = correct evil) the term phytoremediation can also encompass the re-vegetation of disturbed sites such as mine spoil. Phytoremediation is a truly multidisciplinary science, which pulls the threads of soil chemistry, soil physics, plant physiology, soil microbiology and meteorology together to provide solutions for the management and remediation of contaminated environments.

Phytoremediation can be classified into three categories based on contaminant fate. These are degradation, extraction, containment or a combination of these (Cunningham et al., 1996). Degradation includes the breakdown of organic contaminants such as pesticides and hydrocarbons within the rhizosphere or within the plant. Degradation within the soil is primarily due to the naturally occurring microbial populations, numbers of which are significantly increased under a vegetation regime. This occurs due to root-exudates, decomposition of dead roots, and soil aeration, all of which optimise the soil conditions in the valdose zone which favour microbial activity. It is well documented (Gudin and Syrratt, 1975, Reilley *et al.*, 1996) that soil micobiota enhance the degradation of some organic contaminants as part of their metabolic and co-metabolic activity

Extraction by contrast relies on the uptake of contaminants into the shoots and leaves of the plants and through harvesting or copicing, the contaminants including heavy metals and nutrients are removed from the site. This concentration technology does not alter heavy metal contaminants but rather contains it in a much smaller mass, which, in turn, is easier to dispose of. In the case of nutrients there may be opportunities to recycle. An example may be a solution to the 'dirty dairying' problem that is emerging in NZ. Dairy shed 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.

Containment of contaminated sites is of particular importance in New Zealand as failure to prevent or mitigate off site effects from any activity may result in prosecution under the Resource Management Act. The physical containment of the site may be due to the binding of the contaminant in the root or above ground portion of the plants. Alternatively the mode of transport for the contaminant, primarily water, is prevented from leaving the site due to plant transpiration, which alters the water balance, and hydraulically seals the site.

Re-vegetation of challenging sites such as mine overburden is not only important for the remediation of the site but also helps prevent offsite effects such as acid rock drainage and airborne contamination of the surrounded environment with heavy metal laden dust. Mosses are common colonisers of metal contaminated habitats and have the ability to modify the growing environment sufficiently for higher order plants to then establish (Delach & Kimmerer, 2002). Specific examples from work conducted in the Grasberg mine, Irian Jaya are presented here.

Table 1 gives a comprehensive overview of the type of soil and water contaminants that are common in New Zealand and the applicability of phytoremediation as a long-term treatment option. Other factors such as the relative cost of a phytoremediation solution when compared to conventional solutions will also influence treatment option. Generally a phytoremediation solution is likely to cost less, take longer but give a better end result than conventional cleanup technologies. Phytoremediation solutions generally work best on site with a wide spread low to medium level contamination that is too expensive to remediate using the tradition forms of treatment including cap and contain, removal and dump, and chemical or heat treatment. Additionally, phytoremedaition will ensure the site remains fertile. Some traditional solutions determine future use of the site as they may physically alter the site and the soil so it no longer supports plants or other biological systems.

Table 1. Contaminated sites in New Zealand and contaminants likely to be found at these sites

Contaminated Site	Likely Contaminants	Type of treatment
Forestry dump sites	<u>Tannalizing chemicals including:</u> Cr, As, Cu, B PCPs	Stabilisation, extraction, In the longterm, degradation
Landfills	<u>Heavy Metals including:</u> Cd, Pb, Zn, Ni <u>Organic contaminants including:</u> Nitrates due to use of sewage sludge as backfill material	Stabilisation Degradation
Disused Coal Gas sites	Polycyclic aromatic hydrocarbons (PAH's), Pb, Creosote	Degradation
Sheep dips and farm dumps	Pesticides (DDT, Trazines, hexachlorobenzenes, dieldrin) Fertilisers (nitrates, phosphates) Heavy metals such as Cd from fertilisers As PAH's	Degradation Extraction
Disused mine sites	Heavy metals: Particular heavy metals will depend on mine type	Stabilisation, extraction, revegetation for first succession planting
Roadsides	PAH's Heavy metals: primarily Pb, Cu and Cd	Stabilisation Degradation
Horticultural site	Cu, pesticide and herbicide residues	Stabilization
Effluent farms	Heavy metals Nitrates	Extraction, stabilisation

This paper summarises results from our phytoremediation program and presents specific examples of the mechanisms outlined in the introduction

RESULTS

Extraction and Containment

HortResearch has so far focused on the extraction of Cd from soil and B from water. Cadmium is a commonly occurring contaminant of pasture systems in NZ (due to the over zealous use of superphosphate high in Cd) and poses potential problems for the export of lamb meat. Cadmium is readily bio-available and thus accumulates in plants. Figure 1 illustrates accumulation of Cd from the Manawatu fine sandy loam at a resident concentration of 0.3 mg kg⁻¹ soil by various willow clones. This figure not only demonstrates the efficacy of Cd uptake by willow but also that not all willow varieties respond similarly to Cd present in the rootzone. To extrapolate this it may be that clone 14, which accumulates low levels of Cd is a better fodder variety than clone 3 which shows great potential as a phytoremediation species.

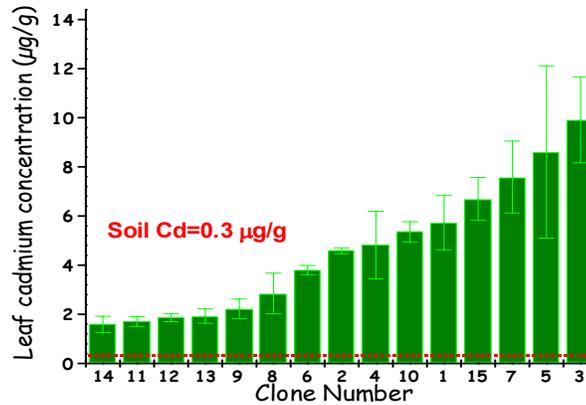


Figure 1. Leaf Cd concentration in 15 different willow clones

Boron is also a common contaminant in New Zealand and primarily comes from former timber treatment plants that use Borax as a wood preservative. With a long history of timber production in NZ we have many sites contaminated with this extremely mobile metal.

We are now two years into the remediation of a contaminated sawdust pile which covers approximately 5 Ha and is up to 15 m deep in places. The sawdust pile contained boron at 20 mg kg⁻¹ and was consistently leaching boron at levels of between 2-3 mg l⁻¹ into receiving waters. Lysimeter studies conducted on the sawdust planted with poplar demonstrate that the volume of water exiting the lysimeter is significantly reduced when compared to bare sawdust but also the concentration of boron in that leachate has been reduced to levels below 1 mg l⁻¹ (Fig. 2). New Zealand drinking water standard for B is 1.4 mg l⁻¹. Figure 3 illustrates the predicted impact of water exiting the sawdust pile with or without trees. Such risk assessment is provided via the use of our Soil Plant Atmosphere Model (SPASMO), a mechanistic model that uses historic meteorological data to predict plant water use and leachate concentrations.

Figure 2. Boron concentration in the leachate from lysimeters containing contaminated sawdust

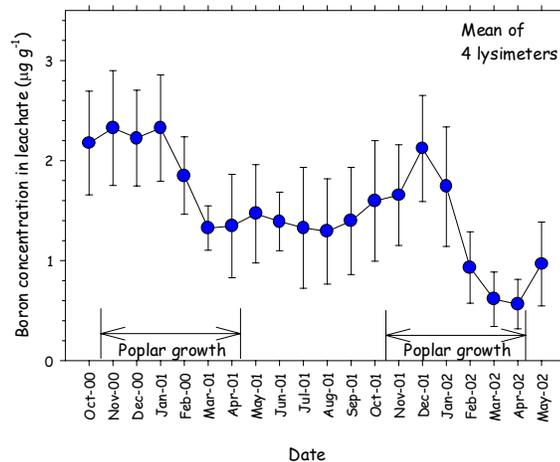
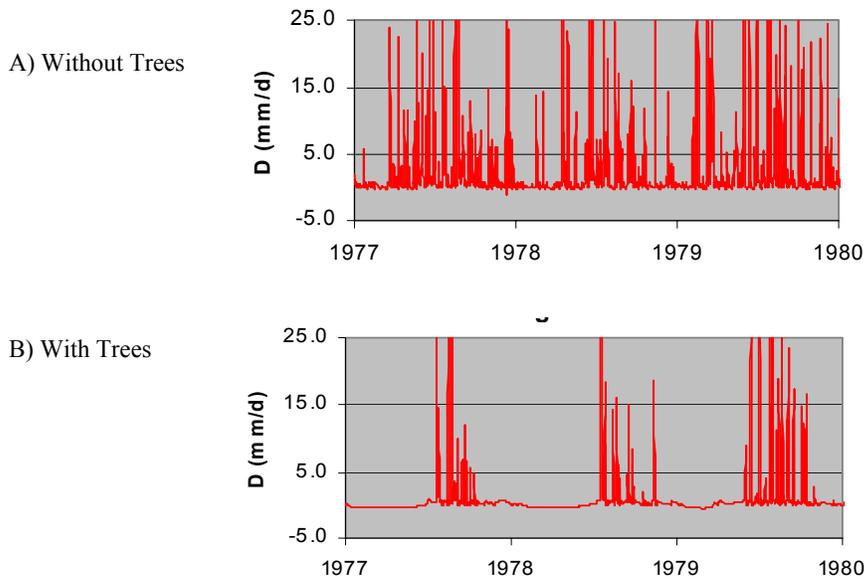


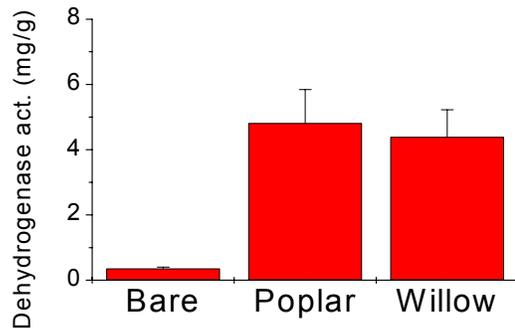
Figure 3. Predicted drainage with and without trees using SPASMO and based on an actual 30 year record of meteorological data for the region.



Degradation

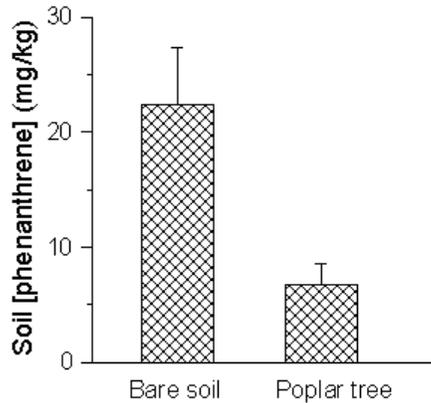
This is the primary mechanism for the remediation of organics in both soil and water systems and primarily relies on soil microbial populations that degrade the contaminants as part of their metabolism. Organic pollutants make up the largest proportion of contaminants world wide (Glass 1999). Figure 4 shows the effect of poplar and willow roots on the dehydrogenase activity in soil (Manawatu fine sandy loam) spiked with an anthracene concentration of 500 mg kg⁻¹. It is well known that dehydrogenase activity is a reliable indicator of microbial population in the soil (Taylor et al., 2002). Methodology for the dehydrogenase assay is outlined by Chander and Brookes (1991). It is clear from Figure 4 that both poplars and willows induce a significant increase in microbial activity of the soil.

Figure 4. Dehydrogenase activity under different vegetation covers.



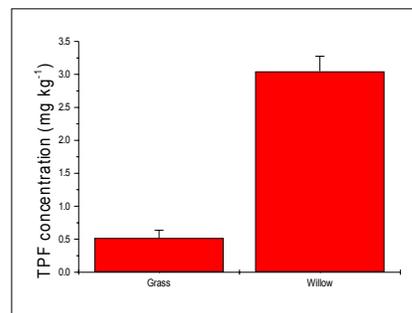
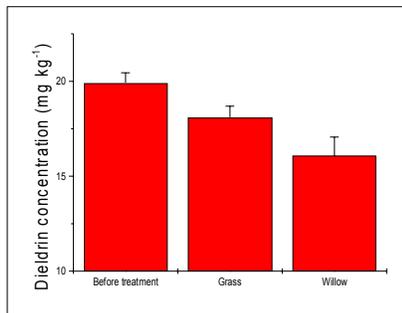
Separate experiments have shown that the degradation of PAH's (polycyclic aromatic hydrocarbons) is enhanced in the presence of poplar roots (Figure 5). Although there is a strong positive correlation between soil microbiological activity and degradation, a causative link has not yet been conclusively established.

Figure 5. The effect of poplars on the degradation of phenanthrene in soil after 6 months of tree growth and an initial phenanthrene concentration of 500ppm.



Similarly, the dieldrin concentration was significantly reduced in soil planted with either poplar or willow when compared to contaminated soil planted with grass (Figure 6A). Soil microbial activity was also significantly greater under trees when compared to grass (Figure 6B).

Figure 6A The effect of willows on dieldrin degradation & 6B Dieldrin concentration under vegetation and associated microbial activity under different vegetation regimes.



Willows caused a significant decrease ($p < 0.05$) in the soil dieldrin concentration over the treatment period (Figure 6A). This reduction was achieved in only five months of growth. The dieldrin degradation by the willows was also greater than that by grass species (Figure 6B), which may colonise many disused sheep dip sites. The impact of phytoremediation willows in the field will be far superior to grass species due to their greater rooting depth (up to 1m) and poplars (up to 3 metres).Revegetation

The Grasberg copper mine in Irian Jaya (West Papua, Indonesia) has approximately 900 Ha of overburden in its current mine plan. The overburden is basically rock containing little or no organic matter and high heavy metal levels. This overburden must be revegetated with native species but due to conditions of low pH, high heavy metal content, low photosynthetic light conditions and low temperatures establishing high order plants is extremely difficult. HortResearch scientists have developed techniques whereby mosses native to the region are used to stabilise the site and to modify substrate conditions to allow other plant species to establish on the site. Results indicate an average increased temperature of 1°C within an established moss mat whilst reducing temperature extremes. This, along with an increase in organic matter, water retention and trapping of silt and sand particles, will in turn enhance the germination and survival chances of other plant species. The addition of nutrients to the overburden had limited effect on moss establishment. This is in stark contrast to higher order plants, which require large amounts of added nutrient before they can establish on such poor growth substrates. Table II illustrates the biomass establishment of different moss species on various rock types found within the Grasberg mine, grown in a controlled environment chamber where the Grasberg environment was reproduced. Interesting to note is the range in levels of biomass production thus demonstrating the importance of selecting the right mosses for particular environments and rock types. New Zealand has significant mining activity, primarily on the West Coast of the South Island and in the Coromandel. HortResearch scientists have extended this research approach using mosses and other early succession plants on one such mine on the West Coast with considerable success so far. The development of indigenous revegetation strategies for mines in NZ is critical for NZ considering our mining activity occurs in areas that are popular with national and international tourists.

Table II. Moss biomass index (area x height) measured at the final harvest for moss species grown on the three rock types, and for all moss species combined on rock that was either weathered or unweathered. (s.e.d. is the standard error of the difference between two means.) Modified from Stanley *et al.*, 2000.

Moss species	Limestone Rock	Mildly acid-generating Rock	Strongly acid-generating Rock
<i>Anomobryum sp</i>	7.5	28.9	16.3
<i>Barbula sp</i>	16.6	17.4	2.8
<i>Breutelia sp</i>	16.8	21.6	0.9
<i>Bryum sp</i>	28.8	37.8	7.3
<i>Racomitrium sp</i>	22.5	42.3	13.1
<i>Schizymerium sp</i>	0.5	5.5	21.2
<i>Splachnobryum sp</i>	4.4	17.4	18.3
All species; weathered rock	16.5	26.8	3.4
All species; unweathered rock	11.2	22.0	19.3

COMMERCIAL APPLICATION

Bioremediation technologies are low cost, increase site fertility and are aesthetically pleasing. Advantages of bioremediation are numerous and include aspects such as public appeal and a broad range of contaminants that can be tackled (Table 1). From a business perspective the relative low cost of bioremediation solutions makes an attractive option.

The scientific processes underpinning bioremediation are interactive and multi-disciplinary. There are often spin-off benefits from a bioremediation solution at a contaminated site such as increased biodiversity and soil fertility, timber products, fuel and fibre following treatment.

Table III Advantages and disadvantages-of bioremediation

Strengths	Weaknesses
Low cost	Limited to low/moderate contaminant levels
Permanent	Long term
In situ	Limited on shallow soil
Managed enhancement of natural processes	Biological limitations
Effective on a range of contaminants	Implementation difficulties to maintain biological function
Can employ a variety of plants/fungi	Incomplete scientific understanding of the entire system
Works with complementary technologies	
Not confined to New Zealand	
Public appeal	

HortResearch's current remediation projects include an old industrial site, a timber treatment dump site, disused sheep dip sites dairy effluent sites, and a mine site. The full range of mechanisms that contribute to the phytoremediation of a site, and which are outlined in the introduction, are now employed in these full scale cleanup operations.

There are limitations with phytoremediation solutions including restriction of application to medium and low-level contamination. The contaminant level must at least allow plant growth. The high cost of physical and chemical remediation technologies often makes remediation prohibitive with medium or low-level contaminated sites. As a result the concept of complementary technologies working together is an attractive commercial option.

CONCLUSIONS

Commercial application of phytoremediation is quickly gaining momentum in New Zealand. It provides a long-term cost effective, green solutions to clients. The Environment and Risk Management Group at HortResearch has applied the fundamental sciences of plant physiology, soil chemistry and physics, plus microbiology to the business

of phytoremediation. This 'green' remediation technology is being advanced globally as an alternative, cost effective, safe and natural technology for the treatment of contaminated soil and water.

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