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Phytoremediation and long-term site management of soil contaminated with pentachlorophenol (PCP) and heavy metals

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Abstract

Pentachlorophenol (PCP) is a persistent organic pollutant (POP) previously used as a timber treatment chemical to prevent sap stain and wood rot. Commonly used in wood treatment industries for the last 50 years, there are now many sites worldwide that are contaminated with PCP. Although persistent, PCP is a mobile contaminant and therefore has a propensity to leach and contaminate surrounding environments.

Both willow (*Salix sp.*, 'Tangoio') and poplar (*Populus sp.* 'Kawa') growing in an open-ended plastic greenhouse were found to tolerate soil PCP concentrations of 250 mg kg^{-1} or less and both species stimulated a significant increase in soil microbial activity when compared to unplanted controls. Both poplar and willow could not survive PCP concentrations above 250 mg kg^{-1} in soil. Pentachlorophenol degradation occurred in both planted and unplanted pots, but a higher rate of degradation was observed in the planted pots.

Soil contaminated by wood-treatment activities often contains co-contaminants such as B, Cr, Cu and As, that are also used as timber preservatives. An additional column leaching experiment, done along side the potted trial, found that PCP, B, Cr, Cu and As were all present in the column leachate. This indicates that although Cu, Cr and As are generally considered immobile in the soil, they were mobilised under our column conditions.

If a contaminated site were to be hydraulically 'sealed' using plants, a reticulation irrigation system should be installed to capture any contaminant leachate resulting from heavy rains. This captured leachate can either be independently treated, or reapplied to the site. Our data demonstrate a reduction in soil hydraulic conductivity with repeated application of leachate containing PCP and metal compounds but the soil did not become anaerobic. This would need to be considered in site remediation design.

Keywords: Boron; Arsenic; Poplar; Willow

1. Introduction

Pentachlorophenol (PCP) has been used as an anti-sapstain treatment in the timber industry worldwide over the last 50 years. In New Zealand, PCP use ceased in 1988 with no import of PCP permitted after 1991. But previous widespread application since the 1940s has resulted in an estimated 600 contaminated timber treatment sites throughout New Zealand (Taylor and Smith, 1997). Soil contamination occurred when sawn logs were treated and stacked in unsealed yards while excess chemicals drained from the timber. Spillage of the chemical stock or working-treatment solutions was also common and contributed to soil contamination in timber yards. Pentachlorophenol was generally applied as a sodium salt or dissolved in oil, diesel and/or creosote (Taylor and Smith, 1997). Therefore, other co-contaminants, including hydrocarbons, boron (B), arsenic (As), chromium (Cr) and copper (Cu) are often

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present in these contaminated soils. The application of PCP within an oily solution such as creosote not only facilitates PCP penetration into the wood, but also increases PCP solubility within soil. It therefore poses an increased risk of groundwater contamination (Christodoulatos and Korfiatis, 1994). Groundwater contamination by Cu, Cr, As and B is also common, but the level of metals and PCP leaching from contaminated soil depends upon many factors including soil type, organic matter content and pH. Sandy soils with low organic matter (OM) content are less able to bind mobile metals, in comparison to heavier soils or those with higher OM content. Similarly, low pH conditions usually favour metal leaching (Armishaw, 1994) but not always (Podlesákova et al., 2001). In contrast PCP is more mobile under high pH conditions (≧7) (Christodoulatos and Korfiatis, 1994).

Pentachlorophenol is a persistent organic pollutant (POP) that is sparingly soluble in water at soil pH values between 5 and 7, which are common. It has strong biocidal activity, which renders it resistant to microbial degradation. The negative effect of PCP on soil microbial populations has been recognised for some time (Brown, 1978) and can occur at levels as low as 4 mg L^{-1} PCP in soil and aqueous systems (Davis et al., 1996).

Pentachlorophenol is regarded as a priority pollutant by the USEPA (United States Environmental Protection Agency, 2004) and its environmental toxicity has resulted in low permitted maximum concentration levels (MCL) being assigned. For example, the USEPA have set an MCL for PCP in groundwater of 0.001 mg L^{-1} (Davis et al., 1996). In New Zealand, the maximum allowable value (MAV) for PCP in drinking water is 0.01 mg L^{-1} (New Zealand Ministry of Health, 2000). Given the environmental and human health threat of PCP and its co-contaminants, and the often-high cost of existing remediation technology, the use of plants to prevent offsite contaminant movement and facilitate the degradation of organic compounds is attractive.

We investigated the ability of both poplar and willow trees to tolerate PCP- contaminated soil, and to assist in its degradation. It is well established that root exudates and improved soil aeration can induce changes in microbial communities, as compared to non-rhizospheric soil (Marschner et al., 2001). These changes in microbial populations may stimulate degradation of organic compounds. We discuss changes in soil micro flora and fauna of contaminated soil under vegetation and the impact this may have on PCP degradation. We also present results from a column leaching experiment using aged contaminated material containing PCP and heavy metals. We report the effect on soil properties and the leachate composition of the captured leachate being re-irrigated onto the contaminated soil column. This leaching experiment provides additional information on long-term strategies required to manage disused timber treatment sites using phytoremediation.

2. Materials and methods

2.1. Plant tolerance and PCP degradation

One hundred litres of PCP contaminated soil/bark mixture (17,000 mg PCP kg^{-1} material) were collected from the now disused Waipa mill site in the central North Island, New Zealand. All experimental work was carried out at research facilities located in Palmerston North (lat. 40.2°S, long. 175.4°E with a cool temperate climate). The contaminated material was diluted with topsoil (Kairanga silt loam, CEC 27.7 $cmol_c$ kg^{-1}) and homogenised using a soil mixer to give PCP concentrations of 250 and 600 mg kg^{-1}. The PCP contaminated soil mixture was stored for one month before planting in order to allow sufficient time for equilibration between the soil and the contaminated material added (Christodoulatos and Mohiuddin, 1996). On the 30th of September 2002 (Day Of Experiment (DOE) 1), 15 L plastic pots (270 mm high × 290 mm top diameter) containing the soil/bark/topsoil mixture was planted with one each of either poplar (*Populus sp.* 'Kawa') or willow (*Salix sp.*, 'Tangoio') poles (500 mm long, 10 mm diameter), or left unplanted (four pots per treatment for six treatments). Eight additional pots containing PCP concentrations of 600 mg kg^{-1} had 10% by volume of commercial compost (Boost organic compost, pine bark/fish product blend, Agrich organics Ltd, Napier, NZ) added to each pot. Of these eight pots, four were planted with the poplar Kawa and 4 were left unplanted. Each treatment had four replicates and a total of 32 pots were prepared for the experiment. Pots were maintained in a plastic-skinned greenhouse that excluded UV radiation. All pots were watered to maintain soil close to pot capacity, with the aim to minimise leaching from the base of the pot. Leachate exiting the pots was trapped in individual trays and re-applied to the soil surface. All pots were regularly (6 weekly) fertilised with Nitrosol™ blood and bone liquid fertiliser (N:P:K 8:3:6) according to the manufacturer's instructions.

Monthly measurements of plant growth were recorded as total shoot length and the general condition of plant growth and condition noted. By day of experiment (DOE) 73, all plants originally planted in the 600 mg kg^{-1} PCP contaminated soil, and including those amended with compost, were dead. A PCP-tolerance test for poplar and willow was then set-up to identify upper limits of PCP tolerance. The contaminated soil/bark mixture was diluted with topsoil (Kairanga silt loam) to give concentrations of 100, 200, 300, 400, and 500 mg kg^{-1} PCP. Three replicates each of the varieties of poplar (Kawa) and willow (Tangoio) was planted for each concentration. These were maintained under the same watering regime as the other pots, until they were destructively harvested at DOE 300. These plants were planted on DOE 132. Dry weights of both roots and shoots were recorded for all treatments.

2.2. Soil sampling and analysis

Monthly soil samples were taken from each pot for analysis of PCP concentration, microbial activity and microbial population demographic determinations. Soil samples were obtained by extracting cores 10 mm in diameter, and approximately 50 mm in length, from each pot. The holes resulting from repeated soil sampling from pots were back-filled using bentonite, an inert filler.

2.3. Soil microbial activity

Dehydrogenase activity has been reported to be a suitable measure of microbial activity in soil (Taylor et al., 2002). Five gram soil samples were collected from each pot at each of the five sampling dates and used to perform a dehydrogenase assay to determine overall soil microbial activity (Chandler and Brooks, 1991). The 5 g-soil samples were individually placed in 30 mL plastic vials with 0.1 g of $CaCO_3$, and 3 mL of 2,3,5-triphenyltetra-zolium chloride added. The sample was mixed and placed in the dark at 30 °C for 24 h. After incubation, 20 mL of methanol was added, the sample shaken and then filtered through Whatman 41 filter paper to extract the triphenylformazan (TPF). Following extraction, the absorbance of the filtered solutions was measured at 485 nm using a spectrophotometer (Beckman DU 640). TPF concentration (mg kg^{-1}) was determined by comparison against a standard curve and TPF concentration per sample calculated to provide a measure of overall microbial activity in the soil. Following individual dehydrogenase evaluations for each pot, the soil from each treatment was amalgamated and diluted serially with sterile water by using the dilution plate method (Parkinson et al., 1971). Dilution plates of media selective for growth of bacteria and fungi were prepared as follows. A peptone-glucose- acid-agar medium containing 1 g of KH_2PO_4, 0.5 g of $MgSO_4$–$7H_2$ 0, 5 g of peptone, 10 g of glucose, 20 g of agar, 1000 mL of distilled water, and 1.0 mL of 80.5 NH_2SO_4 for each 100 mL of medium was used to isolate and grow fungi. The yeast extract agar selective for bacteria contained 15 g of agar, 1.0 g of dextrose, 0.5 g of KNO_3, 1.0 g of K_2 HPO_4 (after autoclaving), 0.2 g of $MgSO_4$ $7H_2$ 0, 0.1 g of $CaCl_2$, 0.1 g of NaCl, 0.01 g of $FeCl_3$, 1.0 g of yeast extract, and 1 L of $H_2$0. The pH was adjusted to 6.8 with HCl or NaOH. A 10^{-1} dilution was prepared by adding 10 g of soil to 90 mL of sterile, deionized, distilled water. Decimal dilutions through 10^{-7} were prepared from the 10^{-1} dilution (Dietrich and Lamar, 1990). Three plates each were made on selective media at dilutions of 10^{-5},10^{-6}, and 10^{-7} for bacteria and 10^{-4}, 10^{-5}, and 10^{-6} for fungi and then incubated in the dark at 23 °C for 5–10 days. Following incubation the number of colonies on each plate was determined and the average calculated. The remaining amalgamated soil was retained and used for PCP determinations.

2.4. Analysis of chlorophenols

2.4.1. Soil residue analysis

Chlorophenols were analysed using a modified method based on US-EPA and US-NOAA protocols (Holland et al., 1993). Between 10 and 20 g of field-wet soil was mixed with sodium sulphate and concentrated phosphoric acid. Chlorophenols were extracted with a solution of hexane/acetone (3:2 v/v) using sonication followed by shake extraction. The hexane containing the chlorophenols was partitioned from the soil–solvent mixture by the addition of water. An aliquot of the separated hexane extract was transferred to a glass culture tube and derivitised to the corresponding acetyl esters using acetic anhydride in the presence of sodium hydroxide. The hexane layer containing the acetylated chlorophenols was transferred to an autosampler vial for analysis

2.4.2. Liquid sample analysis

Chlorophenols were analysed using a modification of the methods of Abrahamsson and Xie (1983); Lee et al. (1984). An aliquot of liquid sample was transferred to a glass flask and spiked with 2,6-dibromo-4-methyl phenol as an internal standard. Disodium hydrogen phosphate, iso-octane and acetic anhydride were added to the contents of each flask, which were shaken vigorously to simultaneously derivitise and extract the chlorophenols present in the samples. After settling, the iso-octane layer was removed from the extraction flasks and transferred directly to a glass auto sampler vial for analysis.

Sap samples were collected following Lang and Volz (1998). Due to small sap sample sizes the samples were diluted further to provide adequate volume for extraction. Chlorophenols in these samples were subsequently derivitised and extracted as described above for leachate samples.

Calibration standards for quantifying liquid/leachate samples were prepared by spiking aliquots of a mixed chlorophenol standard and 2,6-dibromo-4-methyl phenol surrogate standard in methanol into a predetermined volume of Milli-Q water in separate extraction flasks.

The acetylated calibration standards and sample extracts were analysed by gas chromatography and electron capture detection using a Varian 3500 GC and J&W DB-5 glass capillary column (30 m length$\times$0.25 mm i.d$\times$0.5 μm film thickness) with helium carrier gas. The injector temperature was 250 °C and 1 μL of sample and standard was injected in split/splitless mode, the detector temperature was 320 °C and nitrogen was used as make-up gas. The GC column oven was temperature programmed to optimise separation and resolution of the eight chlorophenols and surrogate standard. Detection limits for the measured chlorophenols in each sample matrix are provided in Table 1.

2.5. Column leaching experiment

Two soil columns (dimensions 170 mm$\times$100 mm) were packed with PCP contaminated material diluted with topsoil

Table 1
Chlorophenols measured in soil and sap samples and respective detection limits

Compound	Detection limit		
	Soil (mg kg^{-1})	Sap (μg L^{-1})	Water (mg L^{-1})
2,4,6-Trichlorophenol	5	5	5
2,4,5-Trichlorophenol	5	5	5
2,3,6-Trichlorophenol	5	5	5
2,3,4-Trichlorophenol	5	5	5
2,3,5,6-Tetrachlorophenol	5	5	5
2,3,4,6-Tetrachlorophenol	5	5	5
2,3,4,5-Tetrachlorophenol	5	5	5
Pentachlorophenol,	5	5	5
2,6-Dibromo-4-methyl phenol	10	10	10

to provide a concentration of either 600 mg kg^{-1} or 250 mg kg^{-1} PCP.

A disc permeameter (White and Perroux, 1987) was used to apply the leachate solution to the soil columns at a preset pressure head of −100 mm. Leachate exiting the column was collected under the same pressure head as that applied to the top (Fig. 1). This ensured unsaturated gravity-driven flow of liquid through the soil column. The vacuum-sealed plexiglass case underneath (Fig. 1) was covered with thick brown paper to exclude sunlight and minimise photolytic degradation of any PCP contained in the leachate (Liu et al., 2002). Tap water (2 L, pH 6.8) was initially applied to each column via the disc permeameter. Once soil within the column was fully wet drainage was initiated. Approximately 0.4 L of water was retained in the column at field capacity. Two subsequent leachate events on each column re-applied the leachate collected following the first and second leaching events, respectively. Following each of the three leaching events per column, a 200 mL leachate sub-sample was put aside in glass containers covered with aluminium foil and stored at 4 °C for further analysis.

Flow rate (mm h^{-1}) through each column was calculated from the rate of leachate collection throughout all leaching events for each column. Leachate pH and electrical conductivity were measured after each leachate application event using a Multiline P3 pH/electrical conductivity meter (WTW 82362, Weilheim, Germany). Redox potential was recorded using water test apparatus (Hana Instruments, Portugal).

2.6. Metals in soil and leachate

Analysis of Cr, Cu and B in soil and leachate was carried out by an accredited analytical laboratory (e-lab Limited, Hamilton, NZ). For B and Cu analysis the samples were digested using cold HCl acid. Chromium was determined following boiling N acid digestion. Arsenic was analysed in leachate samples using a graphite furnace atomic absorption spectrophotometer (GFAAS) following acidification of the solution with 1 mL nitric acid in 30 mL of leachate. Soil As levels were determined using the GFAAS following digestion of 0.2 g of soil with 10 mL of nitric acid.

3. Results and discussion

3.1. Potted experiment—PCP as a persistent biocide

Dehydrogenase activity is indicated by the evolution of triphenolformazan (TPF). A sharp drop in dehydrogenase activity is noted for all treatments following addition of PCP contaminated material to topsoil to a level of 250 mg kg^{-1} PCP across all treatment pots one month before DOE 1 (Fig. 2). Initial levels of activity in uncontaminated topsoil

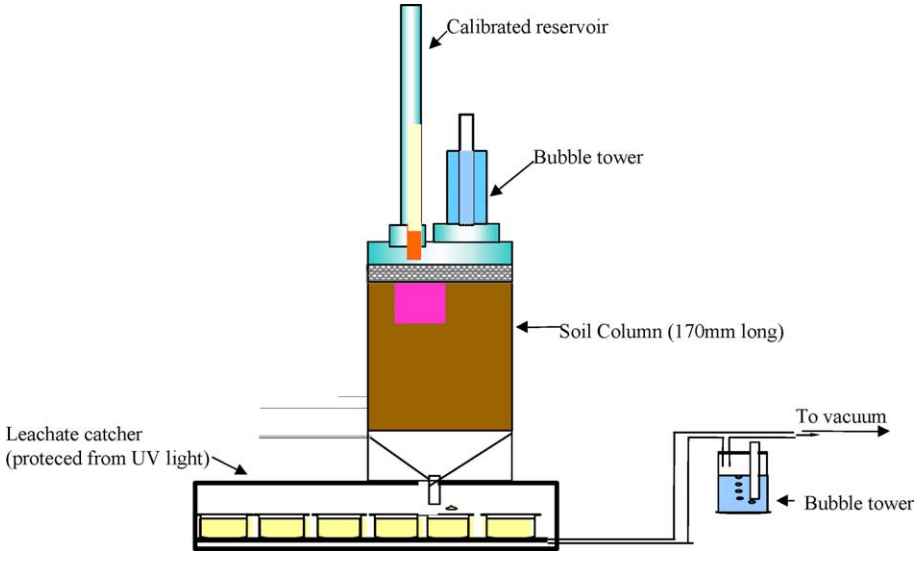

Fig. 1. Column leaching apparatus.

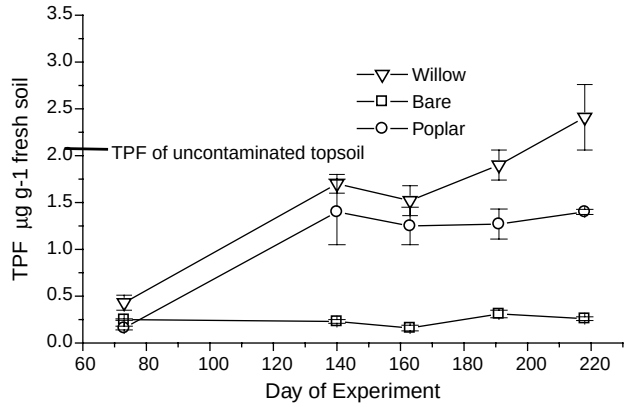

Fig. 2. Dehydrogenase activity as indicated by the transformation of triphenyltetra zolium chloride (TTC) to triphenylformazan (TPF) in contaminated soil (250 mg kg^{-1} PCP) planted with either poplar, willow or left unplanted. Error bars represent standard errors of the mean ($n=4$).

were recorded at 2.05 mg kg^{-1} (Fig. 2, dehydrogenase activity of uncontaminated soil is marked by a horizontal line on the *Y* axis), considerably higher than levels of between 0.2 and 0.5 mg kg^{-1} recorded following the addition of PCP contaminated material one month before DOE 1 (Fig. 2, DOE 73). At DOE 73, microbial activity in the pots planted with willow was slightly higher compared to both the unplanted and poplar treatments (Fig. 2). By DOE 140 there was significant recovery in microbial activity in the planted pots. There was no significant recovery in dehydrogenase activity in the unplanted pots throughout the experimental period.

The continued suppression of microbial activity in the unplanted pots contaminated with PCP was similar to results obtained by McGrath and Singleton (2000) who report no recovery of dehydrogenase activity after 6 weeks in soil contaminated with 250 mg kg^{-1} PCP. The lack of recovery in soil dehydrogenase activity reported by McGrath and Singleton (2000) occurred despite corresponding decreases in PCP concentration during the experiment. We also found this (Fig. 3)

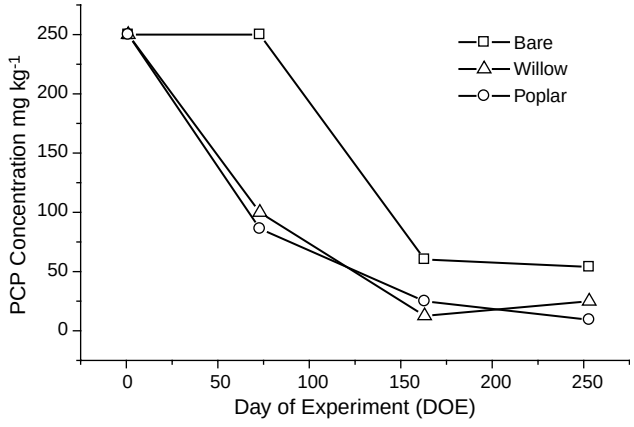

Fig. 3. Change in PCP concentration from initial concentration of 250 mg kg^{-1} with time in pots planted with either poplar, willow or left unplanted.

By DOE 218, the soil of the willow treatment recorded dehydrogenase levels close to those recorded initially for the uncontaminated soil. Soil from the poplar treatment also showed significant recovery in dehydrogenase activity over the experimental period, however, values recorded in the poplar treatment were consistently lower than levels measured for willow. This may be due to the relatively high level of total organic carbon (TOC) extracted from willow roots when compared to poplar roots. Rentz et al., 2004 reported TOC in root extracts of poplar and willow as 25 and 84 mg L^{-1}, respectively, however, these measurements were not made in this study.

3.2. PCP degradation

Over the experimental period PCP levels declined steadily in all treatments. However, a significantly greater and earlier reduction ($p<0.0001$) in PCP concentration occurred in the planted treatments (Fig. 3). A reduction in PCP concentration in unplanted soil was also observed by Puhakka and Melin (1996) and was attributed to microbial activity. McGrath and Singleton (2000) also report a decrease in PCP concentration in non-sterilised unplanted control soils following incubation of soil at 25 °C for 6 weeks. We observed a similar decline in PCP concentration in the soil of unplanted pots, which indicates PCP can be degraded slowly in soils given suitable environmental conditions. In contrast, sterilised unplanted soil spiked with PCP showed no decrease in PCP levels following 6 weeks of incubation at 25 °C (McGrath and Singleton, 2000). These results support our hypothesis, which is that soil microbial populations are able to facilitate PCP breakdown under favourable conditions, even if they have no previous exposure to PCP.

Pentachlorophenol, although only sparingly soluble in soil under normal conditions, has still been reported to be taken up in low concentrations by some plants (Howard, 1991). Sap samples, which were taken from poplar and willow at DOE 173, showed no detectable levels of chlorophenols. The lack of PCP recorded in the sap samples suggests that values of plant uptake are low and therefore not a significant contributor to the PCP disappearance from the pots.

Soil temperatures within the pots regularly exceeded 25 °C during the summer months. These elevated temperatures may have reduced the amount of PCP absorbed by soil and enhanced its dissolution (Divincenzo and Sparks, 2001). This can increase the amount of PCP available in solution for photolytic and microbial degradation (Levinson et al., 1994). No significant loss of PCP through leaching should have occurred in this experiment as leachate was recycled to each pot daily. Similarly, the greenhouse was covered in a polycarbonate material that absorbed UV radiation and this will limit phytolytic degradation of PCP.

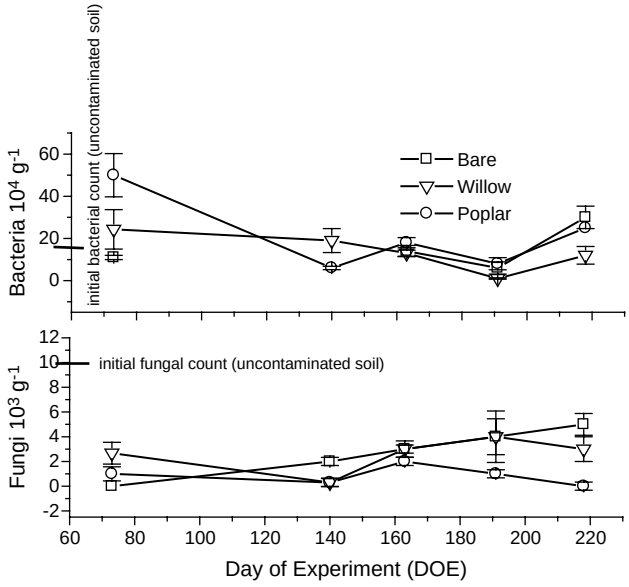

Fig. 4. The change in number of bacteria and fungi present in soil following contamination with PCP at 250 mg kg^{-1} PCP in soil. Error bars represent standard errors of the mean ($n=3$).

3.3. Soil microbial population demographics

Soil microbial populations are often influenced by the presence of contaminants in soil (Nichols et al., 1997; Kelly et al., 1999). Our uncontaminated topsoil had initial counts of 18×10^4 bacterial colonies, and 1×10^4 fungal colonies. Following addition of PCP-contaminated material one month before the commencement of the experiment (30 August 2002), the bacterial colony count remained at levels comparable to the uncontaminated soil at DOE 73 (Fig. 4). However, fungal colony counts were significantly reduced from 1×10^4 in uncontaminated topsoil to between 0 and 3×10^3 once soil was contaminated with PCP (Fig. 4). We might have expected a strong influence of PCP on soil fungal populations as it is an effective fungicide protecting timber against microorganisms responsible for rot and sap stain. Bacteria appear less sensitive to PCP contamination in soil. Other co-contaminants present in the mixture, including As, Cr, Cu and B appear to have a minimal effect on bacteria. Copper however is also a powerful fungicide, which may impact on soil fungal numbers. No consistent trend in either fungi or bacteria numbers were found for any treatment during the experimental period (Fig. 4). This may be due to the limitations in our ability to culture all colonies on the media selected for the dilution plate technique. Approximately, 1% of the soil bacterial population can be cultured by standard laboratory practices. It is not known if this 1% is representative of the bacterial population (Torsvik et al., 1998). Giller et al. (1997) estimate 1.5 million species of fungi exist worldwide but unlike bacteria, many fungi cannot be cultured by current standard laboratory methods (Thorn, 1997; van Elsas et al., 2000). Although molecular methods have been used to study soil bacterial communities, very little research has been undertaken for soil fungi (van Elsas et al., 2000).

Table 2
Total shoot and root dry weight biomass for poplar and willow poles growing in PCP contaminated soil

PCP Concentration (mg kg^{-1})	Plant	Total dry shoot weight for each treatment (g)	Total dry root weight for each treatment (g)
100	Poplar	5.352	18.103
	Willow	9.708	47.469
200	Poplar	2.881	14.30
	Willow	2.838	10.54
300	Poplar	3.902	3.59
	Willow	0	0
400	Poplar	0.394	0.636
	Willow	0	0
500	Poplar	0.353	0.326
	Willow	0	0

3.4. Poplar and willow tolerance to PCP and its co-contaminants in soil

Table 2 presents data illustrating the influence of PCP and its co-contaminants such as Cr, As, Cu and B on plant growth. As PCP levels increased total biomass production in both poplar and willow dropped significantly. Poplar appear more tolerant to PCP than willow. Both are able to survive, but not thrive, at concentrations of 200 mg kg^{-1} PCP. However, willows were unable to grow in soil contaminated with 300 mg kg^{-1} PCP or more. We therefore suggest that phytoremediation of PCP contaminated soil should use poplars rather than willows. Soil properties will influence plant sensitivity to PCP in soil. High clay and organic matter content may allow plants to tolerate higher PCP levels. Under our conditions the addition of 10% compost by volume did not allow either poplar or willow cuttings to survive 600 mg kg^{-1} PCP.

3.5. Column leaching experiment

A column leaching experiment was initiated following our observations of the planted pots after re-irrigation of leachate to the soil surface. Initially, irrigation applied to the pot surface quickly infiltrated the soil. However, following numerous applications of leachate, the solution began to pond and the soil appeared waterlogged. Our leaching experiments were conducted to establish whether or not soil clogging could have a detrimental effect on plant growth.

Fig. 5 shows the leachate flow rate declined in both 250 and 600 mg kg^{-1} PCP contaminated soil columns during the three successive leaching events. Each leaching event following the first event immediately followed the previous one to give a total leaching time of approximately 24 h through each column (Fig. 5). These data indicate soil clogging occurred when leachate was re-applied to the soil surface. Anaerobic conditions did not develop during this

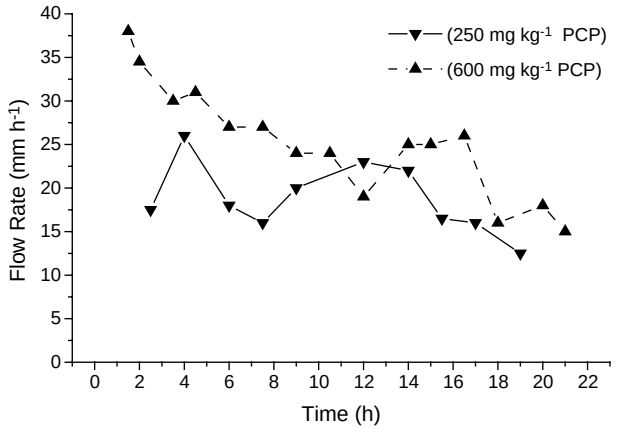

Fig. 5. Change in flow-rate of water and leachate through soil columns contaminated with either 250 mg kg^{-1} PCP or 600 mg kg^{-1} PCP in soil.

experiment as a positive redox potential was maintained in all leachate collected during the experiment (data not shown). However, continued leaching events might eventually result in the development of anaerobic conditions within the soil column.

The pH of the leachate solution remained between 6 and 7 throughout all leaching events in both columns. The first leachate collected from each column was more acidic than subsequent samples. At these pH levels, PCP is not ionised and therefore expected to be moderately bound to soil.

3.6. Heavy metal leaching

Boron, a mobile element and poorly absorbed by soils is therefore prone to leaching (Vogeler et al., 2001). In contrast arsenic, copper and chromium are characterised by low solubility in soil (Podlesákova et al., 2001, pg. 38) and should therefore pose less risk to groundwater or surrounding environments. Traces of B, Cu, Cr and As were detected in the soil and leachate of both columns (Tables 3 and 4).

Boron concentrations were reduced in the soil of both columns following leaching (Table 3). Boron levels in the leachate exiting the 600 mg kg^{-1} PCP column exceed the NZDWS (New Zealand Drinking Water Standard) of 1.4 mg L^{-1} (New Zealand Ministry of Health, 2000) but were below the NZDWS in the leachate from the 250 mg kg^{-1} PCP column.

For As, Cr, and Cu we recorded an increase in soil concentration following leaching of the 250 mg kg^{-1} PCP column. Copper and Cr within the soil of the 600 mg kg^{-1} PCP column showed a sight decline following leaching however As levels in the 600 mg kg^{-1} PCP column were higher in the final compared to initial values. These increase in metal concentrations may indicate that As, Cr and Cu were redistributed within the column profile during the leaching event in the 250 mg kg^{-1} PCP column and also in the 600 mg kg^{-1} PCP column for As. Isolated pockets within the column may have had had initial concentrations of Cr, As and Cu higher than those recorded for the bulk sample. It is likely that the contaminated soil/bark mixture had much higher concentrations of metals associated with bark fragments than the rest of the contaminant material. Arsenic, Cu and Cr are more likely to leach at high concentrations (As and Cr >400 mg $kg^{-1}$and Cu >150 mg kg^{-1} Podlesákova et al., 2001), but leaching of these recalcitrant metals is also dependent on other soil factors including pH and organic matter content. The presence of these metals within the leachate (Table 4) demonstrates that even at relatively low concentrations of metals in the bulk sample, leaching of metals can still occur.

Levels of Cu, Cr and As within the 2nd and 3rd leachate samples did not differ markedly from the first, indicating that metals in solution were probably at at equilibrium with the solid phase of the column.

Chromium was recorded at levels higher than the other metal co-contaminants within the unleached soil. Chromium is only sparingly soluble within soil (Kabata-Pendias and Pendias, 1992) and only low concentrations of chromium were recorded in the leachate exiting the column (Kabata-Pendias and Pendias, 1992). The NZDWS for Cr in drinking water is 0.05 mg L^{-1} (New Zealand Ministry of Health, 2000) and levels of Cr in the leachate do not exceed this (Table 4). Levels of Cr recorded in the captured leachate may however be phytotoxic for both poplar and willow, given that Cr can be taken up by plants and some plant species exhibit toxicity symptoms with Cr solution levels at 0.5 mg kg^{-1}. The concentrations of Cr within the column soil are relatively low compared to levels that may be present at a contaminated site. Armishaw et al. (1994) reports Cr levels of between 500 and 1500 mg kg^{-1} at CCA (copper, chromium, arsenic) contaminated sites in New Zealand.

Both B and Cu are essential plant elements, and Cr is a required element for both humans and animals (Kabata-Pendias and Pendias, 1992). Levels of B and Cu in the leachate from our column experiment are unlikely to be phytotoxic (Kabata-Pendias and Pendias, 1992). Despite its role in human and animal health and its relative immobility in soil, Cr toxicity in plants has been recorded. With Cr present in the leachate it may be readily taken up by plants

Table 3
Concentrations of metals in column soils before and after the leaching events (column length 170 mm)

Sample	Boron (B) (mg kg^{-1})		Copper (Cu) (mg kg^{-1})		Chromium (Cr) (mg kg^{-1})		Arsenic (As) (mg kg^{-1})	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
250 mg kg^{-1} PCP	1.7	1.0	3.1	3.4	18	27	3.0	7.0
600 mg kg^{-1} PCP	3.7	2.0	8.0	6.5	49	40	9.0	46.0

Table 4
Concentrations of metals in the leachate from columns contaminated with either 250 or 600 mg kg^{-1} PCP

Sample		Boron (B) (mg L^{-1})	Copper (Cu) (mg L^{-1})	Chromium (Cr) (mg L^{-1})	Arsenic (As) (mg L^{-1})
PCP (mg kg^{-1})	Leaching event				
250	1	0.83	0.05	0.01	0.02
	2	0.40	0.03	0.01	0.01
	3	0.78	0.02	0.01	0.02
600	1	2.86	0.07	0.03	0.01
	2	1.64	0.05	0.03	0.01
	3	2.62	0.06	0.03	0.01

growing in the soil used for our experiments, or alternatively leached to surrounding environments. If plant uptake of Cr has occurred it is likely that Cr will be retained in the roots of the plants and not translocated to leaves (Ma et al., 2003). Arsenic is not a required plant element, and may also be toxic to plants at levels recorded in the leachate. Our data show As levels in the leachate far in excess of those reported for naturally occurring As in soil solutions which range from 0.004 to 0.012 mg L^{-1} (Kabata-Pendias and Pendias, 1992, pg 35).

Values presented here align closely with data reported by Robinson et al. (2003) for leachate exiting a sawdust pile contaminated with Cu, Cr, As and B. Data on the accumulation of B, Cr, Cu and As in leaves are also presented by Robinson et al. (2003) and indicate that all 4 metals are taken up by plants but that As does not accumulate in the leaves. However, Cr does accumulate with 4.9 mg kg^{-1} DW Cr having been recorded in poplar leaves by Robinson et al. (2003). Normal leaf concentrations of Cr may be between 0.02 and 0.2 mg kg^{-1} DW ((Kabata-Pendias and Pendias, 1992). Copper, an essential plant element, is normally present in leaves. Values of Cu concentrations in poplar leaves growing in contaminated sawdust (Robinson et al., 2003) were not elevated, when compared to concentrations in plant leaves growing on uncontaminated material (Kabata-Pendias and Pendias, 1992). Robinson et al. (2003) also showed *B* is accumulated to high concentrations in poplar leaves ($B = 654$ mg kg^{-1} DW), well above B concentrations in leaves grown in uncontaminated soil. Despite high concentrations of B accumulating in poplar leaves, no toxicity symptoms have been noted. This suggests no phytotoxic effect. Our B leachate concentrations are similar as those reported by Robinson et al. (2003).

Table 5
Pentachlorophenol and tetrachlorophenol concentrations in leachate exiting the column

Sample		PCP mg kg^{-1}	TCP mg kg^{-1}
PCP mg kg^{-1} in soil	Leaching event		
250	1	13.5	0.8
	2	1.6	nd*
	3	1.1	nd
600	1	0.5	nd
	2	7.0	0.5
	3	6.1	0.5

*nd indicates substance not detected

3.7. PCP and semi-volatile organic compounds in column leachate

Both PCP and tetrachlorophenol (TCP) were present in leachate samples collected from the column leaching experiment (Table 5). Concentrations of tetrachlorophenol were low compared to PCP. This indicates little degradation of PCP under the column conditions. All other semi-volatile compounds tested were below detection limits, including creosote, a common co-contaminant at timber treatment sites. An oily film observed on the initial leachate sample collected from each column may have been oil or diesel but measurements of these specific compounds were not carried out. Variation in PCP and TCP levels recorded in the leachate from the two columns, with differing initial PCP concentrations, highlights the heterogeneous nature of PCP contaminated material in the soil. Depending on both organic matter and clay content, PCP and its related degradation products will have differing propensity to leach (Podlesákova et al., 2001). Despite soil and PCP contaminated material being well mixed, variation in PCP concentration within the column is still apparent. These variations are also illustrated by data presented in Tables 3 and 4 where levels of B, Cu, Cr and As are presented. They vary markedly between initial and final concentrations of metals in the soil of both columns.

4. Conclusions

Soil and water contaminated with pentachlorophenol and its associated co-contaminants are widespread. Often concentrations of PCP and metals are high (Armishaw et al., 1994) and this prohibits the use of plants to stimulate the natural degradation of organic compounds. However plants are able to tolerate PCP concentrations of 250 mg kg^{-1} or less. This would allow site remediation of large volumes of low-level contamination once ‘hot spots’, areas high in contaminant concentration, have been removed or diluted by mixing. Column leaching experiments indicate that PCP, Cr, As, B and Cu all leach from soils contaminated with the yard scrapings from timber

treatments sites. This highlights the requirement not only to remediate the site but also to 'seal' the site hydrologically and limit off-site contaminant migration (Mills and Robinson, 2003). Vegetation also prevents wind erosion whereas bare soil may be blown off-site. In order to keep the phytoremediation trees healthy, periodic fertiliser applications would be required. The addition of nutrients to the system would stimulate soil microbial activity but they may also lower the soil pH. This has implications for heavy metal mobility. Metals are more likely to leach under acid conditions. But PCP will be less likely to leach given acid soil conditions (Christodoulatos et al., 1994). We suggest soil pH levels be maintained close to neutral to ensure minimal metal leaching while still favouring the biodegradation of PCP and other organic compounds.

There is a common perception that if contaminants are bound to soil and therefore unable to either leach or be taken up by plants then they pose little environmental threat (Alexander, 1999). By using phytoremediation we not only protect surrounding soil and water from the effects of migrating compounds but the organic contaminants present will more rapidly degrade. The release of PCP and metal contaminants into the soil solution will fluctuate with time and prevailing environmental conditions. Bound compounds are released from decomposing organic matter and rainfall initiates drainage. Site monitoring of leachate is recommended as part of a long-term contaminated site management plan. The use of plants to 'seal' the site and remediate PCP contaminated sites requires careful management to ensure soil and plant health is retained. In using reticulation of captured leachate it would be necessary to ensure that the rates of reapplication do not irreversibly damage soil health and structure, and therefore limit plant health. This would become increasingly easy to manage as plants grow and their water-use increases.

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