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Toxicity of pulp and paper solid organic waste constituents to soil organisms

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ABSTRACT

This study examined the potential biological hazard of pulp and paper waste solids. The solids examined were chosen on the basis of the range of wood-related organic extractives and were either primary solids screened from the effluent stream before secondary treatment, or biosolids from aerated stabilisation lagoons. Acute effects were tested at the level of plants, invertebrates and soil microbes using an oat germination and growth test, earthworm survival and reproduction test, an enchytraeid worm survival and reproduction test, and standard measures of microbial respiration. This was further benchmarked against a marine bacteria toxicity test using extract of the waste solids. Resin acids and resin acid neutrals made up the greatest proportion of organic extractives measured in biosolids whereas resin acids and fatty acids were the main constituents detected in primary solids. Examination of the tissue of earthworms from the tests revealed no net bioconcentration of the organic extractives. The waste solids were not acutely toxic to any of the soil organisms as tested without any dilution. Conversely, extracts of the waste solids demonstrated toxicity in the marine bacteria. In some cases, the solid waste material enhanced the growth of plants, earthworm reproduction and microbial respiration. The only adverse affect was that reproduction of enchytraeids was reduced by some of the waste solid treatments. However these effects did not appear to be associated with concentrations of resin acid neutrals and resin acids in these materials. Overall pulp and paper wastes were relatively benign in terms of toxicity to the soil organisms tested.

1. Introduction

Over 300 million tonnes of wood fibre products are produced in the world each year (Blanco et al., 2004). The management of organic solid waste associated with this industry is an issue of global scale and significance. Environmental regulations such as those in Europe that prohibit the landfilling of organic waste have led to significant reductions in this practice since 1990 (Blanco et al., 2004). The New Zealand pulp and paper industry has traditionally used landfilling as the main means of disposal of solid wastes (Cameron et al., 1997), however government initiatives, consistent with greater awareness of environmental issues regarding disposal of industrial wastes, require industries to explore different solid waste management options (Ministry for the Environment, 2002).

Pulp and paper solid wastes may contain a wide range of potential contaminants and chemical composition should be characterised when considering land application. In New Zealand, the predominant furnish for pulp and paper mills is *Pinus radiata*. The effluents produced from these mills are high in resin acids, which are naturally occurring in conifer species. During secondary treatment of effluent (aerated stabilisation basins), resin acids can be biotransformed to resin acid neutrals, including retene, a polycyclic aromatic hydrocarbon (PAH) (Taverndale et al., 1997). Both resin acids and resin acid neutrals have been implicated in aquatic toxicity derived from pulp and paper mill discharges (Bogdanova and Nikinmaa, 1998; Billiard et al., 1999; Peng and Roberts, 2000). Waste solids can have much greater concentrations of resin acids and resin acid neutrals than the effluent they were derived from due to adsorption of these hydrophobic molecules to suspended solids (Taverndale et al., 1997).

Pulp and paper waste solids may provide a readily degradable source of carbon and supply significant quantities of nutrients to soil biota (Piearce and Boone, 1998). Nitrogen may be high or low in solids depending on their origin, and this will influence nitrogen availability when applied to soil (Catricala et al., 1996). Potassium, phosphorus, carbon and sulphur can also be available in beneficial amounts (Zibilske et al., 2000). There are a number of examples of beneficial effects on soil through land application of pulp and paper wastes (Kananan and Oblisami, 1990; Zibliske, 1997; Piearce and Boone, 1998; Jackson et al., 2000; Magesan

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and Wang, 2003) with little to no adverse impacts on terrestrial organisms (McCarthy et al., 2004; Bostan et al., 2005). However there are also studies showing detrimental effects in aquatic environments (Fragoso et al., 1998; Ali and Sreekrishnan, 2001; Jones et al., 2001) and to a lesser extent in the terrestrial environment (Palmer et al., 1998; Jordan et al., 2002), suggesting that land application of solid wastes be considered on a case by case basis (Bostan et al., 2005). As the relationships between contaminant bioavailability, treatment technology, the nature of pulp and paper residual solids, and resident organism tolerances has not been explored, investigation is warranted in order to relate measures of biological effect to the levels of compounds present in pulp and paper solid waste.

The primary objective of this study was to examine the hazard of pulp and paper-derived waste solids to a range of soil organisms using standard soil toxicity tests. Solid wastes with substantially different wood resin extractives concentrations were chosen in order to allow a preliminary association of contamination and effects. As a benchmark of acute toxicity, the responses of the soil organisms was compared to a bacterial toxicity test conducted on liquid phase extracts (using both water and ethanol as extractants) of the waste solids to evaluate potential toxicity of leachate from the wastes. This research further evaluated whether wood resin extractives, as constituents of pulp-mill waste solids, could bioaccumulate in earthworms. These wastes examined herein are similar to wastes produced in many other countries as pine species such as *P. radiata*, are widely used globally, as are similar wastewater treatment systems. The measured responses were intended to provide indications as to whether exposure to constituents of pulp and paper solid wastes were likely to cause harm to soil organisms and to determine what levels of the wood resin extractives present in the wastes may be detrimental to terrestrial organisms.

2. Materials and methods

2.1. Experimental design

Five different solid wastes were tested from two pulp and paper mills in the North Island of New Zealand. Both mills have primarily used *P. radiata* as the wood furnish, have aerated stabilisation basins for effluent treatment, and bleach with 100% chlorine dioxide substitution. Mill A has both kraft and thermo mechanical pulping (TMP) whereas Mill B exclusively uses kraft pulping.

There has been very little research conducted which specifically addressed the toxicology of pulp-mill wastes with respect to terrestrial organisms. This research endeavoured to provide some initial data on the acute responses of terrestrial organisms to pulp-mill solid wastes, which may be useful to focus further areas of investigation. Bioassays were chosen which were well represented in relevant literature and have been demonstrated as sensitive indicators of a range of organic contaminants in terrestrial (and aquatic – Microtox) systems. As the application scenario in New Zealand is to apply the solids materials directly to the surface without further incorporation (in layers up to 15 cm deep), and as there was limited literature to suggest the response of terrestrial organisms to pulp-mill solids, it was decided to initially expose selected organisms to undiluted material as a worst case scenario, and to further refine this exposure if effects were observed.

Chemical analysis (see below: measurement of pulp and paper wood resin extractives) of wood resin extractives for resin acids, fatty acids, sterols and resin acid neutrals (thought to be the main toxicants) were used to chose a number of wastes with differing contaminant characteristics. Wastes from Mill A included primary solids, washed primary solids, fresh biosolids, and aged biosolids (fresh biosolids that had been removed from the treatment system historically). In this paper the term 'biosolids' distinguishes 'secondary waste solids that have undergone biological treatment' from 'primary waste solids' (i.e. untreated solids). Primary solids were derived directly from the pulping process and were mostly composed of fibre lost during wood processing. The primary solids had a high content of untreated effluent (>80% moisture) and were obtained for the experiments following dewatering using a screw press. The washed primary solids from Mill A were washed with alkali (0.1 M NaOH) to remove readily soluble and acidic compounds, then flushed with water to remove chemical extractives and alkali. This treatment removed the majority of wood resin extractives from the primary solids and provided a reference primary waste material with low extractives content.

Fresh biosolids refers to those collected from a stabilisation lagoon which were drained (2 mm shade cloth inside a perforated container) for 14 d prior to use. Aged biosolids were solid wastes that had been dredged from aerated stabilisation lagoons, drained, and then stockpiled for approximately twelve months in a landfill area as part of normal waste disposal operations carried out at the mill. The fifth waste solid used in the experiments was from Mill B: 'K-Basin biosolids'. These were aged biosolids collected from a treatment basin that had been decommissioned and drained approximately two years previously. The difference between the Mill A aged biosolids and the aged K-Basin biosolids from Mill B reflects the differences in pulping processes between the two mills (see above), as well of the difference in waste outputs that enter the waste treatment systems (e.g. Mill B treatment system previously only received alkaline extraction stream bleachery and foul condensate streams whereas Mill A received integrated TMP/Kraft effluent). All solids had near to neutral pH's ranging from 6.8 to 7.5.

It was not possible to obtain "uncontaminated" waste solids to act as matched reference material for the waste solids described above. A silt loam soil (Templton silt loam – TSL) was used as a reference substrate. This soil was removed from a site where there was no known history of chemical contamination and had the following characteristics; 32% sand, 52% silt, 16% clay, 3.4% organic carbon content, pH 6.3. Biological responses of soil invertebrates and plants in this soil has been previously characterised (O'Halloran et al., 2005), hence it was used in these toxicity tests as a reference to evaluate any toxicity that may occur as a result of exposure to the pulp and paper mill solid wastes. Microbial community respiration was assessed using a loamy sand soil (Tarawera loamy sand – TLS), which matched soil from a related field study – Fraser et al. (2006) and had the following characteristics: 75% sand, 20% silt, 5% clay, 8% organic carbon, pH 5.5.

Maximum water holding capacity (WHC_{max}) of the silt loam reference soil (TSL) was 0.56 g water per dry g of soil (56% water content). This soil was used at approximately 60% WHC_{max} in the bioassays (33% water content). In contrast, the waste solids which had a much greater capacity for holding water (WHC_{max} ranged from 142% to 550% water content), were used in the tests at 80–90% of WHC_{max}, so as not to limit water availability to the test organisms. The WHC_{max} of the loamy sand soil (TLS) used as a reference in the basal respiration was 69% water content and was used at field moisture content (approximately 80% WHC_{max}).

2.2. Measurement of pulp and paper wood resin extractives in tissue and waste solids

The worms for organics analysis were removed from the toxicity tests after 28-d exposure, depurated for 48 h to clear stomach contents and frozen at −20 °C before freeze drying whole tissue. Freeze-dried whole earthworm tissue (from 20 individuals) or waste solids were ground with sodium sulfate, spiked with