

Stockton Mine Acid Mine Drainage and Its Treatment using Waste Substrates in Biogeochemical Reactors

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Abstract

Thirteen acid mine drainage (AMD) sites were monitored at Stockton Coal Mine near Westport, New Zealand to identify and quantify contaminants of concern and delineate their spatial and temporal variability. Metals (primarily Fe and Al) were the key contaminants and measured at concentrations exceeding off-site compliance targets or the Australia and New Zealand Environmental and Conservation Council (ANZECC) water quality guidelines. Dissolved metal concentrations ranged from 0.05-1430 mg/L Fe, 0.200-627 mg/L Al, 0.0024-0.594 mg/L Cu, 0.0052-4.21 mg/L Ni, 0.019-18.8 mg/L Zn, <0.00005-0.0232 mg/L Cd, 0.0007-0.0028 mg/L Pb, <0.001-0.154 mg/L As and 0.103-29.3 mg/L Mn and pHs ranged from 2.04-4.31.

Results of mesocosm-scale treatability tests showed that biogeochemical reactors (BGCRs) incorporating mussel shells, pine bark, wood fragments (post peel) and compost increased pH to >6.7 and sequestered ≥98.2% of the metal load from Manchester Seep AMD at the maximum recommended loading rates determined during this study (0.8 mol total metals/m³ substrate). An average of 20.0 kg/day (7.30 tonnes/year) of metals could be removed from Manchester Seep AMD employing BGCRs. Currently, this AMD is effectively treated further downstream by the Mangatini fine limestone dosing plant; however, in the interest of assessing more cost-effective technologies, this research investigated BGCRs as a passive treatment option.

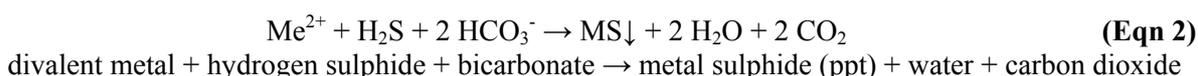
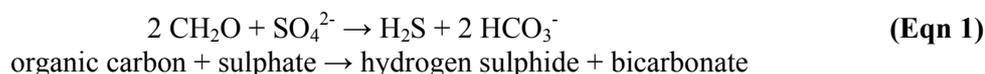
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acid mine drainage (AMD); Stockton Coal Mine; mine-water chemistry; biogeochemical reactors (BGCRs); geochemistry; vertical-flow wetlands (VFWs); biochemical reactors (BCRs); sulphate-reducing bioreactors

INTRODUCTION

The Brunner Coal Measures (BCM), which are present at Stockton coal mine, were geologically formed in a marginal marine setting and consist of carbonaceous mudstones, sandstones, and coal containing abundant sulphide and, subsequently, high acid-generating capabilities (Flores & Sykes 1996; Black et al. 2005; Trumm et al. 2005; Pope et al. 2006; this volume). Acidity generation and Fe release occurs during pyrite (FeS₂) oxidation and hydrolysis, which results from mining activities that expose pyritic overburden to atmospheric oxygen and water (Skousen 1996; Rose and Cravotta 1998; Watzlaf et al. 2004). Under acidic conditions, Al leaches from ubiquitous micaceous and feldspathic-rich rocks (Black et al. 2005) substituting H⁺ acidity for Al³⁺ Lewis acidity (Younger et al. 2002; Watzlaf et al. 2004). Other (divalent) metals such as Cu, Ni, Zn, Cd, As, Pb and Mn also dissolve from minerals present in the BCM (Weber et al., 2006), which causes a compounding metal mobility challenge.

Acid mine drainage (AMD) has impacted an estimated 125 km of freshwater streams throughout the West Coast of the South Island, New Zealand (James 2003). Consequently, stream biodiversity and ecological health have been significantly altered in these systems (Harding and Boothryd 2004; Harding 2005) and invertebrate taxonomic richness is significantly lower (Anthony 1999; Winterbourn et al. 2000). Water chemistry of AMD must be adequately characterised in order to recommend appropriate AMD treatment technologies. Therefore, AMD chemistry for numerous point sources at Stockton Coal Mine was ascertained before the suitability of passive treatment options could be assessed. One AMD seep (Manchester Seep) was chosen as a candidate site for conducting more extensive water chemistry monitoring and related mesocosm-scale treatability tests pertaining to the design and performance of biogeochemical reactors (BGCRs). Similar passive-treatment systems (often referred to as vertical flow wetlands (VFWs), sulphate-reducing bioreactors or biochemical reactors (BCRs) in other studies) showed success in neutralising acidity and sequestering metals from AMD (e.g. Gusek 2002; Gusek and Wildeman 2002; Rose and Dietz 2002, Gusek 2004; Watzlaf et al. 2004; Neculita et al. 2007). These systems typically contain porous media comprised mostly of organics and are sometimes amended with alkaline materials such as limestone or, unique to this study, mussel shells, an industrial by-product with significant acid neutralisation capacity. The primary mechanism associated with divalent metal removal in these systems is often documented as precipitation of metal sulphides during sulphate reduction (Sheoran and Sheoran 2006; Neculita et al. 2007). Stumm and Morgan (1981) summarise these typical chemical reactions (Eqns 1 and 2).



Numerous other biogeochemical processes are also responsible for metal removal in these systems including precipitation or co-precipitation as hydroxide complexes, sulphides, carbonates, silicates or sulphates and sorption to organic matter, carbonates, other metal precipitates or other solid residuals such as sediment (Waybrant et al. 1998; Gusek 2002; Gibert et al. 2003; Zagury et al. 2006). Aluminium, a trivalent metal, was reportedly removed predominately as aluminium hydroxysulphates in VFWs comprised of compost and limestone treating AMD (Thomas and Romanek 2002a).

MATERIALS AND METHODS

Acid Mine Drainage Sampling Locations

Thirteen AMD sites were monitored at Stockton Mine (Fig. 1) during the initial stages of this study to characterise and quantify contaminants of concern in the water and delineate their spatial and temporal variability. A GoogleTM Earth image, showing the AMD sampling locations with respect to their receiving catchments, is presented in Fig. 2. An investigation into AMD sites at Stockton Mine was essential to identify suitable locations for implementing passive treatment technologies. Without conducting water quality and some topographical investigations of each candidate site, passive treatment systems are not recommended. They typically incur larger footprints than an active lime-dosing plant and their effectiveness can be compromised by changing water chemistry affected by upgradient land disturbances.

Acid mine drainage sites sampled initially for three months included Whirlwind Tributaries A, C and D, which drain into the Waimangaroa River. The Whirlwind Tributary A seep daylighted at the base of an overburden embankment, which collected into Pond A1. Water from Pond A1 permeated through a dam embankment into Pond A2 before plummeting down a steep topographic gradient. Whirlwind Tributaries C and D both daylighted at the toe of a dam embankment. The complex hydrogeology associated with these potential treatment areas, proximity of the seeps to an AMD-impacted dam and challenging equipment access deemed these sites as unsuitable for BGCRs so monitoring was discontinued. The A Drive Seep (monitored once) was also excluded as a candidate site due to minimal treatment area in the vicinity. C Drive consisted of two seeps that daylighted on

the side of a slope and drained into a flat area consisting of numerous hydraulically-connected ponds. This area underwent rehabilitation efforts during this study, which was not conducive to the project timeframe, so its monitoring was discontinued. The Collis Seeps consisted of three seeps, which daylighted at the toe of a rehabilitated overburden stockpile and flowed into the same drainage channel. Because of minimal and intermittent flow, Collis Seep 2 was not monitored as part of this study. Monthly monitoring of the Collis Seeps was terminated when it was discovered that metal concentrations would likely exceed the capacity of effective BGCR operation and that available treatment area was inadequate.

Manchester Seep daylighted at the toe of an overburden embankment as a series of braided seeps draining into a flow-equalisation pond (Manchester Pond). Their metal concentrations and pH were conducive for trialling passive treatment. This seep water was also not expected to be influenced by present or future mining activities that could impact its water chemistry. Ample treatment area was available to construct pilot or full-scale treatment systems. Therefore, Manchester Seep was chosen as the most suitable research site for evaluating the performance and feasibility of BGCRs to immobilise metals from its AMD water. Monthly chemistry and flow monitoring was conducted for ten months at this site to assess temporal water chemistry and flow variations over all seasons.

Sample Collection and Water Chemistry Analysis

Surface-water samples were collected following applicable criteria denoted in the Australian and New Zealand Environment and Conservation Council (ANZECC) Water Quality Guidelines (2000). Samples were collected head-space free from surface water either directly in method-specified containers or from a decontaminated 50 mL syringe and then transferred into method-specified containers. Samples were chilled at 2-6°C immediately upon collection until the time of analysis following appropriate criteria specified in APHA (1998).

Dissolved metals samples were analysed by RJ Hill Laboratories Limited using ICP-MS by APHA Method 3125B (APHA, 1998). Samples were filtered during sample collection with 0.45 µm nitrocellulose filters encapsulated in a Pall 47 mm polycarbonate in-line filter holder and preserved with 1:1 nitric-acid to reduce pH to less than 2.0. Sample pH was measured *in-situ* using a YSI Model 60 pH meter field calibrated with pH 4.01 and 7.00 standards (and pH 10.00 standard when applicable) and checked with a pH 1.68 standard.

Flow Measurements

Flow was typically monitored monthly from the Manchester and Collis Dump Seeps using the bucket and stopwatch method. A minimum of five replicates were taken and averaged to determine mean flow during each event.

Water Quality Guidelines and Ecotoxicology

The ANZECC water quality guidelines present “trigger values” that represent concentrations for various contaminants that may be deleterious to the biota of freshwater aquatic ecosystems. These trigger values represent generic effects-based guidelines and are not legally binding compliance levels. Separate values are established at levels of protection including 80%, 90%, 95% and 99%, which signify the percentage of aquatic species expected to be protected at designated contaminant concentrations. The 80% level of protection typically applies to the most disturbed ecosystems such as mine sites; however, they often do not represent site-specific ecotoxicity since most are established based on ecotoxicity tests performed on species present outside of New Zealand and therefore only represent a first indication of whether or not ecosystem perturbation is probable (Niyogi and Harding 2007; O’Halloran et al. 2008). Hardness-dependent algorithms are also provided for calculating thresholds of Cd, Cu, Pb, Ni and Zn toxicity. These guidelines are most applicable to the dissolved metal fraction since this proportion is bioavailable. ANZECC (2000) states that there is “insufficient data” to establish trigger values for Fe and Al (pH<6.5). Current discharge compliance at the Stockton

Mine research site is stipulated to achieve an Al concentration <1 mg/L 99% of the time (off the mine site boundary at the confluence of the Mangatini Stream and Ngakawau River; Fig. 2) based on localised ecotoxicological data such as that reported in Niyogi and Harding (2007) and O'Halloran et al. (2008). To achieve this, a $\text{pH} \geq 4.7$ is typically targeted to precipitate Al. Compliance for future mine sites within the Brunner Coal Measures may require Fe concentrations ≤ 3 mg/L based on localised ecotoxicological studies. The ANZECC water quality guidelines also specify values applicable to contact recreation; however, values specified for the protection of freshwater biota are typically more stringent and applicable to this study.

Mesocosm Biogeochemical Reactor Treatability Tests

Mesocosm-scale treatability tests were performed in a laboratory set-up measuring the effectiveness of seven continuous flow BGCRs for treating Manchester Seep AMD shipped from Stockton mine. Biogeochemical reactor substrates included a mixture of industrial waste products (Table 1) derived from forestry/timber including organic bark (*Pinus radiata*), post peel (untreated by-product from fence post manufacture) and bark compost as well as alkaline materials including limestone, mussel shells (from mussel farming) and nodulated stack dust (NSD) (from cement manufacturing). Two different bioreactor dimensions (337 L trapezoidal containers (440 mm substrate depth) and 138 L cylindrical drums (562 mm substrate depth)) were established. Biogeochemical reactors containing the same substrate mixtures (P2: drum and S4: trapezoidal) were tested to ascertain how reactor shape and substrate depth influenced treatment performance.

The BGCRs were downflow systems with AMD feed at the upper surface and effluent discharge at the bottom outlet. Masterflex peristaltic pumps were used to control and convey AMD into each BGCR at designated flow rates. Influent AMD flow rates were increased incrementally throughout the experiment to test the limits of efficient operation of each BGCR. Influent and effluent sampling was typically conducted on a weekly or biweekly basis and prior to increasing AMD flow rate. Water elevation in each reactor was controlled by adjusting the height of the outlet tubing. Separate pumps were used for trapezoidal and drum reactors due to their differences in substrate volumes, and consequently, design flow rates. Water level was maintained at about 50 mm above the upper substrate surface. Further details about the experimental set-up and treatment efficiencies of these mesocosm-scale systems, which were operated for nearly four months, has been discussed (McCauley et al. 2008; McCauley et al. 2009).

RESULTS

Results from monitoring AMD sites indicated variability in water chemistry at Stockton. Low pH (ranging from 2.04 (Collis Seep 1) to 4.31 (Whirlwind Pond A2)) was prevalent. Metal contaminants were primarily Fe and Al, with Cu, Ni, Zn, Cd, As, Pb and Mn of lesser concern, which are common in AMD derived from pyritic overburden and sulphurous coal.

pH

The primary importance of measuring pH pertains to its influence on metal dissolution and its direct impact on aquatic biota. A summary of pH values measured during this study are presented as Fig. 3. Sample pH values were variable spatially and temporally and followed similar trends to metal concentrations. For example, log molar metal concentration-pH associations showed good linear relationships with coefficient of determinations (R^2) of 0.97 for Fe, 0.83 for Al and 0.95 for the summation of Fe and Al concentrations (plots not presented). Sample pH values were as low as 2.04 (Collis Dump Seep 1) and as high as 4.31 (Whirlwind Pond A2 (WWA Pond 2)) but were typically <3.8 . The most temporal variability was measured at the Manchester Seep (range of 2.49-3.34; median=2.81) and Whirlwind Pond A2 (range of 3.46 to 4.31; median=4.05), which was highly influenced by surface water runoff. Variability at Manchester Seep AMD was likely a consequence of the number of times it was sampled (12) compared to other AMD sites (1-5) and, therefore, may offer a better representation of temporal variability compared to other monitoring sites.

Metals

The primary metal contaminants in AMD were Fe and Al (Fig. 4), which commonly accounted for over 98% of metal loading at each sampling location. Secondary metal contaminants included Cu and Ni (Fig. 5), Mn and Zn (Fig. 6) and; Pd, Cd and As (Fig. 7), which were measured at concentrations exceeding the ANZECC trigger values for 80% level of protection in a freshwater aquatic ecosystem. For metals where hardness dependent algorithms are established (Cd, Cu, Pb, Ni and Zn), trigger values are shown assuming hardness values of 30 (low hardness) and 90 (moderate hardness) mg/L as CaCO₃. With exception of the Collis Seeps, which contained extremely high hardness (1180-1710 mg/L as CaCO₃), average AMD hardness ranged from 6.99 mg/L as CaCO₃ (Whirlwind Pond A2) to 75.5 mg/L as CaCO₃ (Manchester Pond) so were very low to moderate. Thus, effective protection afforded to biota based on ANZECC trigger values would require lower metal concentrations than typically found in the AMD waters at Stockton. For example, 80% of species are not protected from Ni “toxicity” at any of the AMD locations with exception of Whirlwind Pond A2 (WWA Pond 2) as shown in (Fig 5).

There was substantial spatial variability in metal concentrations across AMD locations sampled. For example, dissolved Fe concentrations ranged from 0.31 mg/L (Whirlwind Tributary C) to 1430 mg/L (Collis Dump Seep 1), which represents a difference of over three orders of magnitude (Fig. 4). Dissolved Al ranged from 3.22 mg/L (Whirlwind Tributary C) to 627 mg/L (Collis Dump Seep 1), a difference exceeding two orders of magnitude (Fig. 4). Of the other metals analysed, Cu and Ni (Fig. 5) and Zn (Fig. 6) commonly exceeded the 80% ANZECC trigger values, while Pb only exceeded the ANZECC trigger value from one sample collected from Manchester Seep (Fig. 7). Arsenic was measured at elevated concentrations only from Collis Seep 1 and downstream thereof (Collis DS), whereas Cd exceeded ANZECC trigger values from both Collis Seeps and Manchester Seep (Fig. 7).

Overall, metal concentrations were greatest at the Collis Seeps followed by the Manchester Pond and Seep. Metal concentrations from Whirlwind Tributary A and Pond A1 were greater than the C Drive Seeps, which were greater than Whirlwind Tributaries C and D. The lowest metal concentrations were measured from Whirlwind Tributary Pond A2, likely due to dilution from non-AMD influenced surface water runoff. High metal concentrations at the Collis Seeps were attributed to recent rehabilitation earthworks that exposed pyrite-containing overburden to atmospheric oxygen resulting in the release of proton and metal acidity. Metal concentrations in the other AMD seep waters were dependent on site-specific geology and related past mining activities.

Although metal concentrations were elevated at the AMD sites investigated during this study, they do not give a true indication of the water quality leaving the site. Solid Energy New Zealand Limited has installed and is progressing with treatment options for all AMD generated at Stockton. Solid Energy New Zealand Limited currently mitigates AMD at Stockton via minimisation (e.g. capping mine pits and overburden dumps) and treatment by means of the the Mangatini fine limestone dosing plant, which achieves treatment goals of <1 mg/L Al during 99% of observations at the confluence of the Mangatini Stream and Ngakawau River (Davies et al. 2008; this volume). Further treatment solutions such as this papers work are being investigated.

Metal Loading

Metal loading rates are useful measures for quantifying metal contributions from AMD to receiving water bodies and thus in prioritising AMD treatment. Total metal, Fe and Al loading rates were calculated for the Manchester Seep, the Manchester Pond and Collis Seeps (Seeps 1 and 3 summed). A summary of flow rates and metal loading rates for these sites are given in Table 2. The highest metal loading rates calculated from each AMD source typically correlated with the greatest flow rates (e.g. R² of 0.74 for Manchester Seep and 0.92 for the Collis Seeps). Flow and loading rates followed similar temporal trends from the Manchester and Collis Seeps during the sampling period May to October 2006. Although flow from the Collis Seeps was three to nine times less than flow from the Manchester Seep, its metal loading rates were always greater due to higher metal concentrations. Metal loading rates were less from the Manchester Seep compared with the outlet of the Manchester Pond, which was likely attributed to dissolution of Fe and, to a lesser extent, Al from sediment in the pond. A

sediment sample collected from the pond contained 45.1% Fe and 16.9% Al, which probably contributed towards the higher metal loading from Manchester Pond.

Mesocosm Biogeochemical Reactor Treatability Tests

Influent (AMD) and BGCR effluent Fe and Al concentrations at metal loading rates ranging from 0.23-0.83 mol total metals/m³ substrate/day are given in Fig. 8. Biogeochemical reactors containing 20-30 vol.% mussel shells (P1, S2 and S3) showed the best metal removal for each respective reactor shape (McCauley et al. 2008; McCauley et al. 2009). Metal removal was also good for P3 (containing NSD), but its effluent pH was 9.0-10.5, and therefore considered too caustic for discharge to a freshwater ecosystem so was eliminated from further study. Biogeochemical reactors containing limestone (especially S1) showed the least effective metal removal. The P2 reactor containing 12 % mussel shells and 5 % limestone outperformed S4, the larger trapezoidal reactor with the same substrate complement, indicating cylindrical drum reactors (562 mm substrate depth) perform better than trapezoidal reactors (400 mm substrate depth) for this BGCR design. Metal removal in S2 and S3 (both contained 20 vol.% mussel shells) was similar throughout this study except at the highest loading rates tested of 1.4 mol metals/m³ substrate/day (McCauley et al. 2008). Metal removal from S2 was less than that of S3 at the highest metal loading rates tested, possibly due to increased hydraulic short circuiting caused by the higher percentage of flat, plate-like bark.

Dissolved metal concentrations in the influent (AMD) and BGCRs effluent, along with their calculated removal efficiencies, at metal loading rates of 0.23 to 0.83 mol/m³ substrate/day for systems containing 20-30 vol.% mussel shells (P1, S2 and S3), are shown in Table 3. These systems demonstrated the best metal removal of the feasible options and would likely be candidates for upscaling to pilot or full-scale treatment systems. Metal removal was most effective for Al, Cu, Ni, Zn, Cd and Pb (>98.3-99.9%), but a substantial amount of Fe (96.5-99.8%) was also removed. There was an average net export of 20.8% Mn from the BGCRs indicative of Mn dissolution from substrate materials (McCauley et al. 2009). Since manganese sulfide (MnS) is highly soluble and not expected to form under reduced conditions (Gusek 2002; Watzlaf et al. 2004), it was not expected to be removed in these BGCRs.

DISCUSSION

Water Chemistry

Results of this study demonstrated highly variable AMD water chemistry at Stockton Mine. Metal concentrations varied by about three orders of magnitude between sample locations, while pH values varied by >2.0. Variability was attributed to geological heterogeneity, mining management practices, the prevalence of acid producing rocks and the degree of overburden exposure to atmospheric oxygen and water.

Pope et al. (2006; this volume) detailed mine-impacted water (MIW) chemistry from opencast and underground coal mines in the Brunner Coal Measures (present at Stockton Mine). Iron and Al concentrations and pH from surface waters impacted by coal mining on the West Coast of the South Island in New Zealand are summarised in Table 4. This data shows significant variability in MIWs chemistry with pH spanning five pH units and Fe and Al concentrations differing from three to five orders of magnitude between sites. Data from Whirlwind (tributary unspecified), A Drive and C Drive were also reported in Pope et al. (2006). These results were generally comparable with those measured during this study, which could indicate that spatial variability in AMD chemistry at Stockton is more prominent than temporal variability. The most significant difference between the studies was the pH measured at C Drive which was 3.76 during this study and 3.23 reported in Pope et al. (2006), although Fe concentrations were similar and Al concentrations were 36% greater in this study. Despite chemical variability in AMD across sampling locations, metal concentration and pH relationships strongly correlated indicating that metal dissolution was a result of sulphuric acid produced during pyrite oxidation and hydrolysis.

Pope et al. (2006; this volume) delineated water chemistry based on coal mining impacts from opencast and underground mines and as a function of geology. There was generally a higher Al:Fe

concentration ratio in opencast mines compared with underground mines. This was due primarily to the greater disturbances of overburden and sediments in open mine pits, which allow greater reaction time of AMD with Al-containing minerals (Pope et al. 2006; this volume). Newman (1988) and Pope et al. (2006; this volume) also report that sediment surrounding coal seams is often feldspar depleted and contain less Al compared with sediments further from the coal seams. During underground mining, most sediment disturbance occurs near the coal seam(s), whereas overburden extracted during open-pit mining includes sediment further from the coal seam(s). The exposure of Manchester Seep AMD to sediment as it flowed through the Manchester Pond resulted in an average Fe concentration increase of 36.2% and Al concentration increase of 19%, which shows the influence of greater reaction time of AMD with sediment.

Mesocosm Biogeochemical Reactor Treatability Tests

Overall, treatment performance of the BGCRs exceeded design criteria recommended for similar systems; however, most other systems incorporated limestone as the primary alkalinity amendment whereas this study utilised mussel shells. Wildeman et al. (2006) recommended design criteria of 0.3 moles of metal removal/m³ of substrate/day for SRBRs containing a mixture of organic materials and crushed limestone, which is comparable to the removal rates measured from BGCR S1 in this study (containing similar reactor substrate media including limestone as an alkalinity amendment). This study found metal removal >0.8 moles/m³ substrate/day for BGCRs containing 20-30 vol.% mussel shells (McCauley et al. 2008; McCauley et al. 2009). Effluent pH was also typically >6.7.

Assuming adequate treatment areas are accessible, BGCRs of this design could treat all AMD monitored in this study (with potential exception of Collis Seeps) to discharge compliance levels or to concentrations below ANZECC trigger values (Table 3; Figs. 4-7). Gusek and Wildeman (2002) performed bench-scale treatability tests utilising SRBRs to treat AMD averaging 370 mg/L Fe and 178 mg/L Al, which is slightly more benign compared with the Collis Seeps. Effluent concentration ranges from five different SRBRs utilising different substrate mixtures were 3.7-47.5 mg/L Fe and 0.21-0.67 mg/L Al. Based on results of the Gusek and Wildeman (2002) study, it can be expected that AMD from the Collis Seeps could be treated with a BGCR; however, the treatment from a single BGCR may not be adequate to achieve compliance targets and there is a risk of the system clogging with aluminium hydroxide (Al(OH)₃) or, to a lesser extent, ferric hydroxide (Fe(OH)₃) precipitate, which would require mitigation via regular maintenance.

There has been little research on the implementation of BGCRs or similar passive-treatment systems in New Zealand for AMD treatment. Trumm et al. (2005; this volume) summarised AMD chemistry and results from short-term mesocosm field studies for remediating AMD from Sullivan Mine, an abandoned underground coal mine within the Brunner Coal Measures, and Pike River (refer to Trumm et al. (this volume) for a comparison of results). In general, results of this study showed better (or comparable) metal removal rates and efficiencies with those presented by Trumm et al. (2005; 2008; this volume) and others (e.g. Gusek 2002; Thomas and Romanek 2002b; Gusek and Wildeman 2002; Rose and Dietz 2002; Gusek 2004; Watzlaf et al. 2004; Reisman et al. 2008). Better removal efficiencies and rates demonstrated in this study likely resulted from using mussel shells as alkalinity amendments instead of limestone. Factors including mineralogy, shape, size and reactive surface area of the mussel shells could have contributed to their greater dissolution rates compared with limestone used in other studies.

Potential Metal Load Reduction from AMD Treated with Biogeochemical Reactors

The BGCRs sequestered nearly 99% of total metals from Manchester Seep AMD. A summary of total metal, Fe and Al quantities that would be removed from Manchester Seep, Manchester Pond and Collis Seeps with BGCRs assuming loading rates and removal efficiencies measured during this study (Table 2 and 3) are summarised in Table 5. Biogeochemical reactors have the potential to sequester a substantial amount of metals from the Manchester and possibly Collis Seeps reducing the metal load conveyed into the Mangatini Stream and Ngakawau River. Assuming the BGCRs were implemented to treat Manchester Pond and Collis Seep effluent, a total of 25.7 tonnes of metals including 17.9 tonnes of Fe and 7.4 tonnes of Al could potentially be sequestered per annum. In the interim, AMD

within the Mangatini Catchment is treated by the Mangatini fine limestone dosing plant, which achieves company and community environmental goals of pH >4.0 and < 1 mg/L Al 99% of the time; however, this research has demonstrated that BGCRs are a potential alternative for treating AMD from select seeps.

Conclusions

Results of this study indicated that AMD chemistry was variable on a spatial and temporal basis at Stockton coal mine (by up to three orders of magnitude for major metal contaminants). Despite the variability, Fe and Al were consistently the primary metals of concern (accounting for >98% of metal loading) with Cu, Ni, Zn and Cd considered secondary pollutants of concern, which typically exceeded ANZECC trigger values for protection of 80% of freshwater aquatic species. Although metal concentrations were elevated at the AMD sites evaluated during this study, these are not a true indication of the quality of water leaving the mine site. Currently, this AMD is effectively treated further downstream by the Mangatini fine limestone dosing plant, and Solid Energy New Zealand Limited is progressing with and considering other treatment options for mitigating AMD.

Results of mesocosm-scale BGCRs incorporating industrial waste products as alkaline and carbon substrate materials were successful at neutralising Manchester Seep AMD and sequestering metals (Fe, Al, Cu, Ni, Zn, Cd and Pb) to compliance levels. Design criteria for bioreactors incorporating 20-30 vol% mussel shells was established at >0.8 mol metals/m³ substrate/day, which was about three times greater than similar systems employed overseas that utilised limestone instead of mussel shells.

The BGCRs can likely be employed to treat AMD waters evaluated here with possible exception of the Collis Seeps, which contained metal concentrations that were an order of magnitude greater than that of any other AMD water sampled as part of this study; however, adequate land availability, site topography, equipment accessibility and operational management (including awareness and mitigation of current and future planned mining activities) are required for successful implementation. Suspended solids inherent at any active mine site should not be conveyed to BGCRs. Instead, mitigating sediment transport through settling ponds and pre-treating any AMD that may incur large suspended solid loads, is recommended.

Although BGCRs may not be feasible for treating all AMD-impacted waters, they do have application as a more cost-effective treatment alternative to traditional lime-dosing systems, especially for abandoned and decommissioned mine sites. Overall, water quality discharging from BGCRs should treat most AMD waters substantially and improve biodiversity and ecological health of the receiving water body. Based on results of this study, there is potential to remove an average of 8.97 tonnes of total metals, 6.49 tonnes Fe and 2.38 tonnes Al per annum if BGCRs were employed to treat AMD discharging from the Manchester Pond.

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Figure Captions

Fig. 1 Stockton Mine project site location (West Coast, South Island, New Zealand) (from MapToaster Topo 2007).

Fig. 2 Location of AMD seeps sampled at Stockton Coal Mine and the catchments they drain into including the Waimangaroa River, Mangatini Stream and Ngakawau River (aerial photo from Google Earth (2009)).

Fig. 3 pH ranges from AMD sample locations at Stockton Mine. The variable n represents the number of observations from each sample location. Median concentrations are displayed when $n \geq 3$.

Fig. 4 Dissolved Fe and Al concentration ranges from AMD sample locations at Stockton Mine. The variable n represents the number of observations from each sample location. Mean concentrations are displayed when $n \leq 2$. Median concentrations are displayed when $n \geq 3$. Bolded horizontal lines delineate compliance targets at the confluence of the Mangatini Stream and Ngakawau River.

Fig. 5 Dissolved Cu and Ni concentration ranges from AMD sample locations at Stockton Mine. The variable n represents the number of observations from each sample location. Mean concentrations are displayed when $n \leq 2$. Median concentrations are displayed when $n \geq 3$. Bolded horizontal lines delineate ANZECC trigger values for protection of 80% species. The ANZECC trigger values for Cu and Ni are hardness dependent.

Fig. 6 Dissolved Mn and Zn concentration ranges from AMD sample locations at Stockton Mine. The variable n represents the number of observations from each sample location. Mean concentrations are displayed when $n \leq 2$. Median concentrations are displayed when $n \geq 3$. Bolded horizontal lines delineate ANZECC trigger values for protection of 80% species. The ANZECC trigger value for Zn is hardness dependent.

Fig. 7 Dissolved Pb, Cd and As concentration ranges (hanging bar graphs) from AMD sample locations at Stockton Mine. The variable n represents the number of observations from each sample location. Mean concentrations are displayed when $n \leq 2$. Median concentrations are displayed when $n \geq 3$. Bolded horizontal lines delineate ANZECC trigger values for protection of 80% species. The ANZECC trigger values for Cd and Pb are hardness dependent. The PQLs were 0.001 mg/L As, 0.0005 mg/L Pb and 0.00005 mg/L Cd.

Fig. 8 Influent (AMD) and effluent (P1, P2, P3, S1, S2, S3 and S4) dissolved Fe and Al concentrations from mesocosm-scale treatability tests during metal loading rates from 0.23 to 0.83 mol/m³ substrate/day. Horizontal black lines represent median Fe and Al concentrations. P signifies BGCRs comprised of drums. S denotes trapezoidal-prism shaped BGCRs.

Table 1 Biogeochemical reactor substrate compositions (vol. percent).

	S1	S2	S3	S4	P1	P2	P3
	<i>Trapezoidal Containers - 337 L</i> (Substrate Depth – 440 mm)				<i>Cylindrical Drums - 138 L</i> (Substrate Depth – 562 mm)		
Limestone	12.5	0.0	0.0	5.0	0.0	5.0	2.5
Mussel Shells	0.0	20	20	12	30	12	12
NSD	0.0	0.0	0.0	0.0	0.0	0.0	5.0
Bark	35	40	30	30	30	30	30
Post Peel	37.5	25	35	38	25	38	35
Compost	15	15	15	15	15	15	15

Table 2 Flow rates and calculated metal loading rates from the Manchester Seep, Manchester Pond and the Collis Seeps. Loading rates from the Collis Seeps were computed from either the summation of Collis Seeps 1 and 3 or from the drainage channel directly downstream of the seeps. Data represents mean loading rates \pm standard deviations with the data ranges specified below in parenthesis. The number of observations (n) were: 11 for the Manchester Seep; 4 for the Manchester Pond Outlet; and 5 for the Collis Seeps.

	Manchester Seep	Manchester Pond	Collis Seeps
Flow Rates (L/s)			
Flow	2.36 \pm 2.44 (0.34-10.5)	1.50 \pm 0.48 (0.87-2.00)	0.33 \pm 0.14 (0.15-0.53)
Loading Rates (kg/day)			
Total Metals	20.2 \pm 18.2 (0.44-57.1)	24.8 \pm 9.01 (16.7-31.2)	46.1 \pm 14.7 (27.3-63.4)
Fe	14.7 \pm 15.0 (0.13-45.3)	18.1 \pm 17.5 (11.2-25.1)	31.8 \pm 10.3 (18.4-43.8)
Al	5.26 \pm 3.26 (0.31-11.0)	6.53 \pm 1.72 (5.09-8.87)	13.8 \pm 4.25 (8.59-18.9)

Table 3 Measured pH and influent (Manchester Seep AMD) and effluent dissolved metal concentrations and calculated removal efficiencies from BGCRs containing 20-30 vol.% mussel shells (P1, S2 and S3) at metal loading rates of 0.23-0.83 mol/m³ substrate/day. Data are median concentrations or removal efficiencies with ranges denoted in parentheses. Removal efficiencies for total metals is based on removal of the summation of all metals analysed during this study with exception of Mn, which accounted for <1.0 % of metals in AMD. The number of observations (n) was 21.

	AMD Conc. (pH units or mg/L)	Effluent Conc. (pH units or mg/L)	Removal Efficiency (%)
pH	2.57 (2.51-2.70)	6.71 (6.58-6.89)	NA
Fe	78.4 (54.9-107)	1.04 (0.120-3.46)	98.3 (96.5-99.8)
Al	53.6 (49.6-69.7)	0.031 (0.0170-0.277)	99.9 (99.5-99.9)
Cu	0.209 (0.145-0.272)	<0.0005 (<0.0005-<0.001)	99.9 (<99.7->99.9)
Ni	0.230 (0.187-0.296)	0.001 (<0.0005-0.0020)	99.7 (99.3->99.7)
Zn	1.27 (1.03-1.55)	0.002 (<0.001-0.005)	99.9 (99.7->99.9)
Cd	0.00186 (0.00155-0.00236)	<0.00005 (<0.00005-<0.00005)	98.5 (>98.3-98.9)
Pb	0.0152 (0.0090-0.0284)	<0.0001 (<0.0001-0.0001)	99.7 (99.5->99.7)
Total Metals	NA	NA	98.9 (97.7-99.9)

NA, non-applicable.

Table 4 Water chemistry from seeps and streams impacted by coal mining in New Zealand. Values shown are medians with ranges shown in parenthesis below median values. The variable n represents the number of observations from each sample location. Values from this study are based solely on median concentrations (or averages if n≤2) shown in Figs. 3 and 4.

Mine Type	n	pH	Fe (mg/L)	Al (mg/L)
This Study – Stockton Mine				
Opencast	11-12	3.13 (2.15-4.05)	5.59 (0.09-1410)	17.9 (0.459-607)
Pope et al. (2006) – Brunner Coal Measures				
Opencast	17	3.01 (2.60-5.85)	2.89 (0.56-43.3)	12.3 (0.021-115)
Underground	19-20	2.91 (2.41-3.79)	15.7 (0.91-134)	12.7 (0.21-216)

--, data parameters not measured.

Table 5 Total metal, Fe and Al that would be removed from Manchester Seep, Manchester Pond and the Collis Seeps by BGCRs based on results of the mesocosm-treatability tests. Results presented assume mean loading rates computed during this study. Removal efficiencies used to compute metal removal were based on the median removal rates shown in Table 3 for BGCRs containing 20-30 vol. % mussel shells within their substrate mixture (P1, S2 and S3).

	Manchester Seep	Manchester Pond	Collis Seeps
kg/day			
Total Metals	20.0	24.6	45.6
Fe	14.5	17.8	31.3
Al	5.26	6.52	13.8
tonnes/year			
Total Metals	7.30	8.97	16.7
Fe	5.29	6.49	11.4
Al	1.92	2.38	5.04