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Mobilisation and attenuation of boron during coal mine rehabilitation, Wangaloa, New Zealand

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Abstract

Environmental mobility and fate of boron has been traced from source to discharge waters through the rehabilitated Wangaloa coal mine in southern New Zealand. The boron is derived initially from coal, which has up to 450 mg/kg B. The coal also contains pyrite (2–5 wt.% S), which oxidizes to yield a low-pH environment (typical pH 2–5). Weathering of coal-bearing waste rock liberates B into rainwater that infiltrates into waste rock or evaporates to leave a gypsum crust enriched in B, possibly as boric acid or colemanite as inferred from geochemical modelling. Surface waters dissolve this evaporative material periodically, yielding total B concentrations up to 6 mg/L, at pH < 4.5. Some of the available B is taken up by plants that have been established on the waste rock, resulting in foliage B concentrations of up to 230 mg/kg (dry weight). Partial attenuation of dissolved B by adsorption to iron oxyhydroxide occurs as groundwater passes through waste rock, but this is inhibited by adsorption competition with dissolved sulphate (up to 600 mg/L). Groundwater flows from the mine through a pit lake and wetland, with total dissolved B near 1 mg/kg after dilution and limited adsorption attenuation has occurred. Despite the widespread B mobility throughout the rehabilitated mine, there is little evidence of B toxicity in plants. The B concentrations in discharging waters are in the environmentally safe range for most aquatic organisms, being neither deficient in B as a micronutrient, nor boron-toxic.
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1. Introduction

Boron (B) is a common trace element in coal, especially vitrinite-rich coal (Goodarzi and Swaine, 1994; Williams and Hervig, 2004). This B is mainly distributed through the organic component of the coal, and commonly exceeds 100 mg/kg (Swaine, 1990; Goodarzi and Swaine, 1994; Newman et al., 1997; Williams and Hervig, 2004). Coal mining can expose coal-bearing waste rock and coal-bearing outcrops to oxidation and

leaching by rain and groundwater, allowing enhanced mobilization of B from the coal (Severson and Gough, 1983; Nable et al., 1997; Argust, 1998). This B mobilization can persist when mines close and rehabilitation has occurred, as rainwater continues to percolate through the waste rock.

Discharge of B-bearing waters from coal mines has potential environmental significance because of potential ongoing B toxicity issues for biota, and lowered downstream water quality (Severson and Gough, 1983; Neal et al., 2000; McBeth et al., 2003). Coal-derived B is already widely recognized as a potential pollutant when leached from ash (Carlson and Adriano, 1993;

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Kukier and Sumner, 1996). However, B is both a nutrient and a potential poison for some biota, with a narrow window between deficiency and toxicity (Goldberg, 1997; Howe, 1998), so the magnitude and range of dissolved B concentrations in discharge waters are environmentally significant issues. The potentially negative effects of B in human drinking water have been given little attention in the past, but are now becoming increasingly recognized (Murray and Schlekat, 2004; Parks and Edwards, 2005).

Despite the potential environmental significance of B coming from coal mines, little research has been conducted on the processes of B mobility and attenuation at rehabilitated mine sites. This study provides an account of the B levels and the pathways for B mobilization and attenuation at a coal mine site in southern New Zealand that is currently undergoing remediation. The study follows the B from the coal source, through the surface and ground water system, to its partial discharge from the site, and examines the environmental significance of the B levels at various steps along those pathways.

2. General setting

The coal mine for this study is at Wangaloa, in the southeastern South Island of New Zealand (Fig. 1). The mine was a small (252 ha) open cut operation that was confined to a single stream valley, and all waste rock was dumped within the same catchment (Fig. 1). The mine was active between 1945 and 1989, and extracted high rank lignite from a sequence of Late Cretaceous marginal marine sediments (Harrington, 1958). The lignite was overlain by up to 50 m of fluvial quartz gravels, and this quartz-rich overburden was removed to waste rock dumps in the mine in the latter stages of mining. A veneer of Quaternary loess and loess-rich colluvium 1–10 m thick covered most of the mine area before mining, and this overburden was also dumped, commonly mixed with the quartz gravels. Waste rock contains variable amounts of coal, ranging up to 90% locally, on the 1–10 m scale. Remnants of the principal coal seam form outcrops up to 5 m high beneath benched highwalls of quartz gravels on the margins of the valley (Fig. 1).
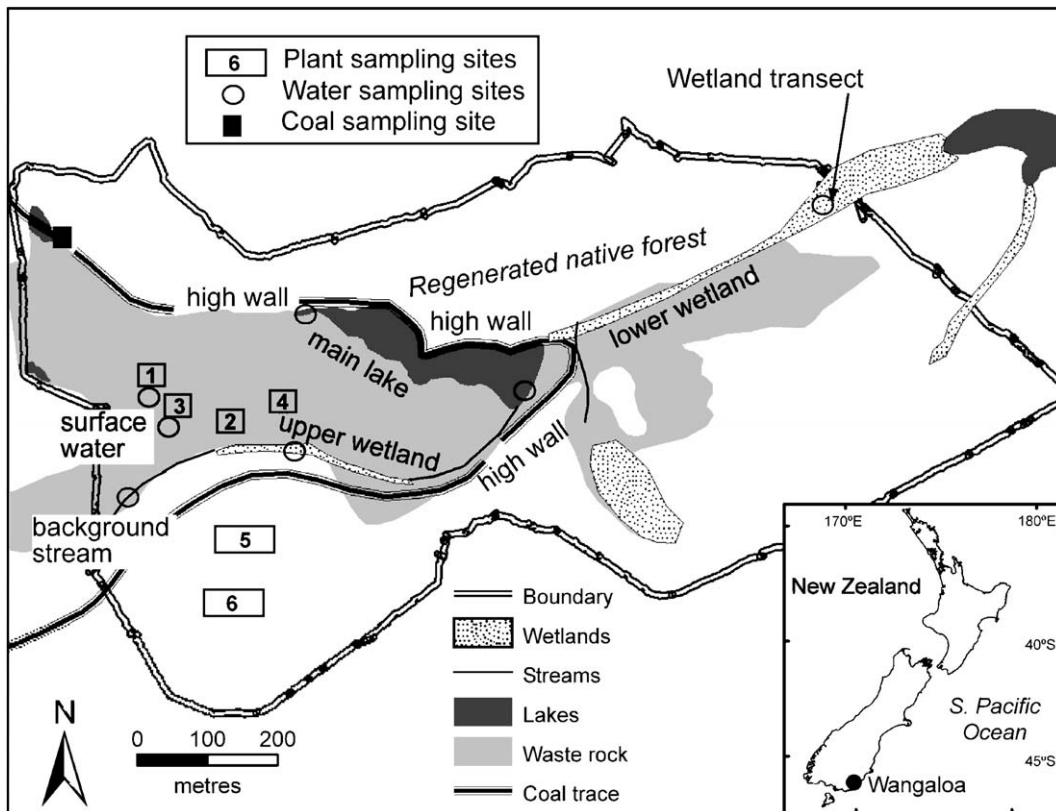

Fig. 1. Map of the Wangaloa mine site, showing the water drainage system (sample sites circled), location of waste rock piles, and the remnant coal outcrops (heavy black lines; filled square shows sample site). Native plant sample sites are indicated with open squares, with numbers referring to data in Table 2. Water sampling sites are open circles. Inset shows the location of the Wangaloa mine in southern New Zealand.

The mine area has a cool temperate maritime climate, and receives ca. 1000 mm of rainfall distributed evenly through the year. There are no major streams crossing the mine area, and most rain water infiltrates the substrate and moves as groundwater. A small tributary stream entering the mine from the west soaks through overburden and contributes to a narrow wetland in the centre of the mine (Fig. 1). An ephemeral stream discharges from that wetland, but this discharge is underground for most of the year. Small pit lakes have formed at the base of the northern highwall, and these are fed by groundwater and surface runoff during rain events. The lower lake discharges from the mine through a wetland at the eastern end (Fig. 1; Black and Craw, 2001). Farther downstream, the discharge water passes through plantation forests, and agricultural land where livestock water extraction can occur.

The quartz gravels consist of rounded quartz pebbles (0.5 to 2 cm) with a matrix of quartz sand and finer grained muscovite and kaolinite. Local cementation of the quartz gravels by pyrite has occurred, particularly near the top of the mined coal seam. Oxidation of pyrite cement and matrix muscovite has resulted in pale brown staining by fine grained (submicron scale) amorphous iron oxyhydroxide (HFO) that pervades much of the quartz gravels. The loess veneer consists of silt-sized windblown quartz, albite, muscovite and chlorite, and the latter two minerals have been variably altered by weathering to clays and HFO. The coal is rich in sulphur (typically 4–5 wt.%) that is partly dispersed through the organic matter (Suggate, 1959), but also occurs in pyrite (FeS_2). The pyrite is present as framboids, cell cavity infills in fossil plant fragments, and as veins (mm scale) along cleats. Pyrite is particularly abundant near to the top of the main coal seam. Oxidation of pyrite in coal results in coatings of gypsum, jarosite, and HFO on coal particle surfaces, and on cleats throughout the coal. Evaporative crusts of gypsum are widespread under dry overhangs in coal outcrops, and similar crusts form on coal fragments in the upper metre of waste rock piles where regular wetting and drying occurs. Evaporative gypsum efflorescences develop locally on coal-rich substrates where surface water accumulates temporarily during and immediately after rain events.

Abandoned parts of the Wangaloa mine area were initially rehabilitated as plantation forest (*Pinus radiata*) in the 1980s, but trees on the waste rock piles showed poor growth. At that stage, the site showed evidence of minor acid rock drainage issues, and the main lake water had pH of 4.8 (Black and Craw, 2001). A renewed plan for site rehabilitation was initiated in 2000, and pine trees were removed. Waste rock recontouring and weed removal ensued, followed by extensive plantings of native New Zealand species in 2003. The native plants were emplaced with individual peat-rich root blocks containing slow-release fertilizer, to ensure maximum establishment success. Despite these precautions, there was 30% mortality of plants over the following two years, and this mortality cannot be directly related to any single environmental issue (Todd, 2005). The present study developed in conjunction with the modern rehabilitation programme, when dissolved boron was identified as a potential environmental issue.

3. Methods

Fourteen samples of coal were taken from mine outcrops of the upper part of the main seam at the Wangaloa mine, and the base of the same seam in a nearby (1 km away) active mine. Additional samples were taken from the same seam where it is freshly exposed in sea cliffs 3.5 km away. Care was taken to remove oxidized surfaces from sampled coal fragments before grinding with an agate mortar and pestle. Samples of coal from waste rock in which sampled rehabilitation native plants are growing were selected for analysis and powdered without removing surface material, to maintain representativity for the growing medium. Total B contents of coal were determined by Eschka fusion of ca. 5 g of powdered coal at the CRL Energy Ltd. laboratory, Wellington, New Zealand, followed by ICP-MS analysis at Environmental Laboratory Services Ltd., Wellington, New Zealand. Detection limit for the method is approximately 25 mg/kg, depending on the properties of the sample matrix. Total sulphur (S) contents of the same powdered samples were determined on 3 mg aliquots using a Carlo Erba Elemental Analyser EA 1108, with a detection limit of 0.1 wt.%, at the University of Otago Chemistry Department Microanalytical Laboratory.

Water samples were obtained from the main lake and the downstream wetland on a monthly basis over nine months in 2004 and 2005. The lake was sampled at its downstream end each month, and one sample was taken at its upstream end where shallow groundwater input is occurring. Puddles of water lying on the surface of coal-rich waste rock were sampled when these were encountered during these sampling trips (eight samples in total). These puddles formed during rain events and evaporated and/or drained away over subsequent days. Water samples for B analysis were collected in acid-washed plastic bottles and preserved with nitric acid in the field. Surface water samples were filtered (0.45 μm), as were some lake and wetland waters. Comparison of results for filtered and unfiltered lake and wetland waters showed negligible

Table 1
Representative analyses of principal waters from the Wangaloa site

	Groundwater (upper wetland)	Lake (outlet end)	Wetland (lower)
pH	4.1	5.9	5.9
Na^+	26	20	20
K^+	2	4	3
Ca^{2+}	13	36	30
Mg^{2+}	8	27	24
Cl^-	51	28	30
SO_4^{2-}	57	202	173
Alk	<1	4	4
B	0.2	0.8	0.6

Alk=alkalinity. Data are in mg/L, except pH.

difference, and so some lake and wetland waters were collected unfiltered. Total dissolved B contents of waters were determined by ICP-MS, using internal laboratory standards, by Hill Laboratories, Hamilton, New Zealand, an internationally accredited laboratory. Detection limit for these analyses is 0.005 mg/L, and sample replication analyses agree within 0.03 mg/L in the range 0.70–1.60 mg/L. Water from the small tributary stream at the west side of the site was used for background and reference purposes, and these waters consistently yielded 0.11 mg/L total dissolved B. Separate water samples (1 L plastic bottles) were taken at all B sampling sites and analysed for dissolved sulphate via ion chromatography by Chemsearch (University of Otago Chemistry Department), with a detection limit of 1 mg/L. Representative major ion water analyses of lake and wetland waters were also obtained from the same laboratory, using methods described by Craw and Beckett (2004). Groundwaters from boreholes in the waste rock were sampled regularly as part of site-monitoring in 2003 and 2004, and a summary of B results from that study (Baker et al., 2004) are included here for comparison.

The pH value of sampled waters was determined in the field with a portable Oakton meter calibrated with standard solutions. Substrate pH was determined as paste pH of slurries of the fine component of surficial material, made in the field by the method of Sobek et al. (1978) and using the same pH meter.

Samples were taken of foliage of native plants growing in quartz-rich and coal-rich waste rock, and on little-disturbed loess-rich substrate. Three to five foliage samples were collected (depending on availability of green matter) from plant species present at each of two sites, for each substrate type, giving a total of 26 samples. The ca. 50 g (green weight) samples were taken in 2004 from specimens that showed sufficient growth since planting in 2003 to withstand this sampling attack. Dead plants from these sites (Todd, 2005) were avoided as they

contained insufficient organic matter for analysis. Foliage samples were oven dried at 50 °C for 48 h, then sent to Hill Laboratories for analysis. There the samples were further dried and powdered with a steel grinder, digested with nitric and hydrochloric acids, and analysed for B, Zn and Cu by ICP-MS. Previous work (Black and Craw, 2001) has shown that the selected metals, Cu and Zn, were readily mobilized and detectable at anomalous concentrations at Wangaloa. Additional plant analytical data on pine needles from trees showing good and poor growth (10 samples each) at the Wangaloa site were provided by Solid Energy (NZ) Ltd. The samples were taken in 2001, and were analysed for nitrogen and B by Landcare Research, Palmerston North, New Zealand, by methods described by Blakemore et al. (1987).

Modeling of geochemical relationships was undertaken with the software package Geochemists Workbench v.3 (Bethke, 1998). The standard software thermodynamic database was used for species predominance diagrams. Adsorption modeling to iron oxyhydroxide used the modified double layer model (Dzombak and Morel, 1990).

4. Results

Substrate pH values in the mine are generally between 4.0 and 6.5, compared to average pH values of 4.2 in background forest soils above the northern highwall (Fig. 1). There are some localized areas of waste rock that have lower pH values, down to 2.6. These low pH areas are dominated by coal-rich substrate and/or quartz gravels with pyrite cement. Water pH values have a similar range
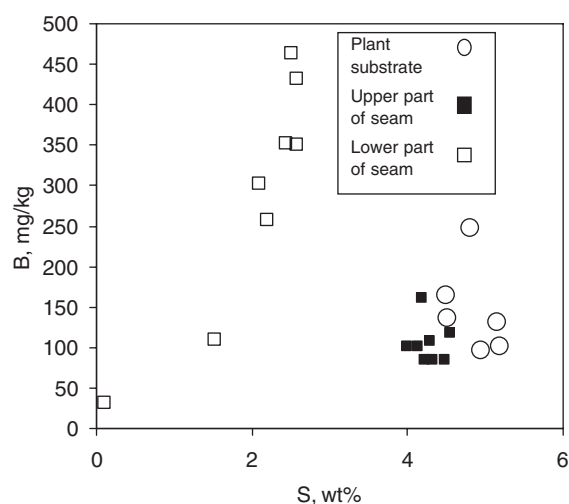

Fig. 2. Total B and total S contents of coal from the main seam that is exposed at Wangaloa mine (squares; see text for sampling sites). Compositions of coal in waste rock beneath sampled native plants (sites 1 and 3, Fig. 1) are shown with open circles.
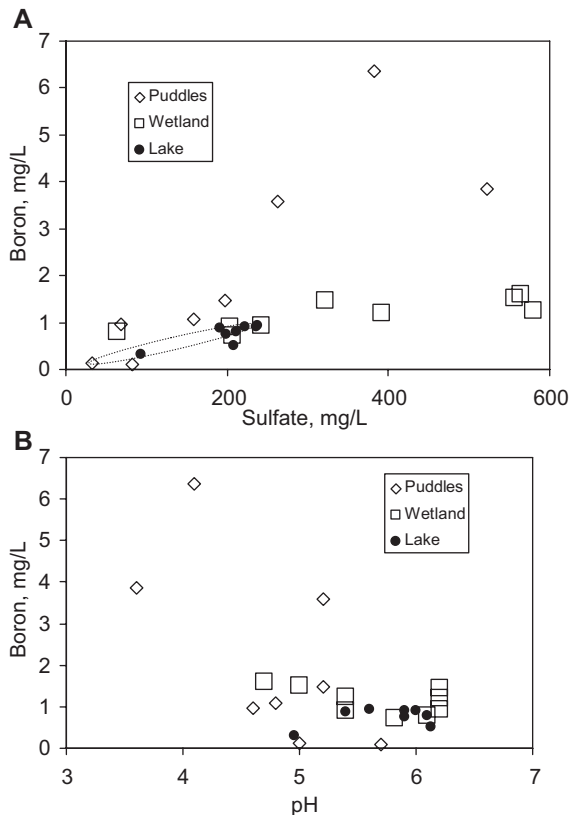
Fig. 3. Total dissolved boron contents of Wangaloa mine waters. A. B–sulphate relationships. The range of groundwater data from Baker et al. (2004) is shown with a dotted ellipse. B. Boron–pH relationships.
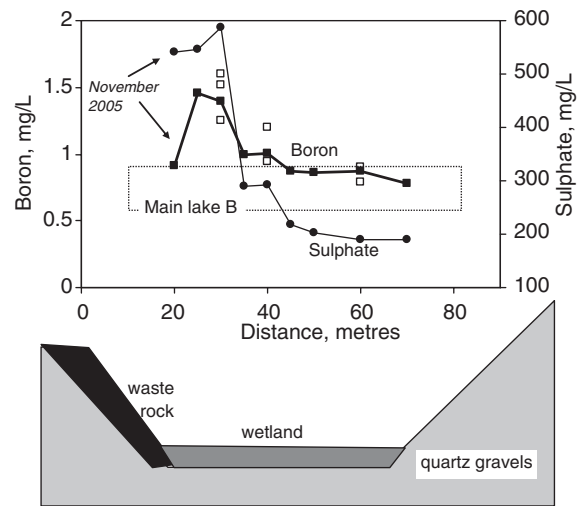

Fig. 4. Total dissolved B contents of waters discharging through the lower wetland at Wangaloa, shown as a transect across the wetland, with cross section sketched below. Typical main lake water total dissolved B concentrations are indicated (dashed box) for comparison.

to those of the substrates. Incoming stream waters have pH values near 6, and most surface and shallow ground waters have pH values between 4 and 5. The lake pH values fluctuated between 5 and 6 over the period of this study, with no clear trends over time. Wetland water pH values immediately downstream of the lake were essentially the same as those of the lake (Table 1). The central wetland and associated ephemeral stream had slightly more acid pH values, between 3.5 and 4.5.

Total B contents of the main coal seam are highly variable, from 84 to 463 mg/kg (Fig. 2). The upper part of the seam still exposed in the Wangaloa mine has relatively low B compared to most of the lower samples (Fig. 2). Samples of carbonaceous mudstone from near the base of the seam also have low B content (Fig. 2). There is no clear relationship between total B content and total S content ($R^2 = 0.13$). The upper part of the seam exposed at Wangaloa has total S up to 4.5 wt.%, whereas the lower part of the seam has total S content down to 2 wt.% (Fig. 2).

Lake waters sampled at the downstream end have consistent total dissolved B contents between 0.5 and

0.9 mg/L (Fig. 3A, B). The downstream wetland has generally similar total dissolved B contents, although some wetland total dissolved B contents are up to 1.6 mg/L (Fig. 3A, B). Total dissolved B contents of wetland waters are higher on the southern side of the wetland, and those from the central and northern part of the wetland have similar total dissolved B contents to the lake (Fig. 4). Surface puddles on coal-bearing waste rock have highly variable total dissolved B contents that are up to 6.4 mg/L
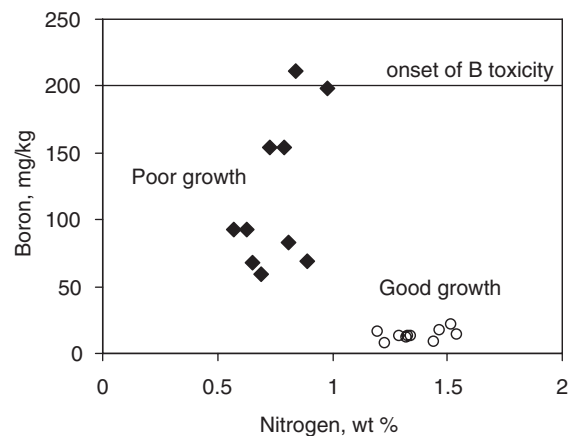

Fig. 5. Comparison of total B and nitrogen contents (dry weight) of needles from pine trees established at Wangaloa mine for initial rehabilitation, and sampled at ca. 15–20 years of age (data from Solid Energy New Zealand Ltd.). Trees that showed good growth (>4 m high; open circles) were on coal-free substrate, and those with poor growth (<3 m high, black diamonds) were on coal-bearing quartz-rich substrate.
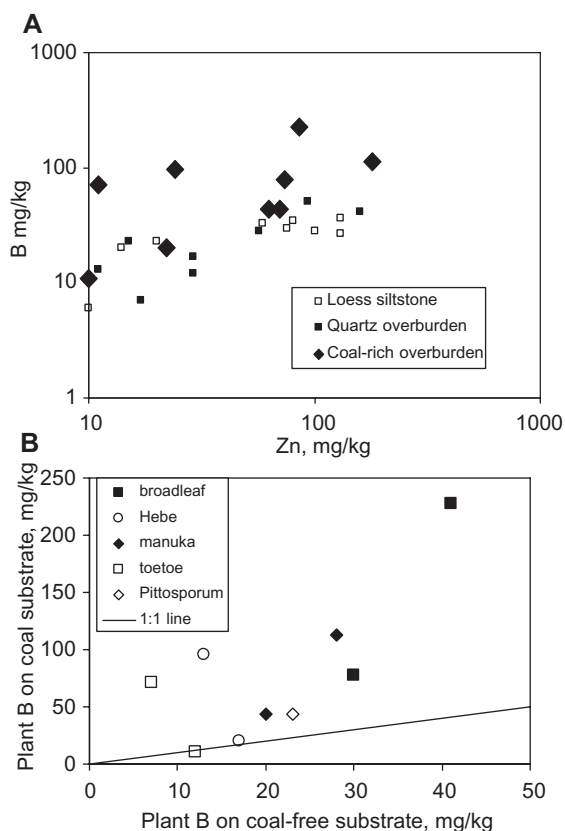
A

B

Fig. 6. Total B contents (dry weight) of native plants established on three different substrates (as indicated) at Wangaloa mine. A. Total B and zinc contents of all analysed plants. B. Comparison of total B contents of the same species on coal-bearing and coal-free substrates (quartz and loess dominated).

(Fig. 3A, B). The highest total dissolved B contents are in low pH water (pH < 4.5; Fig. 3B). All other waters analysed for total dissolved B have pH between 4.5 and 6.2 (Fig. 3B).

Surface waters in lakes and wetlands are enriched in sodium and chloride, reflecting marine aerosol rainout that is common along this coastal area (Craw and Beckett, 2004). Abundant calcium and sulphate (Table 1) are from interaction with pyrite and evaporative gypsum in coal-rich waste rock (Baker et al., 2004). Magnesium and potassium contents (Table 1) reflect water interaction with weathering chlorite and muscovite, respectively. Alkalinity is low compared to other anion contents (Table 1). Groundwater compositions are generally similar to, or more dilute than, those of the main lake (Baker et al., 2004), but the upper wetland sample taken for this study is slightly enriched in sodium and chloride (Table 1). Sulphate contents of surface water puddles are highly variable, but the highest sulphate contents generally coincide with the highest total B contents (Fig. 3A), with $R^2 = 0.70$ for this correlation.

Foliage from poorly-growing pine trees (< 3 m high) collected in 2001 have total B contents between 60 and 211 mg/kg (dry weight), whereas those showing good growth (> 4 m high) at that time have B between 7 and 22 mg/kg (dry weight) (Fig. 5). There was also a similar clear difference, with no overlap of populations, in total nitrogen contents between poorly-growing trees (< 1% N, dry weight) and those showing good growth (> 1% N, dry weight) (Fig. 5). Native species planted in 2003 on relatively intact loess substrate, and on quartz gravel waste rock, have total B contents between 6 and 51 mg/kg (dry weight) (Fig. 6A; Table 2). Species planted on coal-rich overburden contain total B levels between 11 and 228 mg/kg (dry weight), overlapping the results from the other

Table 2
Foliage analyses of native plants established on Wangaloa substrates

Common name	Species	P	Zn	Cu	B
Site 1: coal-bearing waste rock					
Manuka (shrub)	*Leptospermum scoparium*	0.18	180	12	113
Toetoe (grass)	*Cortaderia richardii*	0.08	11	5	71
Koromiko (shrub)	*Hebe salicifolia*	0.2	24	6	96
Broadleaf (shrub)	*Griselinia littoralis*	0.15	86	4	228
Site 3: coal-bearing waste rock					
Toetoe (grass)	*Cortaderia richardii*	0.15	10	5	11
Koromiko (shrub)	*Hebe salicifolia*	0.22	22	3	20
Manuka (shrub)	*Leptospermum scoparium*	0.2	70	6	44
Kohuhu (shrub)	*Pittosporum tenuifolium*	0.18	63	4	44
Broadleaf (shrub)	*Griselinia littoralis*	0.12	74	4	78
Site 2: quartz-rich waste rock					
Toetoe (grass)	*Cortaderia richardii*	0.08	17	6	7
Koromiko (shrub)	*Hebe salicifolia*	0.14	11	5	13
Kohuhu (shrub)	*Pittosporum tenuifolium*	0.26	15	6	23
Site 4: Quartz-rich waste rock					
Manuka (shrub)	*Leptospermum scoparium*	0.14	57	6	28
Toetoe (grass)	*Cortaderia richardii*	0.09	29	6	12
Koromiko (shrub)	*Hebe salicifolia*	0.15	29	4	17
Broadleaf (shrub)	*Griselinia littoralis*	0.11	160	4	41
Kohuhu (shrub)	*Pittosporum tenuifolium*	0.17	93	5	51
Site 6: loess silt					
Manuka (shrub)	*Leptospermum scoparium*	0.12	14	6	20
Toetoe (grass)	*Cortaderia richardii*	0.09	10	6	6
Koromiko (shrub)	*Hebe salicifolia*	0.24	100	6	28
Kohuhu (shrub)	*Pittosporum tenuifolium*	0.21	130	6	27
Broadleaf (shrub)	*Griselinia littoralis*	0.18	76	8	30
Site 5: loess silt					
Manuka (shrub)	*Leptospermum scoparium*	0.12	20	5	23
Koromiko (shrub)	*Hebe salicifolia*	0.34	59	15	33
Kohuhu (shrub)	*Pittosporum tenuifolium*	0.28	130	10	36
Lemonwood (shrub)	*Pittosporum eugenoides*	0.22	80	7	35

P analyses are in wt.% (dry weight); Zn, Cu, and B are in mg/kg (dry weight). Sampling sites are located on Fig. 1.

substrates but extending to much higher total B levels (Fig. 6A; Table 2). The overlap between data from foliage from coal-rich substrate and the other substrates is less when Zn contents are plotted as well, because the higher total B contents are generally accompanied by higher Zn contents (up to 180 mg/kg, dry weight; Fig. 6A; Table 2). Boron is moderately well correlated with Zn for the quartz ($R^2 = 0.66$) and loess ($R^2 = 0.39$) substrates, but poorly correlated with Zn for the coal-rich substrates ($R^2 = 0.21$). Copper levels are generally consistent, between 3 and 15 mg/kg (dry weight), for all substrates (Table 2).

Direct comparisons between different substrates for total B contents of foliage is difficult as the different substrates have some different native species. Species that occur on both coal-rich and coal-free substrates have been compared by matching total B contents in Fig. 6B. The data set is smaller than in Fig. 6A because few species could be matched between substrates. However, this data set shows that for any represented species, total B contents tend to be higher on coal-rich substrate than coal-free substrates; i.e., they lie above the 1:1 line (Fig. 6B).

5. Discussion

5.1. Initial B mobilization

Surface water puddles are ephemeral on a time scale of days, so the B in water in those puddles must also dissolve on that same time scale. Hence, mobilization of B from coal-rich substrate can yield total dissolved B up to 6 mg/kg (Fig. 3A) on a time scale of days. This B is accompanied by abundant dissolved sulphate from oxidation of pyrite and/or gypsum efflorescences (Fig. 3A). Consequently, water infiltrating into the groundwater system through coal-bearing waste rock can rapidly develop relatively high total dissolved B concentrations.

At least some evaporative drying of these surface waters occurs at the site, as gypsum crusts are widespread, particularly on coal fragments, in dry near-surface substrate. Complete evaporation must precipitate some B mineral with the gypsum, although amounts are too small to be detectable. Thermodynamically-predicted phase equilibria (from Geochemists Workbench) for a calcium-bearing B system are depicted in Fig. 7A (partially evaporated) and B (highly concentrated evaporated solution). Dissolved B is present as $B(OH)_3$ under the mildly acid pH conditions observed associated with Wangaloa coal (Fig. 7A). Boric acid will precipitate as the B concentration rises (Fig. 7B). These secondary B minerals may form progressively during weathering of coal via repeated wet/dry cycles, as does gypsum. Precipitation of colemanite under near-neutral pH conditions

at Wangaloa may occur locally (Fig. 7B). It is likely that at least some of the elevated B concentrations observed in ephemeral surface puddles (Fig. 3A) arise because of dissolution of boric acid (and possibly colemanite) from evaporative crusts, as does dissolved sulphate from the gypsum crusts. Hence, B that is released slowly (over years) by weathering of coal can be remobilized from evaporative crusts in hours or days (rain events).

5.2. Plant uptake of B

Boron in coal-rich substrates that is readily mobilized into infiltrating water is also readily mobilized into the
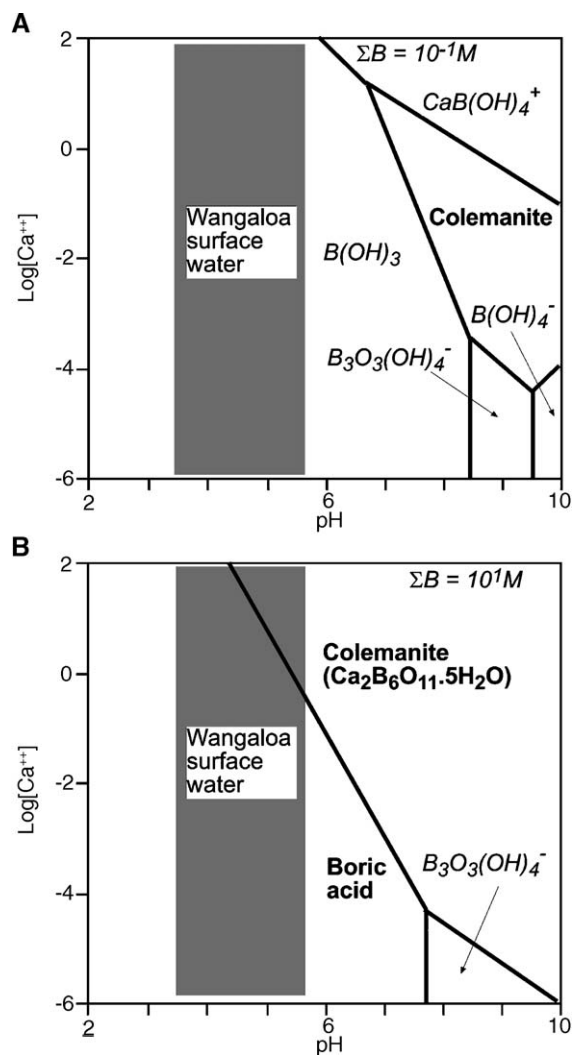

Fig. 7. Boron species thermodynamic stability diagrams (from Geochemists Workbench) in terms of pH and dissolved calcium concentrations, drawn for 25 °C. A. Diagram for partially evaporated water, with dissolved B = 0.1 mol/L. B. Diagram for almost completely evaporated water, with dissolved B = 1 mol/L.

plants established on the substrates. Relatively high total B concentrations in poorly growing (stunted) pine trees at Wangaloa (Fig. 5) show that substantial accumulation of B can occur in needles on the 20 year time scale. However, most of these trees have B at levels below toxicity (Fig. 5; Smidt and Whitton, 1975). Elevated total B levels in native plants established on coal-rich substrates (Fig. 6A, B) show that similar B accumulation can occur in less than two years despite the provision of fertilizer and peat blocks on initial planting. Plant foliage total B contents are generally poor indicators of B toxicity (Nable et al., 1997). Also, the sampled native plants showed the same range of vigour as the same species on neighbouring substrates. Hence, there is no evidence that B toxicity is an issue at the Wangaloa mine. Mortality of some native plants on coal-bearing substrates may be related to B toxicity, but could also be related to low moisture levels in the substrate, low levels of nutrients, or to low pH.

Boron can be accumulated by plants, even to toxic levels, because of limitations in other nutrients. In particular, zinc deficiency can cause enhanced B uptake, and conversely, addition of zinc can ameliorate B uptake (Swietlik, 1995; Nable et al., 1997; Gunes et al., 1999). However, there is a similar range of Zn contents in native plants on coal-bearing and coal-free substrates, and low-zinc and high-zinc native plants show similar degrees of B enrichment on coal-rich substrates (Fig. 6A). Further, Zn is readily mobilized at Wangaloa by the localized acidity, and Zn is locally elevated in waters (Black and Craw, 2001). The crude positive relationship ($R^2 = 0.21$ to 0.66) between Zn and B contents of plants on all substrates (Fig. 6A), rather than a negative relationship, suggests that Zn deficiency is not driving the B uptake. It is possible that low substrate macronutrient levels, such as low nitrogen, contributed to strong B uptake by the pine trees that were originally planted on the mine (Fig. 5). Macronutrient data were not gathered for native plants to test this suggestion because of the provision of macronutrients to each individual at planting time.

5.3. Boron transport and attenuation through the mine

Boron that is not retained on substrate surfaces by evaporation, or taken up into plants, is transported, mainly by groundwater, towards the main lake and downstream wetland (Fig. 1). Despite the highly variable total dissolved B and sulphate concentrations in surface waters, the lake waters are remarkably uniform in composition (Fig. 3A). There is a consistent positive relationship ($R^2 = 0.91$) between total dissolved B and sulphate contents of groundwaters (Fig. 3A; Baker et al.,

2004). The main lake waters fall at the upper end of that trend, apart from the shallow groundwater-affected sample from the upstream end of the lake (Fig. 3A). These data confirm that the main lake is derived predominantly from groundwater percolating through the waste rock. The total dissolved B contents of the groundwaters and the main lake are generally lower than those of the surface water puddles on coal-rich substrate (Fig. 3A).

Most waters from the wetland immediately downstream of the lake have essentially the same total dissolved B and sulphate contents as the lake, and the same positive correlation between total dissolved B and sulphate over time. Hence, these wetland waters are assumed to be derived from discharging lake water. Samples from the southern side of the wetland have distinctly elevated sulphate contents, and generally higher total dissolved B contents (Figs. 3A and 4). These waters are probably derived from groundwater emanating from the waste rock on the southern side of the wetland area (Figs. 1 and 4). This lateral groundwater and the main lake discharge water merge within the wetland, and the total dissolved B and sulphate contents mix in the centre of the wetland (Fig. 4).

5.4. Boron adsorption

Dissolved B is readily adsorbed by minerals with high reactive surface areas, such as HFO and clays (Goldberg, 1997) that are abundant in the Wangaloa mine substrates. Hence, some attenuation of dissolved B by adsorption is to be expected as groundwater passes through the waste rock. Boron adsorption to clay minerals is greatest under alkaline conditions, which do not occur at Wangaloa. In addition, the amount of adsorption to kaolinite, which is the predominant clay at Wangaloa, is relatively low under acid conditions (Keren and Mezuman, 1981; Goldberg, 1997). Hence, B adsorption to clay minerals in the acidic substrates at Wangaloa is likely to be only minor. Boron adsorption to HFO is most pronounced at circumneutral pH and decreases towards lower pH, but is still significant at pH > 4 (Bloesch et al., 1987; Goldberg, 1997), and this type of attenuation is the most likely to dominate at Wangaloa.

Boron adsorption to HFO can be estimated with surface models (e.g., Goldberg, 1997) using Geochemists Workbench. For this study, models were set up to estimate the decrease in dissolved B with varying solution pH (Fig. 8A) from an assumed initial concentration of 3 mg/L (based on surface puddle waters; Fig. 3A, B). The models passed the B-bearing solution through rocks containing HFO. Increasing distance of travel through these rocks is approximated by increasing amounts of HFO (in grams)
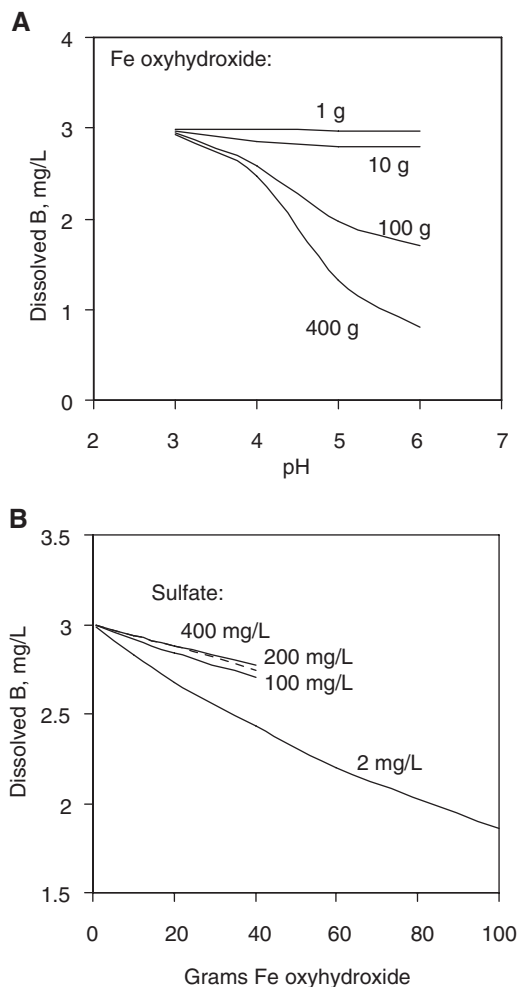
A

B

Fig. 8. Results from modeling (Geochemists Workbench) of B adsorption to HFO (see text). Amount of adsorption of B is expressed as dissolved boron remaining from an initial solution B content of 3 mg/L (Fig. 3A, B). A. Adsorption models at a range of solution pH relevant to Wangaloa waters, and a range of amounts of HFO (grams) available as adsorption substrate. Adsorption models are at pH=5 with a range of available HFO substrate (grams), and a range of solution sulphate concentrations (2 to 400 mg/L) for adsorption competition.

that the water interacts with (Fig. 8A). These models show that with increasing distance of travel (greater mass of HFO encountered), the amount of B lost from solution by adsorption is negligible at a pH of 3, but increases dramatically as pH rises. At a pH of 5, common at Wangaloa, almost all the dissolved B can be adsorbed from solution by HFO if the water passes sufficient HFO. Since HFO is abundant in all the Wangaloa waste rocks, substantial attenuation by adsorption to HFO is implied.

Adsorption to HFO is hindered by competing ions, particularly anions (Bloesch et al., 1987; Goldberg, 1997). At Wangaloa, sulphate is the most abundant competing

anion, and sulphate concentrations are locally high in B-bearing waters (Fig. 3A). Adsorption competition from sulphate is relatively low compared to many other anions (Goldberg, 1997). However, the high levels of sulphate at Wangaloa can be expected to have a strong effect on B adsorption, at least locally. This competitive adsorption has been modeled with Geochemists Workbench for B-bearing waters (3 mg/L) at pH of 5, for increasing amounts of interaction with HFO (Fig. 8B). Models were run for different concentrations of dissolved sulphate that cover the observed range of data at Wangaloa (Fig. 8B). These models confirm that the competing effect of sulphate is small when the dissolved sulphate concentration is similar to that of dissolved B (2 mg/L; Fig. 8B). However, the high levels of dissolved sulphate commonly observed in Wangaloa waters (Fig. 3A) result in substantial adsorption competition between dissolved B and sulphate, and the amount of B adsorption strongly decreases (Fig. 8B). These models became numerically unstable at high amounts of HFO interaction, but the gradients of results that were obtained (Fig. 8B) imply that even with long distances of travel through HFO-bearing rocks, the dissolved B content of waters would decrease by only small amounts.

The models presented above provide some support for minor amounts of adsorption of B to HFO as B-rich surface waters infiltrate into and through waste rock at Wangaloa. The decrease in total dissolved B contents from >3 mg/L (surface waters) to near 1 mg/L (main lake), despite passage through coal-bearing waste rock with elevated B contents, may reflect this adsorption. However, dilution by low-B waters that have not passed through coal-bearing waste rocks is also likely to have contributed to the lower B in the lake. The relatively high total dissolved B contents of waters discharging directly into the downstream wetland from waste rock (Fig. 4) may be a result of sulphate adsorption competition associated with these relatively sulphate-rich waters (Fig. 3A).

5.5. Environmental significance of dissolved B levels

The background stream at Wangaloa (Fig. 1) has total dissolved B concentration that is typical of background streams elsewhere (0.1 mg/L; Tartari and Gamusso, 1988). The highest dissolved B contents measured in this study, 6.4 mg/L, is similar to high B levels reported downstream of a boron mine (Okay et al., 1985), but the Wangaloa waters are ephemeral only. The low but significant total dissolved B concentrations emanating from the Wangaloa mine are slightly greater than World Health Organisation drinking water guideline for B of 0.5 mg/L (WHO, 2003). However, there is no evidence

for B toxicity to humans at such low levels, and the drinking water guidelines are based on lifetime exposure (Murray and Schlekat 1994; Parks and Edwards, 2005). Long-term exposure to total dissolved B concentrations as high as 8.5 mg/L in drinking water would probably not have an adverse effect on human health (Parks and Edwards, 2005). Hence, based on the data available, the observed B discharges at Wangaloa coal mine are unlikely to have any significant effect on human health, should the water be used for drinking. The human population downstream of the Wangaloa site is small, and the water is used to only a limited extent for agricultural purposes. Recommended maximum B content in water for agricultural uses is 5 mg/L (ANZECC, 2000), and the current mine discharges are lower than this.

Boron is a micronutrient to many aquatic organisms, with a narrow window between deficiency and toxicity. The level at which B is toxic is poorly defined, and some apparent toxicity to aquatic organisms at low B levels may be a result of B deficiency (Fort et al., 1998; Rowe et al., 1998; Loewengart, 2001). A dose–response curve for aquatic organisms in waters with differing B concentrations is U shaped, with adverse effects at low and high concentrations reflecting deficiency and toxicity, respectively (Fig. 9; Rowe et al., 1998; Loewengart, 2001). The curve in Fig. 9 is for trout, but similar curves, at similar magnitudes, can be defined for other fish, and for frogs (Fort et al., 1998; Rowe et al., 1998). New Zealand environmental guidelines suggest 0.09 mg/kg dissolved B for 99% protection of aquatic organisms (ANZECC,

2000), but this level is at the edge of the B deficiency part of the dose–response curve (Fig. 9) and should be treated with caution. All waters described in this study have B concentrations well within the safe range of exposure for studied aquatic organisms (Fig. 9; Butterwick et al., 1989; Rowe et al., 1998). However, Bringmann and Kuhn (1980) suggest that B concentrations as low as 0.2 mg/L can have minor adverse effects on some microorganisms such as green algae and protozoans. Clearly, the environmentally safe levels for dissolved B are as yet poorly defined, but most organisms appear to readily tolerate the levels of dissolved B being derived from the Wangaloa mine. Since the total B levels in coal at Wangaloa, and the processes of B mobility and attenuation described above, are similar to those expected in most coal mines elsewhere in the world, B-bearing water discharges from coal mines may not be a significant environmental issue.

6. Conclusions

This study describes the passage of B from source to discharge through the partially rehabilitated Wangaloa coal mine. Boron is distinctly elevated in high-sulphur (2–5 wt.%) coal but total B levels (100–450 mg/kg) are comparable to marginal marine coals found elsewhere in the world (Goodarzi and Swaine, 1994). This boron is released from the coal by weathering on a time scale of years, in a low-pH environment (pH values typically between 2 and 5) generated by pyrite oxidation. Boron is locally concentrated in evaporative crusts with gypsum, and geochemical modeling suggests that this B occurs as boric acid (at low-moderate pH) and/or colemanite (at circumneutral pH). The evaporative crusts redissolve rapidly (hours to days) in surface waters during rain events, and total dissolved B concentrations up to 6 mg/L occur in moderately acid waters (pH < 4.5) that arise from pyrite oxidation. This readily-mobile B in surface waters is strongly bioavailable, and plants established on rehabilitated waste rock take abundant B into their foliage. Pine trees (*Pinus radiata*) established on waste rock for 15–20 years took up B to near toxic levels (ca. 200 mg/kg, dry weight), possibly because of low nutrient status of the quartz-rich substrate, and those trees have been removed. Native plants subsequently established on the waste rock also incorporated boron to similar levels in their foliage over only two years, but analysed plants show no specific signs of B toxicity. Zinc and copper, two trace metals readily mobilized in the waste rock at the site, are apparently not deficient either, and there is a crude positive relationship between B and Zn in plant foliage.
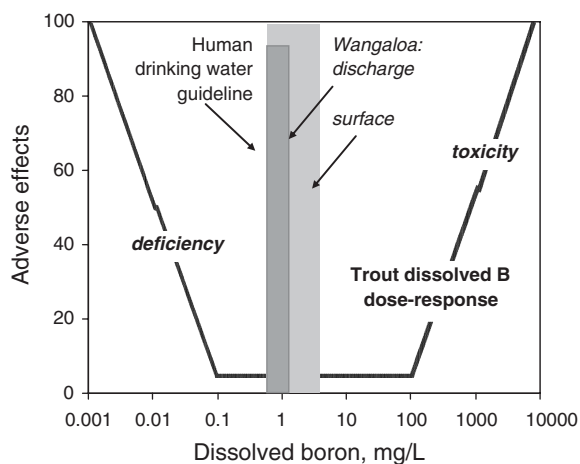

Fig. 9. Dose–response curve (heavy stippled line and bold lettering) for trout in B-bearing water (after Rowe et al., 1998). Note logarithmic horizontal scale. Vertical scale is relative only, and derived from sources referred to in the text. Human drinking water guideline from WHO (2003) is a vertical dashed line. Wangaloa mine waters are indicated with shaded vertical blocks: surface waters are light grey, and discharge waters are dark grey.

Most of the water discharging from the Wangaloa mine has percolated as groundwater through waste rock that contains variable amounts of coal. This groundwater passes through a pit lake and wetland before leaving the site. Boron concentrations in groundwater, lake and wetland are distinctly lower than those observed in surface waters. Dilution within the waste rock is responsible for some lowering of B concentrations. In addition, adsorption of B on to iron oxyhydroxides in the waste rock causes some B attenuation. This B attenuation is only minor in moderately acid waters (pH < 5), but can be important at pH 5. However, B adsorption is further limited by competition by sulphate ions, which locally exceed 200 mg/kg in the mine waters. Nevertheless, the combination of dilution and adsorption results in attenuation of B concentrations to near 1 mg/kg in discharge waters. This boron concentration poses no environmental threat to aquatic organisms, as it is sufficiently high to provide essential B as a micronutrient, but not high enough to be potentially toxic. The processes that are described in this study of B dissolution followed by limited B adsorption via attenuation to HFO should occur in most coal mines with pyrite-bearing coals. Hence, similar dissolved B concentrations (near 1 mg/L) should be expected from mines with similar elevated B concentrations elsewhere in the world.

Acknowledgements

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