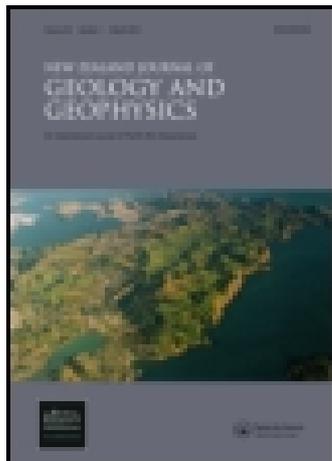


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Stratigraphic controls on water quality at coal mines in southern New Zealand

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Stratigraphic controls on water quality at coal mines in southern New Zealand

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Abstract Water quality at four coal mines in southern New Zealand can be related directly or indirectly to the geology and mineralogy of the stratigraphic sequence in which the coal mines occur. The Late Cretaceous Taratu Formation of the Kaitangata coalfield formed in a marginal marine setting during regional marine transgression, and marine incursions punctuated coal formation. Abundant authigenic and remobilised pyrite at the Wangaloa mine (typically 4 wt% S in coal) in the Kaitangata coalfield has oxidised and caused acidification of mine waste rocks (to pH 1) and mine waters (to pH 3). Similar or even greater amounts of pyrite occur locally at the nearby Kai Point mine, although the mined seam typically has <2 wt% S. However, dissolution of carbonate concretions in marine sediments immediately overlying the mined seam at Kai Point mine ensures that acid generated by pyrite oxidation is neutralised, and the site generally has substrates and waters with near-neutral or alkaline pH. The close stratigraphic association between coal and marine sediments at Kai Point mine has resulted in high B contents in coal (up to 500 mg/kg) about 10 times higher than at the nearby Wangaloa mine. Both mines have elevated dissolved B contents in mine waters (up to 6 mg/L at Wangaloa). The Late Cretaceous coal-bearing sequence at Ohai is entirely nonmarine, pyrite is rare or absent, and no environmental acidification occurs. Likewise, the Miocene coal-bearing strata at Newvale coal mine have negligible pyrite and no acidification occurs from these rocks. However, iron sulfide cements have formed in Pliocene gravels from groundwater derived from rain with marine aerosols. Oxidation of this sulfide material has caused localised acidification at Newvale mine. Acidification

has caused localised and generally short-term elevation of dissolved trace elements at Wangaloa and Newvale mines, with dissolved Al up to c. 2.5 mg/L at Newvale. Suspensions of clay minerals cause turbidity at all mines. Well-washed, coarse (>1 µm), detrital kaolinite at Kai Point, Wangaloa, and Newvale mines settles readily (within days). Chlorite from disaggregated labile clasts in overlying Pliocene gravels dominates longer term turbidity at Newvale, but the turbidity decreases rapidly on a time-scale of months. Fine-grained (including sub-micrometre) poorly sorted authigenic kaolinite from labile clasts in the coal-bearing strata at Ohai causes long-term turbidity, with negligible setting over 9 months. The stratigraphically controlled processes quantified in this study can be used to predict the nature and scale of potential water quality changes in new coal mines in southern New Zealand.

Keywords AMD; pyrite; boron; turbidity; chlorite; kaolinite; stratigraphy; mining

INTRODUCTION

Modern open-cut coal mining results in large-scale surface disturbance and locally deep excavations (Sengupta 1993; Skousen et al. 1997; Lottermoser 2003). Waste rock is dumped in large piles for long-term storage (Hutchison & Ellison 1992; Sengupta 1993). These operations result in exposure of large amounts of fresh rock to atmospheric weathering and rainfall runoff, which can give rise to lowered water quality (Sengupta 1993; Monterroso & Macias 1998; Hewlett et al. 2005). Prediction of the nature of these environmental effects before mining begins is an essential part of mine planning, so that these effects can be anticipated, minimised, and ameliorated throughout the mining and mine closure periods (Hutchison & Ellison 1992; Sengupta 1993; Skousen et al. 1997; Lottermoser 2003). Most changes to water quality around coal mines arise as a direct result of the rock types present in excavations and waste rock piles (Sengupta 1993; Skousen et al. 1997; Black et al. 2005). These rock types, in turn, are related to the stratigraphy of the sedimentary sequence in which the coal occurs. Hence, it should be possible to predict the nature and severity of water quality changes associated with a coal mine, as long as the stratigraphic setting of the mine, and hence the rock types associated with that stratigraphy, are known in advance (Skousen et al. 1997; Wisotsky & Obermann 2001; Weber et al. 2004).

This study provides four examples of coal mines (Fig. 1) from four different stratigraphic settings (Fig. 2A–D), and identifies the key changes to water quality that have arisen in those coal mines (Table 1). We relate these environmental effects directly to the local stratigraphy, and show how local stratigraphy controls the environmental effects. The four studied coal deposits occur in four different detailed stratigraphic settings in Late Cretaceous (Ohai mine; Wangaloa and Kai

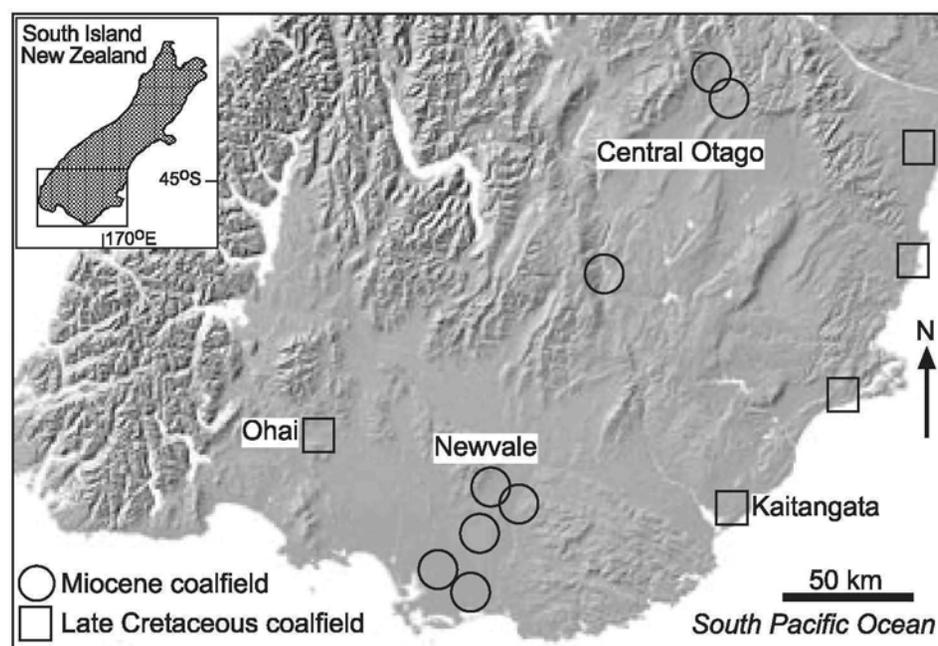


Fig. 1 Location map for coal deposits in southern South Island, New Zealand (see inset), based on a digital terrain model from www.geographx.co.nz. Principal coalfields of Late Cretaceous (squares) and Miocene (circles) age are indicated. The four coalfields discussed in the text are labelled; Kaitangata coalfield includes Wangaloa and Kai Point mines.

Table 1 Summary comparison of principal stratigraphic and environmental water quality parameters of the four studied coal mines, southern New Zealand.

Mine (host unit, age)	Lithological and depositional setting	Acidification	Boron	Turbidity	Dissolved trace metals
Wangaloa (Taratu Fm, Late Cretaceous)	Mature fluvial, marginal marine	Extensive, substrate to pH 1, water to pH 3	Moderate in coal (<100 mg/kg); dissolved up to 6 mg/L, discharge water <1 mg/L	Temporarily high, rapid decrease (days); >1 μm detrital kaolinite	Cu, Zn, As occasionally slightly elevated
Kai Point (Taratu Fm, Late Cretaceous)	Mature fluvial, strong marine influence above	Local substrate and waters to pH 3, waters neutralised by ankerite concretions	High in coal (500 mg/kg), moderate in discharge water (<2 mg/kg)	Temporarily high, rapid decrease (days); >1 μm detrital kaolinite	Low, near detection limit
Ohai (Morley Coal Measures, Late Cretaceous)	Immature fluvial, labile alteration, nonmarine	Nil	Low in coal and mine waters (<0.2 mg/L)	Moderate, persistent, submicrometre kaolinite	Low, near detection limit
Newvale (Gore Lignite Measures, Miocene)	Mature fluvial, nonmarine. Overburden immature and pyritic	Local, water to pH 4, from overlying pyritic sediment	Low in coal and mine waters (<0.4 mg/L)	Occasionally high, rapid decrease (months), micrometre-scale chlorite	Minor localised Fe, As, Al elevation

Point mines of Kaitangata coalfield) and Miocene (Newvale mine) sequences (Fig. 1; Table 1). The aim of this study is to provide a stratigraphic basis for prediction of water quality changes that are likely to arise in new coal mines in southern New Zealand.

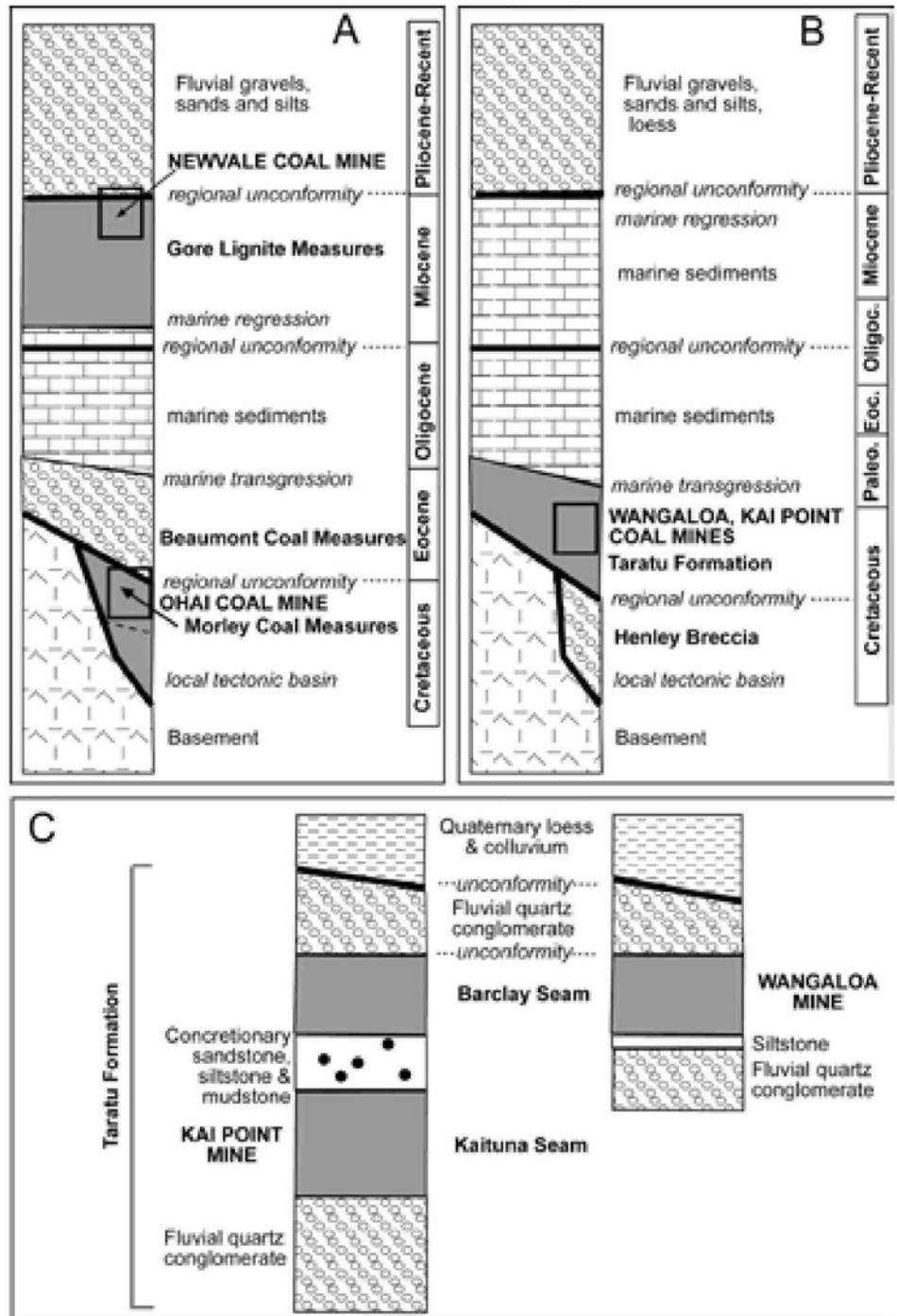
GENERAL GEOLOGY

Regional stratigraphy

Coal in the southern South Island of New Zealand occurs within a Cretaceous–Cenozoic sedimentary sequence that rests unconformably on Paleozoic–Mesozoic greywacke

basement (Fig. 2A,B). This lower part of this sedimentary sequence formed during regional extension and associated regional subsidence that began in the early Late Cretaceous and continued to the Oligocene (Carter & Norris 1976; Norris & Carter 1982; Shearer 1995). Late Cretaceous topographic and tectonic depressions hosted fluvial sediments, including coal measures (Carter & Norris 1976; Douglas & Lindqvist 1987; Shearer 1995). The regional subsidence resulted in marine transgression, and some of the fluvial sediments were deposited in a marginal marine setting (Harrington 1958; Douglas & Lindqvist 1987; Lee et al. 2003). Maximum marine transgression occurred in the Oligocene, and compressional deformation associated with development of the present collisional plate boundary was initiated in the

Fig. 2 Summary stratigraphic columns for the four coal mines discussed in the text. **A**, Column for the Ohai-Newvale area (Fig. 1) (after Bowen 1964; Isaac & Lindqvist 1990) showing the relative stratigraphic positions of the Gore Lignite Measures and Ohai Group coal-bearing units. Stratigraphic positions of Ohai and Newvale mines are indicated with open squares. **B**, Column for the Kaitangata region (Fig. 1) (after Harrington 1958; Lee et al. 2003) showing the general stratigraphic relationships for the Taratu Formation, which hosts the Wangaloa and Kai Point mines (open square). **C**, Columns for the Kai Point and Wangaloa mines, showing the principal mine units and the relative stratigraphic positions of the two mines within the Taratu Formation.



late Oligocene to early Miocene (Carter & Norris 1976). This compressional deformation has deformed and locally uplifted the Cretaceous–Oligocene sediments and underlying basement.

Uplift of mountain ranges in the southern South Island was initiated in the early Miocene (Carter & Norris 1976). Tectonic basins adjacent to these ranges provided sites for accumulation of fluvio-lacustrine sediments including coal measures (Norris & Carter 1982; Isaac & Lindqvist 1990). Continued uplift caused localised deformation of these basins, and the Miocene sediments became unconformably overlain by younger fluvial deposits (Carter & Norris 1976; Isaac & Lindqvist 1990; Youngson et al. 2006). Continued uplift and

erosion of the whole sedimentary sequence has resulted in the present complex topography (Fig. 1). There has been localised unconformable deposition of Pliocene–Pleistocene tectonic and glaciofluvial sediments on the earlier sequence, including a veneer of late Pleistocene loess (Bruce 1973; Craw et al. 2007).

Alteration by groundwater

All the fluvial sedimentary rocks have been affected to some extent by post-depositional alteration (Craw 1984, 1994; Chamberlain et al. 1999). This alteration is a result of chemical interaction between the rocks and percolating groundwater, especially in the more permeable beds such as gravels

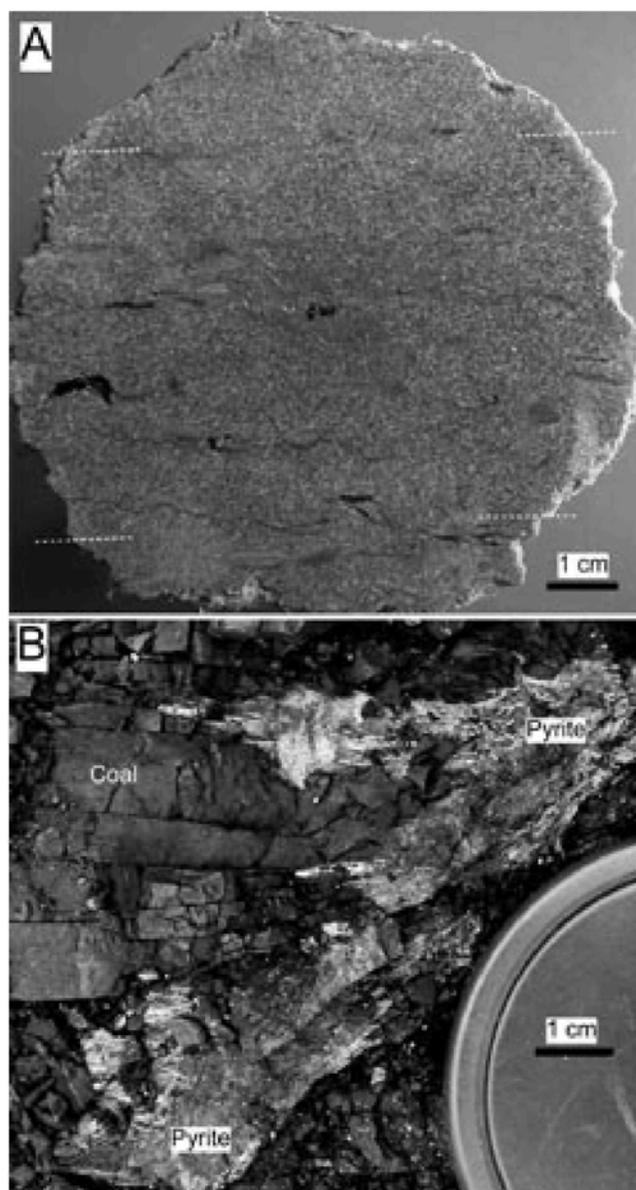


Fig. 3 Photographs of pyrite occurrences at the Kai Point mine. **A**, Pyrite concretions in marine sandstone of the concretionary unit overlying the Kaituna Seam (Fig. 2C). Bedding is horizontal, as indicated with white dashed lines. The white speckled texture of the concretion is quartz sand that has been cemented with pyrite. **B**, Coal at the top of the Kaituna Seam, with pale pyrite veins following fractures.

(Craw 1994; Chamberlain et al. 1999). Alteration is most pronounced in immature sediments derived from nearby basement during tectonic evolution of sedimentary basins. These immature sediments contain abundant clasts of quartzofeldspathic greywacke and other feldspathic basement rocks. In addition, these greywacke clasts contain abundant labile lithic clasts, which have been altered as well. The alteration process also affected basement rocks underlying the fluvial sediments, to depths of up to 20 m below the unconformity (Craw 1994).

The alteration minerals formed during this rock/water interaction depend on the chemical conditions prevailing during the alteration process. Kaolinite is the most common alteration mineral in strongly altered rocks, and this has been derived from feldspars and/or muscovite in the original rock

(Craw 1984, 1994). Chlorite commonly remained unaltered in unoxidised rocks and has been transformed to a variety of smectites in more oxidised conditions (Craw 1994; Chamberlain et al. 1999). More mature sedimentary rocks in the Cretaceous–Pleistocene sequence of southern South Island are dominated by quartz and kaolinite, and alteration is less obvious in these rocks although silica cementation was widespread (Craw 1994). Authigenic pyrite and/or marcasite has formed in a wide variety of both mature and immature fluvial sediments, particularly in and near organic matter, and some of this pyrite extends into the underlying basement (Youngson 1995; Clough & Craw 1989; Chamberlain et al. 1999).

MINE STRATIGRAPHY AND ROCK TYPES

Kaitangata coalfield

The Kaitangata coalfield has been developed in the Late Cretaceous Taratu Formation (Harrington 1958) (Fig. 2B). The Taratu Formation varies in thickness from c. 100 m to almost 1 km across the Kaitangata coalfield. The two Kaitangata coalfield mines of interest in this study, the Wangaloa and Kai Point mines (Fig. 2C,D), have been developed in the thickest part of the Taratu Formation, in a syn-depositional extensional basin (Harrington 1958; Youngson et al. 2006). The Taratu Formation unconformably overlies immature greywacke-dominated fluvial sediments of the Henley Breccia, which formed at the base of the same extensional basin (Harrington 1958; Youngson et al. 2006). In contrast to the underlying Henley Breccia, the Taratu Formation is dominated by quartz-rich mature sediments, with matrix kaolinite and kaolinite-rich siltstone and mudstone. The mature nature of the Taratu Formation is a result of derivation from groundwater-altered basement rocks and pre-existing sediments such as the Henley Breccia (Youngson et al. 2006). Rare clasts of silica-cemented quartz conglomerate in the Taratu Formation attest to the existence of pre-Taratu mature quartz-rich sediments as well, and these have been recycled into the Taratu Formation. The mature quartz and kaolinite rich sediments have numerous well-defined coal seams interspersed through the Taratu Formation (Harrington 1958). The Kai Point coal mine is being developed in the Kaituna Seam (Fig. 2B,C), although the overlying Barclay Seam was mined in the early stages of development of this mine. The Wangaloa coal mine was developed in the Barclay Seam (Fig. 2D), c. 3 km south-east of the Kai Point mine.

The Taratu Formation is overlain conformably by Late Cretaceous–Paleocene sediments deposited during the regional marine transgression (Fig. 2B) (Harrington 1958; Douglas & Lindqvist 1987; Lee et al. 2003). The upper members of the Taratu Formation, including the Kaituna and Barclay Members, contain evidence of marginal marine sedimentation with periodic marine incursions into the fluvial basin (Douglas & Lindqvist 1987; Lee et al. 2003). In particular, a distinctive concretionary unit, formed during incursion of sea water, consists of quartz-kaolinite sandstone, siltstone, and mudstone and immediately overlies the Kaituna Seam at the Kai Point mine (Fig. 2C) (Lee et al. 2003). The sandstone layers in this unit contain abundant spherical concretions, up to 10 cm across, in which pyrite cements the rock (Fig. 3A). Siltstone and mudstone layers in this unit contain ellipsoidal concretions up to 1 m long (long axis) and 50 cm thick in which ankerite cements the rock. These carbonate concretions

have undergone some post-formational fracturing, and most fractures have also been filled with ankerite. This concretionary unit has only localised distribution and is not present beneath the Barclay Seam at the Wangaloa mine (Fig. 2C).

Both the Kaituna and Barclay coal seams are up to 10 m thick, although minor partings with siltstone and mudstone occur locally. Both seams have been coalified to the boundary between lignite and sub-bituminous coal (Harrington 1958; Suggate 1959; Lee et al. 2003), and individual (organic) constituents are largely obscured by this coalification. The coal contains abundant sulfur, both as part of the organic component and as syn-depositional authigenic pyrite (Suggate 1959; Black & Craw 2001; Begbie et al. 2007). In addition, post-depositional groundwater has remobilised pyrite to form veins locally up to 5 cm thick in the coal seams (Fig. 3B), and cement in immediately overlying quartz gravels up to 2 m from coal seam tops (Begbie et al. 2007).

The uppermost Taratu Formation members and the overlying marine-influenced sediments have been removed from the Wangaloa and Kai Point mine sequences during Cenozoic–Recent uplift and erosion. Both mine sequences are capped by a veneer of Pleistocene loess silt and colluvium derived from that loess. This veneer is 1–4 m thick and is irregularly distributed across the landscape. The loess was derived from the east or southeast when a low-relief coastal plain was exposed during sea-level lowstands (Bruce 1973). Hence, the loess is typically thickest on leeward (west-facing) slopes. Colluvial channels on these slopes further thickened the loess deposits locally.

Ohai coalfield

The Ohai coal mine (Fig. 1) is developed in the Morley Coal Measures, part of a Late Cretaceous fluvial sequence that accumulated in an extensional tectonic basin (Fig. 2A) (Bowen 1964; Shearer 1995; Lee et al. 2003). The fluvial sequence is dominated by immature sandstones, with some immature conglomeratic horizons, especially at the base (Bowen 1964). Clasts in these sediments include greywackes and some granitoids, and feldspars in these clasts have been extensively altered by groundwater to kaolinite, and mafic minerals have been altered to kaolinite and montmorillonite. Organic matter in the Morley Coal Measures has been coalified to near the sub-bituminous/bituminous rank boundary (Suggate 1959; Lee et al. 2003). The coal is interlayered with sandstones, with minor siltstone, and these latter rocks are excavated as waste rock. There is no evidence for marine incursion into this fluvial tectonic basin during coal accumulation.

The Morley Coal Measures are unconformably overlain by Cenozoic sediments with Eocene Beaumont Coal Measures at their base (Fig. 2A) (Bowen 1964; Shearer 1995; Lee et al. 2003). These coal measures include immature fluvial sediments and some low-rank (lignite) high ash coals that are not mined. The unconformity between the Cretaceous and Cenozoic coal measures is angular but typically does not exceed 20°. The Beaumont Coal Measures are conformably overlain by marine sediments of a rapid marine transgression associated with a major extensional basin to the west (Norris & Carter 1982).

Eastern Southland coalfield

The Newvale coal mine (Fig. 1) is extracting lignite from the Miocene Gore Lignite Measures. These sediments accumulated in a fluvial tectonic basin from Miocene river(s) draining Central Otago (Fig. 1) and consist of nonmarine sandstone,

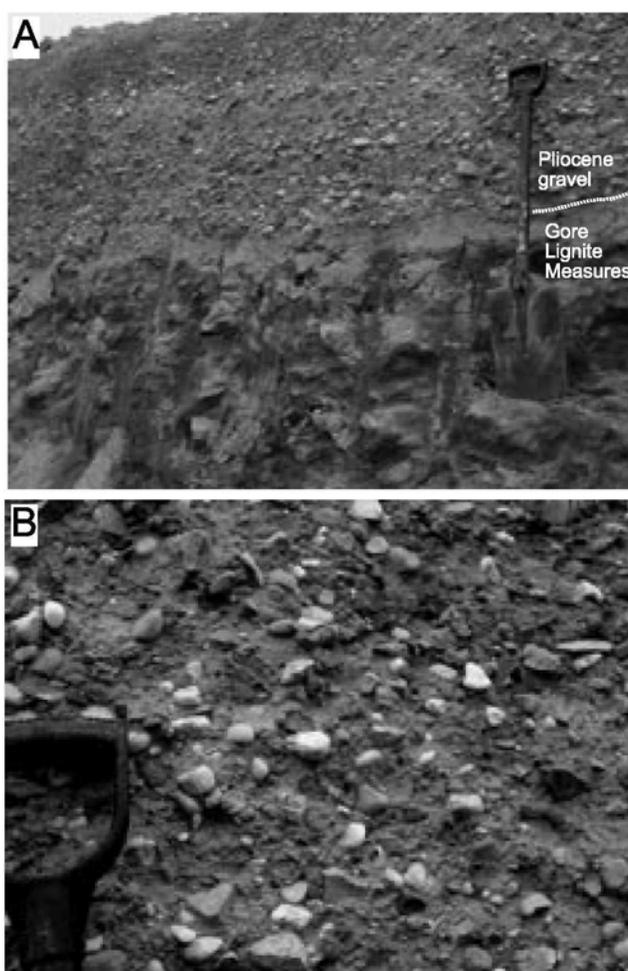


Fig. 4 Photographs of immature Pliocene gravels that overlie the Miocene Gore Lignite Measures at Newvale mine and constitute a major component of mine waste rock. **A**, Unconformity between the Pliocene and Miocene units indicated with dashed white line on right, showing the contrast in sediments between fluvial carbonaceous siltstone (below) and poorly bedded gravel (above). Spade is 90 cm tall. **B**, Close view of clast-supported Pliocene gravels (as in upper part of A) showing rounded quartz clasts separated by variably disaggregated labile greywacke clasts that form a pseudomatrix.

siltstone, and mudstone. The sediments are dominated by quartz and kaolinite derived from pre-existing mature sediments in Central Otago and from uplifted and eroded basement rocks altered by groundwater (Chamberlain et al. 1999; Youngson et al. 2006). Thick (commonly 10 m) lignite seams are irregularly distributed through this fluvial sequence (Isaac & Lindqvist 1990). The Newvale mine has been developed in a seam that occurs close to the surface on the western side of the tectonic basin (Fig. 1). The Gore Lignite Measures conformably overlie marine sediments as part of the marine regression associated with Miocene compression (Fig. 2A) (Isaac & Lindqvist 1990).

The Gore Lignite Measures at the Newvale mine are unconformably overlain by Pliocene gravels (Fig. 4A) derived from the uplifting mountain margins to the tectonic basins (Clough & Craw 1989). These sediments contain mainly immature greywacke clasts, with some quartz clasts recycled from older mature sediments (Fig. 4B). The greywacke clasts have been extensively altered by groundwater, and are largely

disaggregated, creating a labile pseudomatrix (Fig. 4B). This pseudomatrix contains authigenic smectite and chlorite disaggregated from the greywacke clasts. In addition, authigenic cementation by pyrite and/or marcasite has occurred in these gravels (Clough & Craw 1989).

METHODS

Data for key environmental parameters specific to each mine were gathered to provide quantification of appropriate magnitude, variability, and trends through the sites. Field mapping and sampling at Wangaloa mine occurred over several years (Black & Craw 2001; Craw et al. 2006, 2007; Begbie et al. 2007). Pit lakes at Wangaloa mine were sampled for turbidity and chlorophyll-*a* in October 2007, 12 h after the end of a week of intermittent rain totalling 26 mm. Mapping and sampling of parameters relevant to water quality at Kai Point mine occurred over 3 months in early 2005. Pit lakes at Ohai and Newvale mines were sampled extensively, at surfaces and from several depths, in October/November 2005, March 2006, and July 2006.

The pH and conductivity of waters were determined in the field with portable meters calibrated with standard solutions. Substrate pH was determined as paste pH: slurries prepared with distilled water on-site (Sobek et al. 1978). Water samples were obtained from accessible streams and pit lakes through each mine site. Water samples from depth in pit lakes were obtained with a 3 L Go-Flo water sampler that was acid-cleaned and stored in sterile plastic bags for transport. Major ions in Kai Point mine waters were analysed by ChemSearch, an internationally accredited laboratory in the Chemistry Department, University of Otago. APHA (1998) Method 3111B (flame atomic absorption spectrometry) was used for Ca²⁺, Mg²⁺, Na⁺, and K⁺; Method 4500-Cl C for chloride; and Method 2320B was used for dissolved carbonate. Sulfate was analysed by ion chromatography using Metrohm column (ASupp-5) with bicarbonate eluent and a Metrohm conductivity detector (IC Model 819) with chemical suppression, at ChemSearch. Detection limits for these ions are c. 1 mg/L, and analyses for these ions are reproducible to <1% error in the compositional ranges observed in this study. Major cations in Ohai and Newvale waters were determined by ICP-MS. Water samples for trace element analysis at Kai Point, Ohai, and Newvale were collected through syringe filters (0.45 µm) into acid-washed plastic bottles and preserved with nitric acid in the field. The total dissolved trace element contents of waters were determined after nitric acid digestion by ICP-MS at Hill Laboratories, Hamilton, New Zealand, an internationally accredited laboratory, using Method APHA 3125.

Samples of sediment from the bottom of pit lakes were collected with a grab-sampler lowered onto the lake bed. These were bagged immediately on recovery in acid-clean plastic bags. Suspended matter in pit lakes was left to settle for 5 months before decanting water and collecting the sedimented material which was then dried at 70°C. These samples were analysed mineralogically via standard X-ray diffraction techniques on a PANalytical X'Pert instrument with CuKα radiation, in the Geology Department, University of Otago. Turbidity of water samples from Wangaloa, Newvale, and Ohai mines was determined within 24 h of collection using a HACH 2100N Turbidimeter, using reference method APHA 2130B at ChemSearch. Samples were tipped on end 20 times to redistribute settled material, and measurements

were compared to Gelex Secondary Turbidity Standards. Chlorophyll-*a* contents of turbid waters were determined after acetone extraction and HCl acidification by fluorescence with a Sequoia-Turner Model 450 fluorometer.

Total B contents of coal were determined by Eschka fusion of c. 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 this analysis is c. 25 mg/kg, depending on the properties of the sample matrix. Total sulfur (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.

RESULTS

Some environmental data for the Wangaloa mine have been compiled previously by Black & Craw (2001), Craw et al. (2006, 2007), and Begbie et al. (2007). Relevant results from these studies are summarised herein and are used as benchmarks for comparison with the other mines in this study. Detailed data for some parameters were not gathered at mines where these parameters were of little or no environmental significance (Table 1). Instead, limited data for these parameters are used for comparison only, to show the greater significance of these parameters in other mines. Data are summarised in Fig. 5–9, and Table 2, and representative analyses of key parameters are presented in Tables 3 and 4. Data from some sites are not plotted in diagrams where the results are at or near analytical detection limits. Detailed information on stratigraphic variations of sulfur and boron contents are presented for Wangaloa and Kai Point mines only, as these parameters affect water acidity and dissolved boron, the most environmentally significant water quality parameters at these two sites (Table 1). The differing topographic settings of the four studied sites hindered gathering of datasets that are directly comparable among all the sites. Both Wangaloa and Kai Point mines are located in well-defined valleys, so that water compositions can be followed through the sites to distinct discharge points (e.g., Fig. 6A; Table 3), whereas Ohai and Newvale mines have mainly internal drainage to pit lakes. Wangaloa, Ohai, and Newvale mines have pit lakes that are inactive or rarely disturbed, whereas Kai Point mine has only one pit lake that is in the centre of the active mine, precluding comparison of lake turbidity data from Kai Point mine.

Table 2 Mineral species and their relative abundances (qualitative) in suspended material and material settled on pit lake floors in southern New Zealand coal mines.

	Ohai	Wangaloa, Kai Point	Newvale
Quartz	common	common	common
Feldspar	absent	rare	rare
Muscovite	rare	common	common
Chlorite	absent	absent	dominant
Kaolinite	dominant	dominant	absent
Montmorillonite	rare	absent	absent

Wangaloa mine

The Wangaloa mine was active from the 1940s to 1989, and has been rehabilitated since 2003 (Begbie et al. 2007). The principal features of environmental significance are site acidification, low pH, and elevated boron levels in site discharge waters (Begbie et al. 2007; Table 1). The acidification arose because of oxidation of pyrite in coal and waste rocks (Begbie et al. 2007). Sulfuric acid from this oxidation process also caused localised mobilisation of Cu and Zn, and some dissolved As was released from solid solution in pyrite (Black & Craw 2001). These trace element effects were minor and intermittent, and may have been enhanced by rising water tables after periods of low rainfall (Black & Craw 2001).

Pyrite, oxidation of which causes the low pH of substrates at the Wangaloa site, occurs primarily in coal fragments scattered through the waste rock. Total S concentrations in the Barclay Seam, from which these coal fragments were derived, is near 4 wt% (Fig. 5A). This total S content includes both pyritic and organic S, and changes little through the seam (Fig. 5A). Hand specimen observations suggest that pyrite is most common, but irregularly distributed, near the top of the Barclay Seam. Hence, the data in Fig. 5A show typical or background S contents, and locally higher S contents (up to 7 wt%) can occur. In addition, pyrite-cemented quartz conglomerate that immediately overlies the Barclay Seam has caused strong acidification (down to pH = 1) of some waste rock at Wangaloa (Begbie et al. 2007).

The surface and ground waters at the Wangaloa site have generally lower pH than background waters (Fig. 6A). In particular, waters that have been in contact with pyrite-bearing waste rock have pH as low as 3 (Fig. 6A). Almost all surface and ground waters at the Wangaloa site pass through a large pit lake before leaving the site, and this lake facilitates mixing of site waters. The lake pH was near 4 at the beginning of site rehabilitation, and rose during rehabilitation to near 6 (Fig. 6A) (Begbie et al. 2007). Consequently, waters discharging from the site also rose from below pH 4 to pH 6 during rehabilitation (Fig. 6A) (Begbie et al. 2007).

Boron contents of the Barclay Seam, like the S contents, are broadly uniform through the upper part of the seam (Fig. 5B). Typical B contents are c. 50 mg/kg (Fig. 5B). B contents of Barclay seam coal are locally as high as 450 mg/kg, and may have been enhanced by secondary mobilisation and evaporative concentration in surface waters (Craw et al. 2006). Boron content of surface and ground waters at Wangaloa are highest (up to 6 mg/L) in acid waters that have chemically interacted with coal-bearing waste rocks (Fig. 6B) (Craw et al. 2006). Higher pH site waters have relatively lower B contents (Fig. 6B), and the lake and discharge waters had B contents of c. 0.9 mg/L in the latter stages of site rehabilitation in 2006 (Begbie et al. 2007).

Wangaloa waters have low dissolved cation concentrations (typically <100 mg/kg Ca²⁺, Mg²⁺, <30 mg/kg Na⁺, and <7 mg/kg K⁺ (Fig. 7A,B). Consequently, conductivity of Wangaloa mine waters is generally low (<800 μ S/cm; Fig. 8A). Dissolved trace metals are typically low, although dissolved Cu is up to 0.018 mg/L (Fig. 8C), and temporarily elevated dissolved As up to 0.7 mg/L and Zn up to 1 mg/L have been recorded (Black & Craw 2001). Dissolved Al is up to 6 mg/L (Fig. 8C).

Wangaloa mine waters become highly turbid during heavy rain events, but that turbidity eases rapidly as the suspended matter settles. The main pit lake loses turbidity rapidly (days

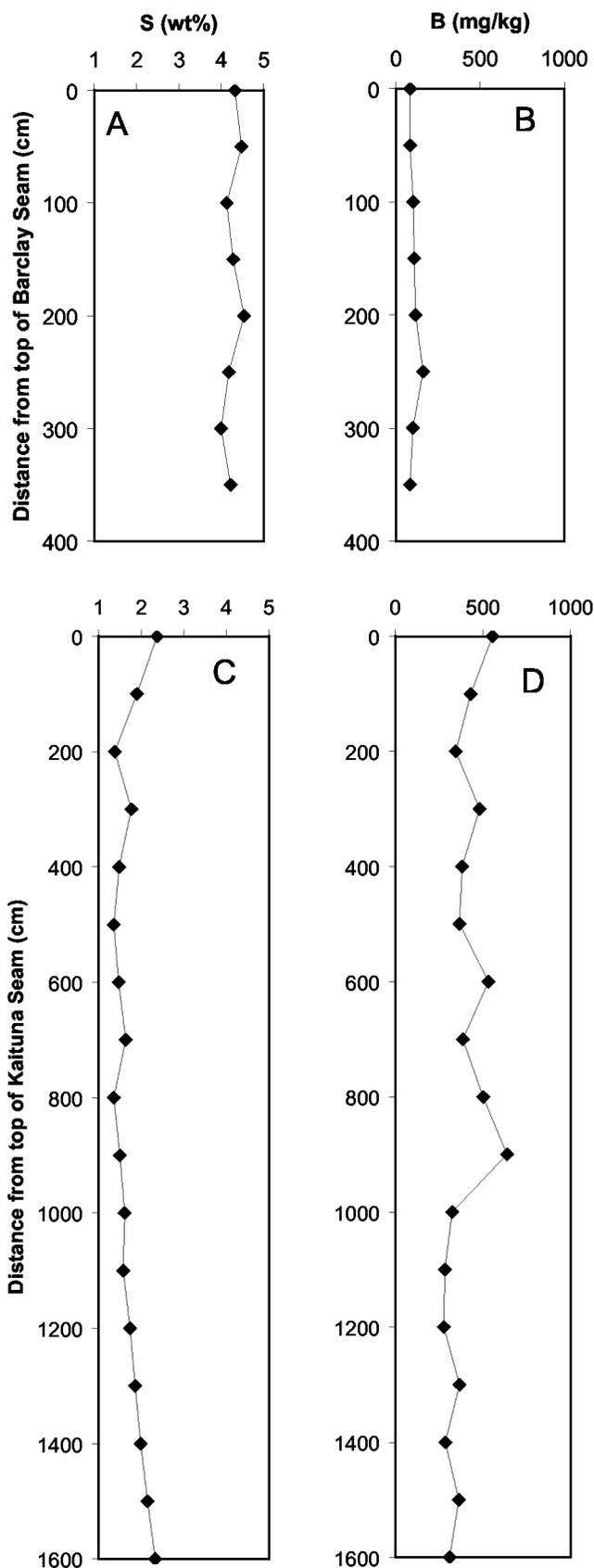


Fig. 5 Variations with depth through coal seams of sulfur and boron in the Kaitangata coalfield. A, S content of Barclay Seam at Wangaloa mine. B, Boron content of Barclay Seam at Wangaloa mine. C, S content of Kaituna Seam at Kai Point mine. D, Boron content of Kaituna Seam at Kai Point mine.

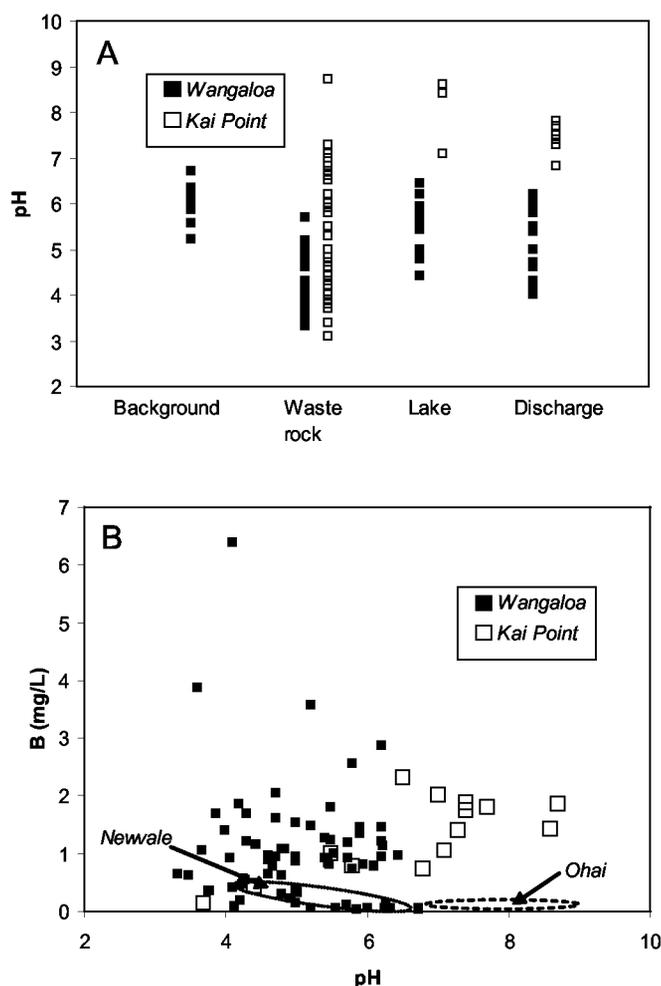


Fig. 6 The pH and boron contents of mine waters in the Kaitangata coalfield. **A**, Variations of pH of mine waters, arranged with incoming water at left, and discharging water at right. **B**, Covariation of pH and dissolved boron content of mine waters.

to weeks), and turbidity persists in two smaller lakes for hours only, despite abundant unvegetated waste rock in their catchment areas. The settled suspended matter on the main pit lake floor is dominated by kaolinite, with subordinate quartz and muscovite (Table 2). Long-term turbidity in all lakes is low (5–15 NTU; Fig. 9A). The lake with the highest turbidity also has the highest chlorophyll-*a* content (4.6 $\mu\text{g/L}$; Fig. 9A), indicating that a significant proportion of the turbidity is a result of the presence of phytoplankton (cf. Jamu et al. 1999).

Kai Point mine

Initial mining at Kai Point focused on the Barclay Seam (Fig. 2C), and waste rock from that mining stage has been stored on-site. The Barclay Seam at Kai Point is chemically similar to the same seam at Wangaloa, with strongly elevated S (up to 5 wt%) and moderate boron levels (c. 50–450 mg/kg). Most mining at Kai Point has extracted coal from the Kaituna Seam (Fig. 2C), which is chemically distinct from the Barclay Seam (Fig. 5C,D). Kaituna Seam coal contains less S than the Barclay Seam, with most of the seam having <2 wt% S (Fig. 5C). The S content of Kaituna Seam rises slightly above 2 wt% at the top and bottom of the seam (Fig. 5C). As for the Barclay Seam, the S content of the Kaituna Seam depicted in Fig. 5C reflects a typical or background level. Abundant but localised secondary pyrite occurs in fractures in the upper 1–2 m of the Kaituna Seam (Fig. 3B), substantially raising the S content locally. The low overall S content of the Kaituna seam reflects generally lower pyrite content compared to the Barclay Seam, and less acidification of waste rock occurs during storage than at Wangaloa. However, the pyrite-rich upper part of the Kaituna Seam is generally removed as waste rock, and this pyrite can contribute to acidification of site substrates. In addition, pyritic concretions in sandstone overlying the Kaituna Seam (Fig. 2C) also contribute to localised acidification of waste rock piles.

Waters that have interacted with waste rock have a wide range of pH across the mine site (Fig. 6A), reflecting the variable waste rock compositions described above. However, the pit lake in the active mine, which receives some of the waste rock drainage and drainage from active mine excavations, has a pH between 7 and 9 (Fig. 6A; Table 3). This is distinctly more alkaline than the pit lake at Wangaloa (Fig. 6A).

Table 3 Water analyses through the Kai Point mine, from waste rock piles, through the main pit, to wetlands on the discharging creek. All analyses are mg/L except conductivity (cond.), which is in $\mu\text{S/cm}$, and pH (pH units). LLD = detection limit; bd = below detection; alk = alkalinity as HCO_3^- .

Sample	KP2	KP3	KP6	KP9	KP14	KP12	KP11	LLD
Site	waste rock	waste rock	waste rock	waste rock	pit	waste rock	discharge	
Water	stream	stream	pool	stream	lake	wetland	wetland	
Ca ²⁺	81.0	45.5	195	258	51.0	19.4	50.0	1
Mg ²⁺	60.0	32.0	199	253	50.0	16.5	49.0	1
Na ⁺	42.0	9.7	56.0	62.0	83.0	12.4	32.0	1
K ⁺	6.56	4.46	13.1	12.1	11.4	5.62	5.90	1
Cl ⁻	14.4	12.0	28.5	26.6	24.4	10.0	28.8	1
SO ₄ ²⁻	547	270	1190	1600	267	129	315	1
alk ⁴	bd	bd	320	305	279	6.8	57	1.2
As	bd	bd	bd	bd	bd	bd	bd	0.001
B	0.44	0.144	2.00	2.29	1.43	0.999	1.04	0.005
Cond.	973	595	1943	2225	877	323	722	
pH	4.4	3.7	7.0	6.5	8.6	5.5	7.1	

Likewise, waters discharging from the Kai Point mine site have a pH value near 7, distinctly higher than Wangaloa waters even after rehabilitation (Fig. 6A). Kai Point mine waters have a large range in conductivities (up to c. 2000 $\mu\text{S}/\text{cm}$; Fig. 8A; Table 3), with anions dominated by sulfate and alkalinity (Table 3). There is locally elevated dissolved Ca^{2+} and Mg^{2+} (up to 250 mg/L of each; Fig. 7A), probably resulting from interaction of acid waters with ankerite concretions.

Kai Point mine waters have relatively high Na^+ and K^+ (up to three times higher) compared to Wangaloa mine waters (Fig. 7B; Table 3). Dissolved trace metals, including As (Table 3), are near to, or below, analytical detection limits. Boron levels are strongly elevated in the Kaituna Seam (up to 640 mg/kg) compared to the Barclay Seam (Fig. 5B,D). Consequently, dissolved B contents of Kai Point mine waters are generally higher (up to 2 mg/L) than Wangaloa waters, excepting local waste rock waters at Wangaloa (Fig. 5B). Discharge waters at Kai Point have between 1 and 2 mg/L dissolved B at near-neutral pH. Environmentally acceptable levels of dissolved B for aquatic organisms are poorly defined because B is also a micronutrient at low levels (Rowe et al. 1998; Parks & Edwards 2005; Craw et al. 2006). However, the dissolved B contents of Kai Point discharge waters are at levels below fish toxicity and are safe for human drinking water (Rowe et al. 1998; Parks & Edwards 2005).

Rapid runoff of rainwater results in localised stream turbidity at the Kai Point mine, and the pit lake is commonly turbid when active mining is occurring around it. However, this turbidity eases rapidly (commonly over hours to days) as the suspended matter, which is mainly kaolinite, settles when water motion ceases (Table 2). No turbidity measurements were taken at the Kai Point site because the only lake is part of the active mining zone.

Ohai coal mine

Coal and associated fluvial sediments of the Morley Coal Measures do not contain pyrite, and overall S content is low (typically <0.1 wt%). Consequently, there has been no acidification of substrates in waste rock piles, or acidification of mine waters (Fig. 8A). Surface streams draining mine excavation surfaces and waste rocks, and a large pit lake, all have pH values between 7.0 and 9.5 (Fig. 8A).

Dissolved load of the Ohai waters is low (Table 3), and conductivity is correspondingly low (<600 $\mu\text{S}/\text{cm}$; Fig. 8A). Dissolved Ca^{2+} and Mg^{2+} concentrations at Ohai are low (<50 mg/L; Table 3), and the Ca/Mg ratio is higher than for Kaitangata coalfield waters (Fig. 7A). Dissolved K^+ is low (<5 mg/L), but dissolved Na^+ is distinctly elevated (up to 160 mg/L) compared with all other mine waters in this study (Fig. 7B). Dissolved trace metal concentrations are generally near to analytical detection limits in Ohai waters (Table 4). Both dissolved Al and Cu concentrations, for example, are distinctly lower than at the Wangaloa mine site (Fig. 8C). Dissolved boron levels of mine waters are low (c. 0.1–0.2 mg/L) (Fig. 8B; Table 4).

The most environmentally significant water quality feature at the Ohai mine is turbidity of mine waters, especially in the large pit lake (Fig. 9A,B). The lake has near-constant turbidity over time, although turbidity increases slightly with depth (Fig. 9B). This turbidity is due to the presence of a suspension of sub-micrometre kaolinite, with minor smectite (Table 2), and chlorophyll-*a* contents are low (<1 $\mu\text{g}/\text{L}$; Fig. 9A).

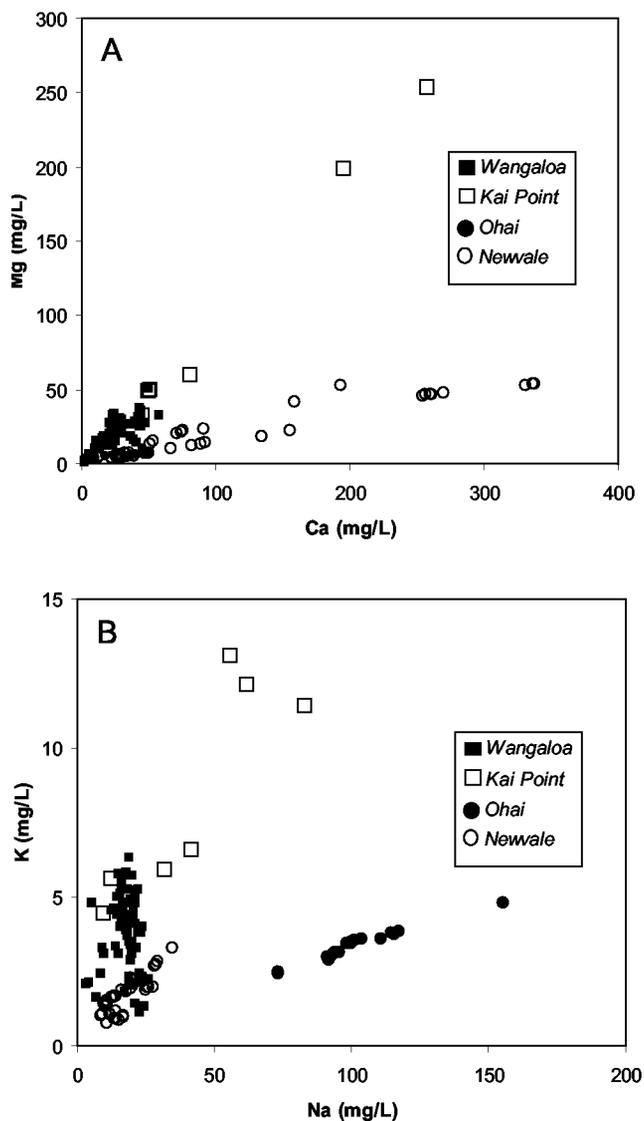


Fig. 7 Major cation concentrations in mine waters from the four studied mine sites. A, Covariation of Ca^{2+} and Mg^{2+} . B, Covariation of Na^+ and K^+ .

This suspension apparently settles only slowly, if at all, and affects the quality of potential discharge waters. Despite this suspension of extremely fine grained kaolinite, there has been little dissolution of that kaolinite, as dissolved Al concentration remains low (<0.5 mg/L) in Ohai mine waters (Fig. 8B). However, elevated dissolved Na^+ (Fig. 7B) may reflect dissolution of smectite (Table 2) or the abundant decomposing feldspar in the adjacent waste rocks.

Newvale coal mine

Lignite and the fluvial sediments of the Gore Lignite Measures at Newvale mine have low S (typically <0.1 wt%) and pyrite is rare or absent. Hence, acidification from these rocks is negligible, and most mine waters have circumneutral pH (Fig. 8A). However, oxidation of pyrite and/or marcasite in the overlying Pliocene gravels (Fig. 4A) has caused minor localised acidification of substrates and mine waters down to pH 4 (Fig. 8A).

Table 4 Representative set of trace metal analyses of pit lake waters with slightly elevated dissolved trace element contents (mg/L) from Ohai and Newvale coal mines, southern New Zealand. LLD = detection limit; bd = below detection. Cond. = conductivity ($\mu\text{mho}/\text{cm}$). Last column has ANZECC (2000) recommended trace metal limits for 95% protection of aquatic species.

Site	Ohai		Ohai		Ohai		Ohai		Newvale		Newvale		Newvale		ANZECC	
	N side	E side	active	disused	active	disused	active	disused	95%							
Water	pit lake															
Depth (m)	20	10	5	25	35	10	5	10	10	3	10	10	3	3		
Date	6 Oct 05	7 Dec 05														
pH	7.2	7.3	7.3	7.3	7.3	6.2	6.0	6.7	6.7	5.3	6.2	6.7	5.3	5.5		
Cond.	515	510	514	514	514	910	610	1256	1256	689	349	29.2	702	27.5		
Na ⁺	104	99.0	100	100	100	34.9	20.5	29.2	29.2	25.5	2.0	2.0	27.5	2.0		
K ⁺	3.6	3.4	3.4	3.5	3.4	3.3	2.1	2.8	2.8	2.0	2.0	2.8	2.0	2.0		
Ca ²⁺	24.3	17.6	17.7	18	17.7	193	91.1	159	159	73.9	75.7	75.7	75.7	75.7		
Mg ²⁺	5.5	5.1	5.2	5.2	5.2	52.5	23.3	41.4	41.4	20.9	21.8	21.8	21.8	21.8		
B	0.005	0.124	0.127	0.132	0.132	0.146	0.123	0.134	0.134	0.348	0.322	0.322	0.322	0.322		0.370
Fe	0.02	bd	bd	bd	bd	20.3	4.63	14.1	14.1	0.06	0.96	0.96	0.96	0.96		
Mn	0.0005	bd	bd	bd	0.0008	1.09	0.554	0.943	0.943	0.617	0.651	0.651	0.651	0.651		1.9
Al	0.01	0.016	0.017	0.017	0.016	0.07	0.094	0.076	0.076	0.016	0.015	0.015	0.015	0.015		0.055
Cu	0.001	bd	bd	bd	bd	0.048	0.01	0.034	0.034	bd	0.002	0.002	0.002	0.002		0.013
As	0.0005	0.0018	0.0025	0.0019	0.0019	0.0005	bd		0.0014							
Ni	0.0005	0.0006	0.0008	0.0006	0.0005	bd	0.0056	0.001	0.001	0.0017	0.0017	0.0017	0.0017	0.0017		0.011
Pb	0.0001	bd	0.0003	0.0003	0.0005	0.0002	bd	0.0002	0.0002	bd	bd	bd	bd	bd		0.0034
Zn	0.001	0.001	0.001	0.001	0.001	0.006	0.014	0.008	0.008	0.02	0.004	0.004	0.004	0.004		0.008

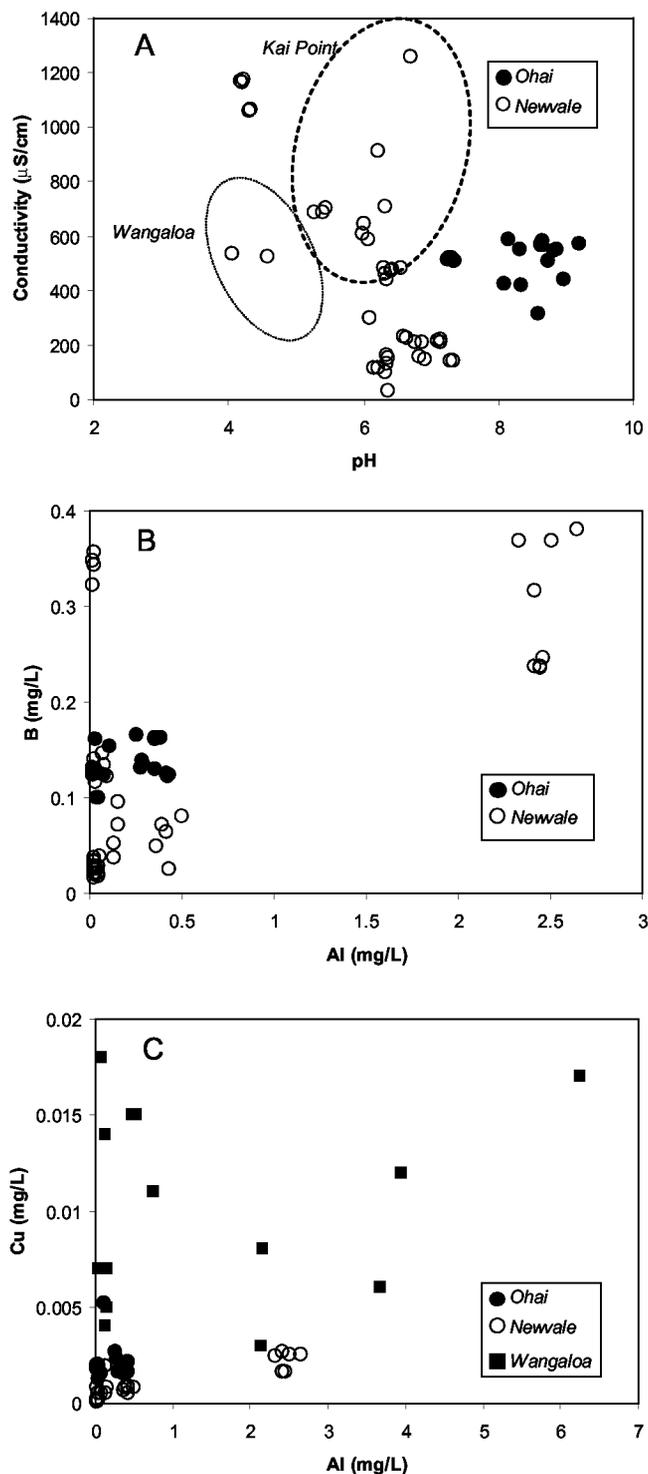


Fig. 8 Chemical characteristics of mine waters from the studied sites. A, Water pH versus conductivity data for Ohai and Newvale mines, compared to the observed range for mine waters at Kai Point (dashed ellipse) and Wangaloa (small ellipse). B, Covariation of dissolved Al content and dissolved B contents for Ohai and Newvale mine waters. Wangaloa and Kai Point waters are not shown at this scale because of their relatively high B contents (Fig. 6B). C, Covariation of dissolved Al and Cu contents of Wangaloa, Ohai, and Newvale mine sites.

Pit lake waters at Newvale mine exhibit a wide range of compositions, with conductivity data extending from <100 $\mu\text{S}/\text{cm}$ (less than at Ohai mine) up to 1200 $\mu\text{S}/\text{cm}$ (Fig. 8A). The high conductivity waters all have relatively low pH. The Newvale waters are characterised by a trend towards elevated dissolved Ca^{2+} (up to 340 mg/L), with a Ca/Mg ratio that is similar to Ohai mine waters and distinctly higher than at Kai Point mine (Fig. 7A). In contrast, Newvale mine waters have low dissolved Na^+ and K^+ that is comparable to the Wangaloa mine, and there is no enrichment of Na^+ like that seen at Ohai mine (Fig. 7B).

Newvale mine waters typically have low dissolved trace metal concentrations, near to analytical detection limits (Table 4). Dissolved B levels are typically 0.1 mg/L (Table 4; Fig. 8B), and higher B levels in some waters (up to c. 0.4 mg/L ; Fig. 8B; Table 4) occur mainly in a pit lake that has been weakly acidified by oxidation in the overlying Pliocene gravels. Likewise, the more acid waters (pH near 4) have dissolved Al near 2.5 mg/L , which is higher than at Ohai mine, but lower than at Wangaloa mine (Fig. 8B,C). Elevated Fe and As occurred in some samples of waters from a pit lake into which waste rock was being actively deposited (Table 3), but these elevated concentrations were not apparent 3 months later.

Turbidity data for Newvale pit lakes (Fig. 9B) show that there is considerable spatial and temporal variability in this parameter. The highest turbidity (near 90 NTU; Fig. 9B) occurred in a pit lake adjacent to an active waste rock pile that had occasional incursions of waste rock into the lake. This turbidity decreased markedly on a time-scale of months (Fig. 9B). The lowest Newvale turbidity data (Fig. 9B) were gathered in the oldest inactive pit lake. All Newvale lake waters have higher chlorophyll-*a* contents than Ohai lake waters (Fig. 9A). Moderate turbidity (c. 10 NTU) Newvale lake waters have a wide range of chlorophyll-*a* contents up to 21 $\mu\text{g}/\text{L}$ (Fig. 9A). The pit lakes are all shallow and no significant variations of turbidity with depth were discernible. The mineral component of turbidity in the younger pit lakes is a result of suspended silicates dominated by chlorite (Table 2). This chlorite is derived from the disaggregated greywacke clasts in the Pliocene gravels that form the overburden for the mine (Fig. 4A,B). Kaolinite from Gore Lignite Measures associated with the mined lignite is apparently an inconsequential contributor to the suspended matter in the pit lakes. Dissolution of suspended mineral matter has occurred to a limited extent only (Table 4; Fig. 8C). Elevated Ca^{2+} concentrations in waters that have been acidified by pyrite oxidation in overlying Pliocene sediments may result from dissolution of Ca-bearing minerals in labile greywacke clasts in those sediments (Fig. 4A,B).

DISCUSSION

Marine influences

Pyrite is the predominant precursor and cause of acidification associated with coal mines (Sengupta 1993; Weber et al. 2004; Begbie et al. 2007). Pyrite in coal-bearing sedimentary sequences is commonly associated with marginal marine sedimentation (Sengupta 1993; Hughes et al. 2007). These generalisations are correct for the Wangaloa mine, and acidification at that mine is largely a result of oxidation of syn-depositional pyrite formed in coals deposited in close

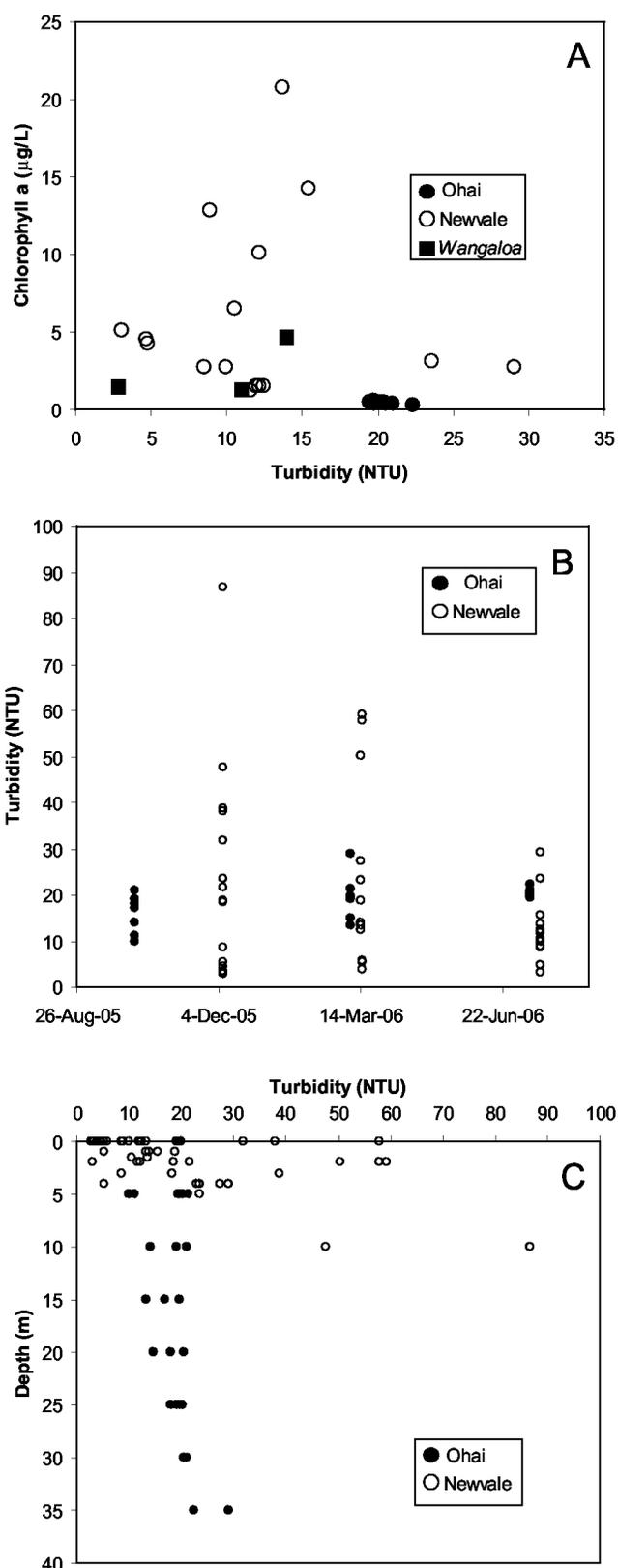


Fig. 9 Turbidity data for pit lakes at Wangaloa, Ohai, and Newvale coal mines. **A**, Covariation of turbidity and chlorophyll-*a* in pit lake waters from Wangaloa, Ohai, and Newvale coal mines. **B**, Variations of turbidity with time through three sampling campaigns at Ohai and Newvale mines. **C**, Variations of turbidity with depth for pit lakes at Ohai and Newvale mines.

proximity to marine incursions (Douglas & Lindqvist 1987; Lee et al. 2003). Remobilisation of some of that pyrite has also extended the pyritic mineralisation to the overlying fluvial quartz gravels as well (Begbie et al. 2007).

Localised acidification at Kai Point mine is predictable from the similar stratigraphic setting to that of the Wangaloa mine. The indications of sea-water incursion in the unit immediately overlying the Kaituna Seam confirm the marginal marine setting for deposition of that coal (Lee et al. 2003). Oxidation of pyrite in the coal and in the overlying concretionary unit causes localised acidity (Fig. 6A). However, the concretionary unit overlying the Kaituna Seam contains abundant large ankerite carbonate concretions (above). These concretions are the only carbonate material on the Kai Point mine site, and constitute a major lithological difference from Wangaloa mine, where no carbonate is present. The carbonate in the concretions facilitates neutralisation of sulfuric acid generated by pyrite oxidation, and many waste rock substrates have near-neutral pH. It is not possible to quantify mine site acid generation potential and acid neutralisation capacity (cf. Skousen et al. 1997; Weber et al. 2004; Hughes et al. 2007) at the hand specimen or outcrop scale at Kai Point because of the irregular distribution of pyrite and carbonate on the 1–10 m scale. However, it is clear from the site water pH data (Fig. 6A) that there is sufficient neutralising capacity in the carbonate concretions in the concretionary unit to counter acid generated from what are locally substantial amounts of pyrite. The neutralisation reaction also contributes to elevated dissolved Ca^{2+} , Mg^{2+} , and alkalinity in mine waters (Fig. 7A; Table 3). The discontinuance of this carbonate-bearing unit between Kai Point and Wangaloa mines accounts for the contrast of net acidification at Wangaloa and net acid neutralisation at Kai Point (Fig. 6A; Table 3).

Ohai mine, despite being of similar stratigraphic age to both Wangaloa and Kai Point mines, has negligible pyrite content and no acidification because the Ohai sedimentary sequence was entirely nonmarine during deposition (Bowen 1964; Shearer 1995; Lee et al. 2003). The Ohai tectonic basin apparently developed above sea level and/or was not open to the coast (Bowen 1964), in contrast to the Kaitangata coalfield which hosted several marine incursions during the Late Cretaceous (Lee et al. 2003).

The coal-bearing sequence at Newvale was fully nonmarine during deposition (Isaac & Lindqvist 1990), and pyrite is rare and so acidification is not a consequence. However, some marine influence may have occurred, with associated pyrite, in deeper parts of the Gore Lignite Measures, as these are underlain by marine sediments (Isaac & Lindqvist 1990). In addition, even though the overlying Pliocene gravels are fully nonmarine, authigenic iron sulfide has formed, and oxidation of this sulfide causes localised acidification (Falconer & Craw 2005). The iron sulfide forms from groundwater, with the dissolved S supplied via marine aerosols in rainwater (Youngson 1995). This phenomenon is widespread in southern South Island nonmarine Cenozoic–Recent gravels (Clough & Craw 1989; Youngson 1995; Falconer & Craw 2005). Hence, this indirect marine-sourced sulfide material, as well as sulfides from direct marine incursion, can be responsible for coal mine acidification.

In addition to pyrite formation, marine incursions in close stratigraphic proximity to coal seams typically result in elevated levels of boron in coals (Goodarzi & Swaine 1994). This is apparent in the Kaitangata coalfield (Craw et al. 2006).

Kai Point mine, in particular, has strongly elevated B levels in the Kaituna Seam, and this has led to elevated dissolved B levels in mine waters. The Kaituna Seam was formed in close stratigraphic proximity to marine-influenced sediment (immediately overlying concretionary unit), and therefore has generally higher B content than the Barclay Seam at Wangaloa (Fig. 4B,D), where the stratigraphic link to marine sediments is less direct (Lee et al. 2003). However, some portions of the Barclay Seam do have elevated B (up to 450 mg/kg), despite the generally low levels in the upper part of the seam (Fig. 4B).

Acidification of mine substrates and waters following pyrite oxidation has the follow-on effect of facilitating dissolution of trace metals (Black & Craw 2001; Falconer & Craw 2005). Metals such as Al, Cu, and Zn are essentially insoluble, from an environmental quality perspective, in near-neutral waters, but become more soluble with decreasing pH (Langmuir 1997; Lottermoser 2003). The transiently elevated dissolved Cu and Zn levels reported at Wangaloa (Fig. 8B) (Black & Craw 2001), and the present localised elevation of dissolved Al at Wangaloa and Newvale (Fig. 8B), are therefore indirect results of pyrite formed from marine influences in the stratigraphy. Low pH can also enhance B dissolution (Fig. 5B, 6B), although the chemical reasons for this are poorly understood (Severson & Gough 1983; Craw et al. 2006). Elevated Fe concentrations in Newvale waters are unlikely to be a result of true dissolution of Fe, as Fe^{3+} is extremely insoluble at circumneutral pH (Langmuir 1997). More likely, this Fe represents colloidal iron oxyhydroxide material finer grained than the 0.45 μm filters used in sampling. The same samples contain elevated As levels (Table 4), and this As is probably preferentially adsorbed onto the iron oxyhydroxide colloidal material (Langmuir 1997; Hewlett et al. 2005). These elevated concentrations did not persist, and were probably derived from waste rock being dumped in the pit lake near the time of sampling.

Sources of suspended minerals causing turbidity

Clay minerals that have formed from alteration of labile sediments and underlying basement by groundwater dominate the clay mineral component of Cretaceous–Cenozoic sediments in the southern South Island (Craw 1994; Youngson et al. 2006). These various clay minerals form with a wide range of grain sizes that are partly controlled by the minerals they are replacing and partly by the nature of the rock permeability that allowed water incursion (Craw 1994). When these clay minerals are transported in water, additional grain-size sorting occurs (Davies-Colley & Smith 2001). Initial mobilisation of these clay minerals results in turbid water with a wide range of grain sizes entrained mainly in suspension (Davies-Colley & Smith 2001). Transport of the clay minerals in a river system results in transfer of the finest material to the ocean in turbid water, whereas coarser and well-sorted clay mineral bearing sediments are retained in fluvial sediments. Hence, a coal mine developed in a sedimentary sequence consisting of mature fluvial sediments will cause disturbance and mobilisation of relatively coarse grained well-sorted clay minerals.

The two mines in the Kaitangata coalfield have facilitated mobilisation of micrometre-scale fluvial kaolinite into mine waters. This kaolinite readily settles again, on a time-scale of days or weeks, and turbidity is not a significant environmental issue at either mine. Relict turbidity in Wangaloa mine lakes is at least partially a result of phytoplankton (Fig. 9A).

In contrast, the waste rock at Ohai contains clay minerals formed *in situ*, from labile minerals in the immature host sediments. It is the fine-grained (sub-micrometre) component of this clay fraction that caused significant turbidity in Ohai mine waters, and this turbidity did not decrease on a time-scale of months (Fig. 9A,B). There is a negligible phytoplankton contribution to the Ohai lake water turbidity (Fig. 9A). Turbidity at Newvale has been dominated by chlorite disaggregated from the overlying immature Pliocene gravels (Fig. 4B; Table 2). This chlorite is mainly of moderate grain size (1–10 μm scale), as it is a widespread low-grade metamorphic mineral. These sediments have not been altered by groundwater for sufficiently long to transform the feldspars to kaolinite, as has occurred at Ohai. Hence, the Newvale turbidity decreases on a time-scale of months as suspended chlorite settles. Remnant turbidity at Newvale (Fig. 9A,B) is probably a result of suspension of neo-formed clay minerals in the disaggregated Pliocene clasts, and variable amounts of chlorophyll-*a* (Fig. 9A). Future mining at Newvale may mobilise kaolinite from within the Gore Lignite Measures themselves, but since this is fluvially transported kaolinite (as for Kaitangata coalfield, above), long-lived turbidity is unlikely to arise.

CONCLUSIONS

Water quality at southern South Island coal mines is directly or indirectly related to the immediate stratigraphic setting of each mine. Consequently, environmental water quality is predictable in advance of mining as long as the specific stratigraphy is known. The principal environmental water quality parameters and their stratigraphic controls for four examples of established coal mines in the southern South Island are summarised in Table 1. Acidification results from oxidation of authigenic pyrite that is formed when there is a marine influence on the mine stratigraphy. This marine influence ranges from direct marine incursion, indicated by carbonate and pyrite bearing sediment overlying coal, as in the Late Cretaceous Taratu Formation of Kai Point mine, to indirect as in the Miocene coal measures at Newvale where marine aerosols in rainwater have facilitated pyrite formation in unconformably overlying Pliocene nonmarine gravels. Carbonate concretions in the marine-influenced unit overlying the mined coal seam at Kai Point mine have sufficient neutralisation capacity to maintain near-neutral pH over most of the mine site and its discharge waters. This marine-influenced unit does not occur at the nearby Wangaloa mine site, and acidification of substrates and mine waters has occurred to various degrees since mining ceased in 1989. This acidification has resulted in localised and temporary mobilisation of Al, Cu, Zn, and As from waste rock.

Proximity of coal to marine incursions in the stratigraphic sequence affects the boron content of the coal, and also the amount of dissolved boron in mine waters. The coal seam immediately beneath the marine-influenced unit at Kai Point mine has up to 640 mg B/kg, whereas coal at the nearby Wangaloa mine, also formed in a marginal marine setting, has 50–450 mg B/kg. Waters in these coal mines have dissolved B contents more than 10 times higher than those in mines in nonmarine coals at Ohai and Newvale (Fig. 6B, 8B).

Turbidity in mine waters readily settles on a time-scale of days when the suspended matter is fluvially transported clay minerals, such as the kaolinite that dominates the clay fraction

of Late Cretaceous and Miocene coal measures. In contrast, clay minerals liberated from immature sedimentary detritus have a wide range of grain sizes including sub-micrometre particles. These latter particles in particular contribute to long-term turbidity of mine waters.

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