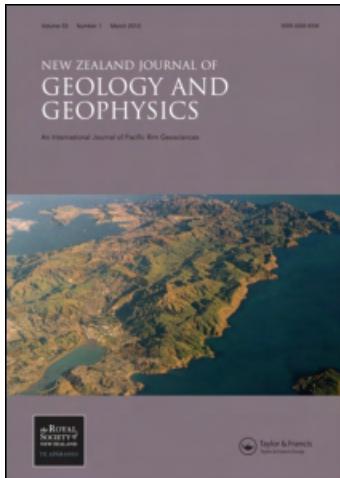


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Field quantification and characterisation of extreme arsenic concentrations at a historic mine processing site, Waiuta, New Zealand

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Field quantification and characterisation of extreme arsenic concentrations at a historic mine processing site, Waiuta, New Zealand

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Abstract The mining and roasting of the arsenopyrite ore in the Waiuta area (c. 30 km south of Reefton, Westland) has left a legacy of arsenic-rich material. The scale and extent of elevated arsenic concentrations were established with field portable X-ray fluorescence measurements. The principal source of environmental arsenic at the Prohibition Mill site is the roasting by-product arsenolite, which is very toxic and more environmentally mobile than arsenopyrite in original ore. Resultant arsenic-rich run-off (c. 30 mg/L) is temporarily immobilised by the formation of the secondary arsenic mineral scorodite, which cements the ground around the roaster system. Within the roaster system and the scorodite-rich substrate, arsenic concentrations can be up to 40 and 30 wt%, respectively, and high levels (wt% scale) can persist below 60 cm depth of the substrate. Arsenic in the soil surrounding the site can still exceed 0.1 wt%, and this arsenic is derived from atmospheric fall-out of arsenolite dust, rather than dispersion of arsenolite. The arsenolite dust in the soils has dissolved over the past 60 yr resulting in persistent elevated levels of arsenic adsorbed onto natural iron oxyhydroxide in the soil. An area of c. 32 500 m² around the Prohibition Mill site has arsenic levels above the recommended guideline for commercial/industrial sites of 0.05 wt%. On a regional scale, arsenic concentrations do not generally exceed the guideline for commercial/industrial sites, with the exception of a few localised anomalies related to arsenopyrite-rich waste rock.

Keywords Blackwater Mine; Waiuta; arsenolite; scorodite; arsenopyrite; arsenic mobilisation; portable XRF

INTRODUCTION

Arsenic (As) is a trace metalloid element that is commonly associated with metallic mineral deposits, especially mesothermal gold deposits. It can be naturally enriched up to levels of hundreds to thousands of times above respective average crustal abundance (1.7 mg/kg, Wedepohl 1995). Arsenic is considered to be toxic in the environment at relatively low (ppb) levels (e.g., Foy et al. 1978; Loebenstein 1993; Turner 1993; Gebel 1997; Smedley & Kinniburgh 2002). Thus, As

mobility from mineralised rocks is of considerable environmental significance. Furthermore, mining activity can aid As mobilisation through the excavation and processing of As-rich ore. Percolating rainwater can then oxidise and dissolve As from the mine wastes and excavations and is discharged into the environment at potentially toxic levels for the downstream biota (Foy et al. 1978; Loebenstein 1993; Turner 1993; Gebel 1997; Smedley & Kinniburgh 2002).

New Zealand has a long history of mining, with the earliest mining activity focused on alluvial gold. The alluvial gold was sourced from upstream quartz veins, which were soon discovered and extracted in underground mines. The mines were generally economically marginal, and mine sites were abandoned without rehabilitation when profitability waned. These mines have varying levels and sources of As. A geochemical study is generally necessary to chemically characterise a potentially toxic site. Furthermore, in order to plan and implement appropriate remediation options, understanding the full scale and extent of toxic material is necessary, which can be costly and time consuming when it involves a large-scale sampling campaign followed by laboratory analyses. This study presents an example of the successful field quantification of As at a historic mine site by the application of a field portable X-ray fluorescence (FPXRF) instrument. The site has previously been investigated for As mineralogy, mobility, and level of As contamination in solids and water (Craw et al. 2007; Haffert & Craw 2008a,b). The FPXRF data, in conjunction with the previous work, provides a holistic site, and regional characterisation with respect to As.

GENERAL SETTING

The Prohibition Mill site (lat. 42°17.49'S, long. 171°49.64'E) is part of the historic Blackwater mine at the former mining town of Waiuta on the West Coast of New Zealand's South Island (Fig. 1). Waiuta is located on a plateau c. 400 m a.s.l., whereas the Prohibition Mill site is on the crest of a nearby ridge, 120 m above the surrounding terrain (Fig. 1B). The studied area is located within the Blackwater River catchment, which drains into the Grey River flowing southwards and discharging into the sea at Greymouth.

The Blackwater mine extracted gold from mineralised structures hosted within the lower Paleozoic Greenland Group of the Buller Terrane (Cooper 1974). Greenland Group rocks consist of alternating mudstones and sandstone with detrital grains of quartz, rock fragments, muscovite, plagioclase, and biotite, of which the last two have been altered to albite and chlorite, respectively, during greenschist facies metamorphism. Subsequent hydrothermal alteration of the sandstone has developed a mineral assemblage of K-mica, carbonate (dolomite-ankerite and ferroan magnesite-magnesian siderite, minor calcite), chlorite, pyrite, and arsenopyrite (Christie & Brathwaite 2003). Gold and associated arsenopyrite (up to

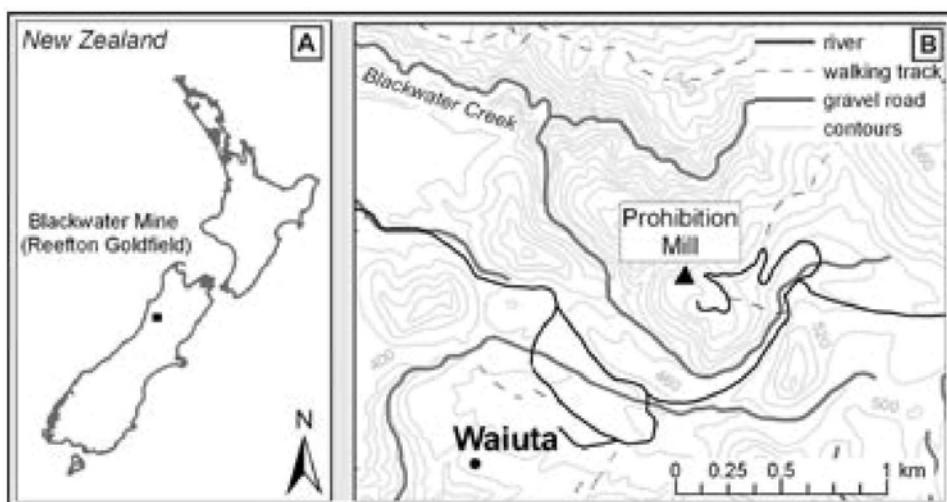


Fig. 1 A, Map of New Zealand showing the location of the Blackwater Mine. B, Topographic map showing the setting of the historic mine town of Waiuta and the Prohibition Mill site at the Blackwater Mine.

1 wt%) enrichment occurred in quartz veins in poorly veined, non-brecciated host rock.

The basement rocks are overlain locally by remnants of a Cretaceous–Tertiary sedimentary sequence (Suggett 1957), which contains non-marine sections that include coal seams (Brunner Coal Measures), and marginal marine sediments that are locally calcareous and pyritic (Hewlett et al. 2005).

The region is characterised by high orographic rainfall, averaging 2300 mm annually. Seasonal distribution of rainfall has spring and autumn maxima, and minima in late summer and midwinter (Mew & Ross 1994). The mean annual temperature is 12°C, with prevailing westerly winds. Dense rainforest originally clothed the steep terrain, and forest has regenerated over much of the mined areas since mining ceased more than 50 yr ago. Most regenerated forest is dominated by southern beech (*Nothofagus* spp.), but early stages of forest regeneration have abundant shrubs, particularly manuka (*Leptospermum scoparium*) and kanuka (*Kunzea ericoides*). Soils in regenerated forest areas typically have pH between 5 and 6, and many surface waters have similar pH. However, groundwater in the underlying basement typically has pH near 7 (Hewlett et al. 2005).

SITE DESCRIPTION

Processing of arsenopyrite-rich ore took place at the Prohibition Mill site between 1938 and 1951 and no rehabilitation was undertaken after mine closure. The present site includes concrete foundation remains and scattered timber and iron debris (Fig. 2A). The most distinct feature is the condenser tower from the Edwards Roaster. Large areas of the site are not vegetated, especially in the vicinity of the roaster and flue system (Fig. 2A). Site runoff drains into an adjacent wetland (c. 10 × 100 m) immediately below the processing plant site. The wetland was originally a tailings impoundment constrained at the northern side by an artificial dam (Fig. 2A). The wetland has been naturally revegetated since the site was abandoned and the surface consists of variably saturated vegetation mats overlying a substrate of processing plant residue and sediment washed off the surrounding slopes. The dam wall is composed of angular boulders of mineralised Greenland Group. Water percolating through the dam emanates on the other side at the foot of a scree slope and eventually enters

Blackwater Creek (Fig. 1B). The most contaminated areas of the site are presently fenced off while more permanent site management options are considered. The fence location was based on the results of the study presented here.

To the northeast of the site there is an elevated plateau (70 × 100 m), which is built on local rock debris with steep scree slopes at the northern end.

ORE PROCESSING AND ARSENIC CHEMISTRY

At Waiuta, As occurs mainly as the sulfide arsenopyrite (AsFeS), and the release of As into the environment occurs naturally by oxidation of exposed sulfide minerals (e.g., Bowell 1992; Ashley & Lottermoser 1999; Clark & Raven 2004; Haffert & Craw 2008b). At the Blackwater Mine the natural process of As mobilisation was accelerated through the mining and beneficiation of gold, which is commonly intergrown with the sulfide phases (Haffert & Craw 2008b). Processing techniques involved the crushing, flotation, cyanidation, and, most importantly, the roasting of the ore. The roasting broke down the sulfide phases thereby liberating the gold for subsequent leaching. A by-product of the roasting is arsenolite ($\text{As}^{\text{III}}_2\text{O}_3$), which emerged from the furnace as arsenic trioxide vapour and dust. The collection of the dust and condensation of volatile arsenic trioxide was performed to save the As. Complete removal of arsenolite from any of the dust-collecting chambers was difficult to achieve, resulting in a build-up of arsenolite throughout the roaster gas discharge system (Hutton 1947), and this was disposed of on-site.

At present, very As-rich processing residues (up to 40 wt%, Fig. 2B) persist on-site and arsenolite crystals are still exposed in the condenser tower of the roaster system. This mineral is reputedly very soluble (up to 12 g/L, Vink 1996) and substrate runoff has concentrations of up to 30 mg/L dissolved As (Haffert & Craw 2008a). Upon oxidation, some of the dissolved As is immobilised by formation of scorodite ($\text{FeAs}^{\text{V}}\text{O}_4 \cdot 2\text{H}_2\text{O}$). The scorodite precipitate cements the substrate downstream from the roaster system, thereby encapsulating and immobilising some of the eroded arsenolite (Fig. 2B). Arsenic mineralogy and mobility of these As minerals has been studied in detail by Haffert & Craw (2008a).

The As-rich site runoff and further dissolution of arsenolite in the tailings sediments (up to 10 wt% As) ensures that

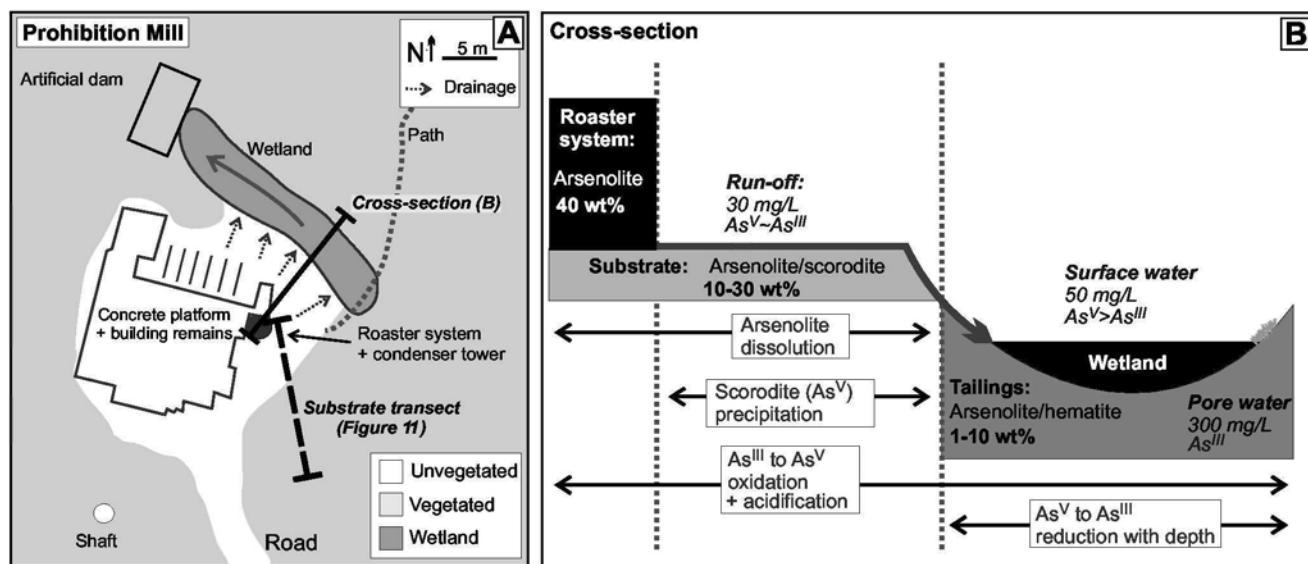


Fig. 2 A, Outline of the Prohibition Mill site based on aerial photographs. White areas are largely unvegetated, whereas light grey areas are vegetated. The dark grey area delineates the extent of wetland water. The position of the substrate sampling transect is also shown. B, Cross-section spanning the immediate downstream environments from the roaster, including the substrate and wetland. Arsenic minerals and associated As concentrations in solid (wt%) and water (italics, mg/L) are indicated. Processes relating to As chemistry and their environments are also shown (after Haffert & Craw 2008a).

dissolved As concentrations in the wetland water remain high. During previous sampling campaigns, concentrations reached up to 52 mg/L, which exceed the World Health Organisation (WHO 2004) drinking water guideline of 0.01 mg/L by over three orders of magnitude. The overall site pH in water and substrate is low (pH 4–5), caused by the oxidation of As^{III} produced during arsenite dissolution (Haffert & Craw 2008a). This distinguishes the Prohibition Mill site from most other gold mine sites, where acidification is generally due to the oxidation of sulfide minerals, particularly pyrite (FeS_2) and arsenopyrite (FeAsS).

Once the wetland discharge percolated through the artificial dam, As concentrations dropped by over an order of magnitude to 2.4 mg/L (pH 7.6) during previous sampling campaigns (Haffert & Craw 2008b). Further downstream, As concentration continues to decrease due to dilution, which is especially pronounced at the confluence of tributaries.

METHODS

Analytical sample points

At the Prohibition Mill site FPXRF readings were taken at 730 positions on a 1 m sampling grid (Fig. 3A). The grid was aligned along the north (N) and east (E) axis and the centre of the grid (N00 E00) was positioned at the condenser tower, where the highest As concentrations were found during previous sampling campaigns. In areas where As concentrations dropped below 0.1 wt% (1000 ppm), readings were taken sporadically at larger intervals along the grid. The surrounding region of the site (kilometre-scale) was sampled where access was possible. Co-ordinates of all samples were obtained using a differential Geo Explorer CE series Trimble GPS system.

Before analysis of a substrate point, vegetation and/or surface debris was removed, followed by the compaction and smoothing of the material surface with a trowel (Fig. 4).

Information on material type, moisture content, and vegetative cover was recorded for each reading.

About 20 holes were drilled up to a depth of 80 cm (Fig. 3B). Subsurface samples, as well as water-covered samples, could not be measured *in situ* and c. 50 samples of this kind were extracted into plastic sampling bags before measurement. Another 60 samples were extracted for inspection and assessment of the performance of the FPXRF. All extracted samples were re-analysed by FPXRF in the laboratory and then weighed and dried to establish the range of moisture contents. Based on material type and As content, 40 representative samples were additionally crushed and analysed again by FPXRF to establish the influence of the preparation method on the results.

Along a transect covering the upstream transition from As-dominated unvegetated substrate to grass and bush covered siliciclastic natural soil, five samples of 2–3 kg over a distance of c. 20 m were extracted from the surface layer (up to 15 cm depth) (Fig. 2A). These samples were air dried and subsequently sieved by an automated shaker (20 min) into seven size categories (φ): <−2, −2–0, 0–1, 1–2, 2–3, 3–4, >4. After 5 min of shaking, the material was inspected for aggregates and manually disintegrated where applicable. With the exception of the two largest size fractions (>2 φ and −2–0 φ), samples were subsequently analysed for As and Fe content by acid digestion and inductively coupled plasma mass spectrometry (ICP-MS).

Analytical techniques

An INNOV-X alpha series FPXRF was used for As analysis in the field. The unit weighs <2 kg with dimensions of c. 20 × 30 cm. The analysis is based upon the emission of X-rays generated from an X-ray tube inside the FPXRF unit. The sample is placed in front of a window with a shutter. When the shutter is open, the X-rays from the tube are absorbed by the atoms in the sample, generating fluorescence as the atoms relax and release energy. The instrument reads the total counts

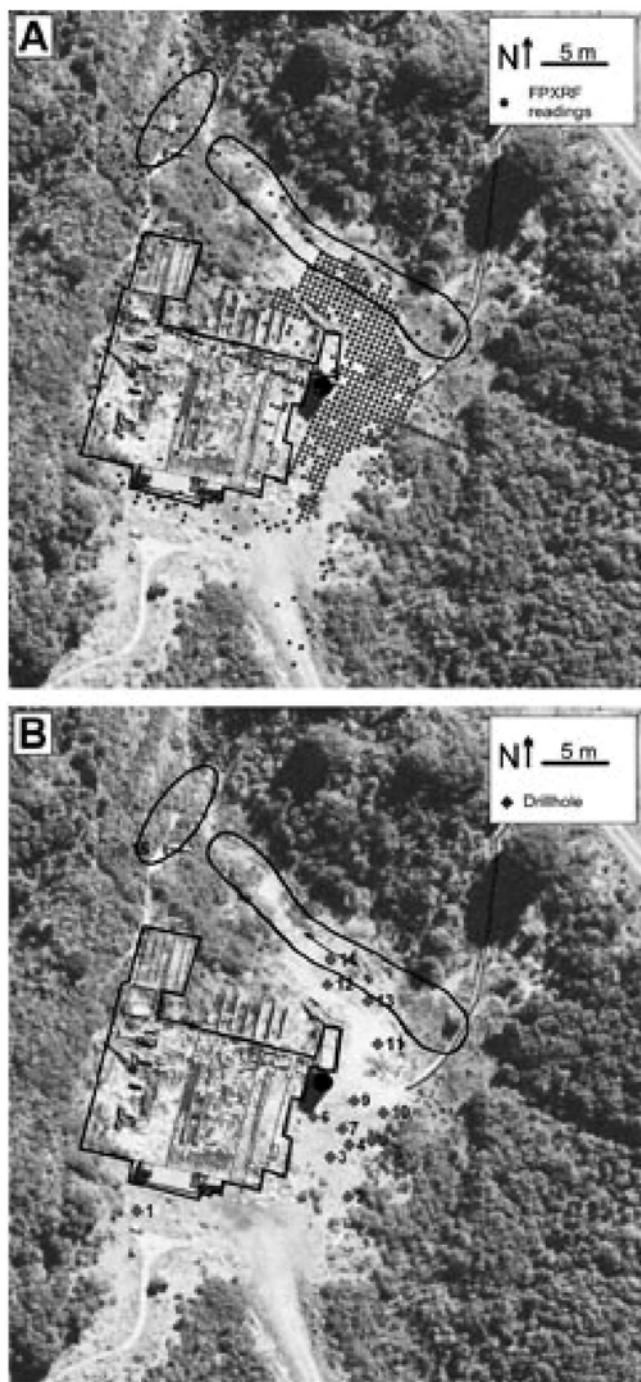


Fig. 3 Aerial photograph of the Prohibition Mill with *in situ* FPXRF reading locations (A) and drillhole locations (B).

received by a detector for a wavelength that is specific for each element. Lead, which is known to interfere with As analysis (US-EPA 1998), is present at concentrations about two orders of magnitude lower than As at the Prohibition Mill site and in the greater Waiuta area, and is therefore not concentrated enough to interfere with the As analysis.

Two analytical modes of the FPXRF were used during this work. For the <10 wt% As range, the inbuilt *soil mode* was used, which was regularly calibrated with a one-step calibration lid provided by the manufacturer. For concentrations >10 wt% As, the *empirical mode* was applied. The empirical mode is based on an individual calibration with six standards.

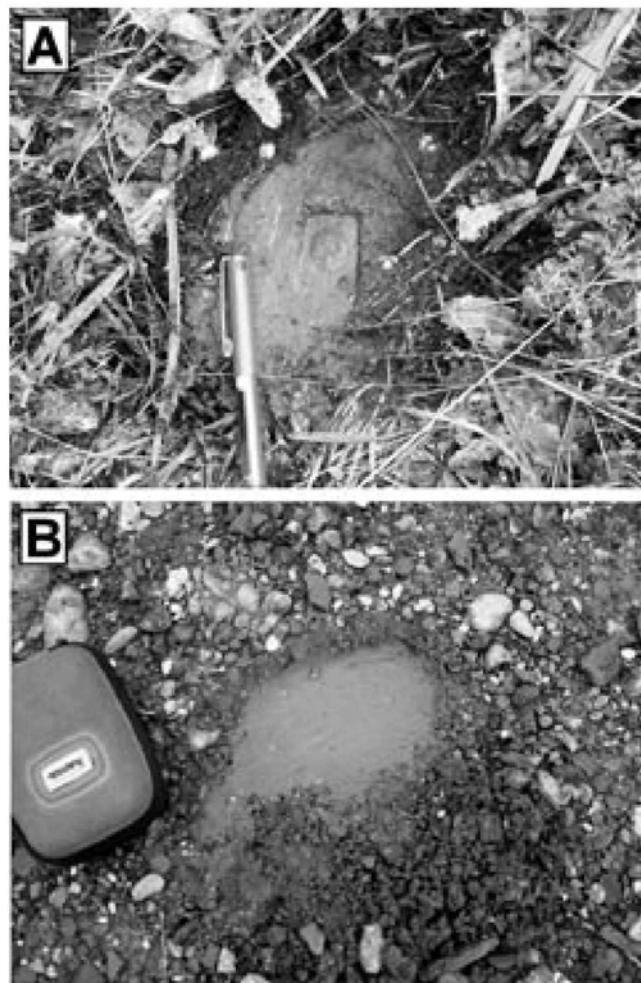


Fig. 4 Surface preparation for *in situ* FPXRF readings. A, For silicate-rich vegetated substrate the grass is removed first and the soil compacted before analysis. B, For unvegetated As-rich substrate, large clasts are removed and the surface is compacted before analysis.

The standards are made up of material from the Prohibition Mill site which had been previously sampled and analysed by acid digestion and ICP-MS (Haffert & Craw 2008a).

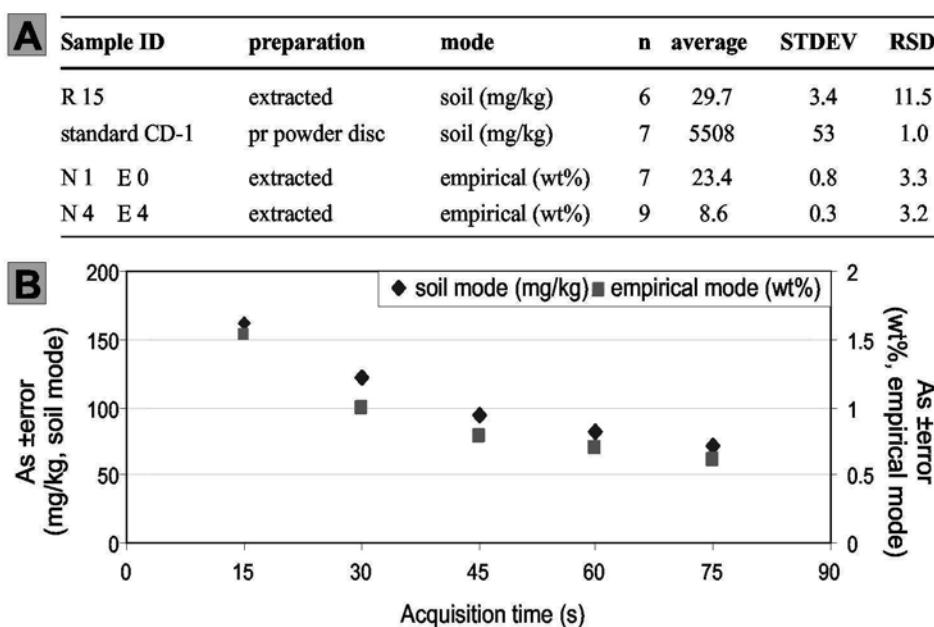
The representative samples and the sieved size fractions were manually ground by mortar and pestle. The samples were then analysed for total recoverable As and in some cases Fe by nitric/hydrochloric acid digestion (EPA 200.2, US-EPA 1994) followed by solution analysis by ICP-MS (Hill Laboratories, Hamilton, New Zealand). Interference of $^{40}\text{Ar}^{35}\text{Cl}$ on ^{74}As analysis was corrected by measuring ^{77}Se and ^{82}Se and establishing the interference of $^{40}\text{Ar}^{37}\text{Cl}$ on ^{77}Se . This was then related to the $^{40}\text{Ar}^{35}\text{Cl}$ interference by adjusting for the natural abundance of both Cl isotopes.

OPERATION OF FPXRF

Data quality

The effect of acquisition time on the quality of the analysis was tested in both soil and empirical mode and the results are presented in Fig. 5. In both modes the analysis error decreases with increasing acquisition time. For the purpose of this study, an acquisition time of 30 s was applied, which

Fig. 5 A, Table showing the precision of FPXRF in soil and empirical mode using standard deviation (STDEV) and relative standard deviation (RSD) calculated from a certain number of samples (*n*). The sample “standard CD-1” refers to a reference standard pressed powder disk (Antimony-Arsenic Ore CANMET) containing 0.66 wt% As. B, Graph showing the influence of acquisition time on error margins for soil and empirical mode.



represents a compromise between time management and analysis quality.

At least one precision sample was run per day. The instrument precision was tested in both the soil and empirical modes across a range of concentrations. Generally the precision was highest (= low Relative Standard Deviation, RSD) in the soil mode, with a RSD of 1% in samples with As concentrations above 0.01 wt% (Fig. 5). However, the precision dropped by an order of magnitude at concentrations below 0.01 wt% As. The empirical mode was generally less precise than the soil mode, with relatively constant RSD values (c. 3%) across a wide range of concentrations. The RSD of all precision tests stayed below the recommended 20% (US-EPA 1998).

The detection limit of the FPXRF was determined based on counting statistics, in particular standard deviation (SD), provided by the FPXRF instrument with each analysis. The SD for a target analyte peak is calculated from the net counts (*N*) for the peak of the analyte of interest (i.e., gross counts minus background under the peak): $SD = (N)^{1/2}$. Multiplying the standard deviation (SD) by 3, provides the value for the detection limit (US-EPA 1994). Detection limits for FPXRF are not fixed for a particular element and are influenced by, for example, measurement time, matrix effect, and concentration of the analyte.

During this study, analyses of samples with concentrations close to the guidelines provided by the National Environment Protection Council in Australia (NEPC 1999) for standard residential ground (100 mg/kg) and for commercial/industrial sites (500 mg/kg), have detection limits of below 20 and 40 mg/kg As, respectively (Fig. 6). Concentrations approximating the NEPC interim urban ecological investigation level for As of 20 mg/kg (NEPC 1999) are in the same order of magnitude as the detection limit (Fig. 6) and should therefore be used with care. Samples with As concentrations of <10 mg/kg typically fell below the detection limit of the analysis (Fig. 6). The detection limit calculated that way only indicates instrument performance for one particular sample. Minimal sample preparation and, therefore, errors arising from variations in the physical character of the sample introduce larger

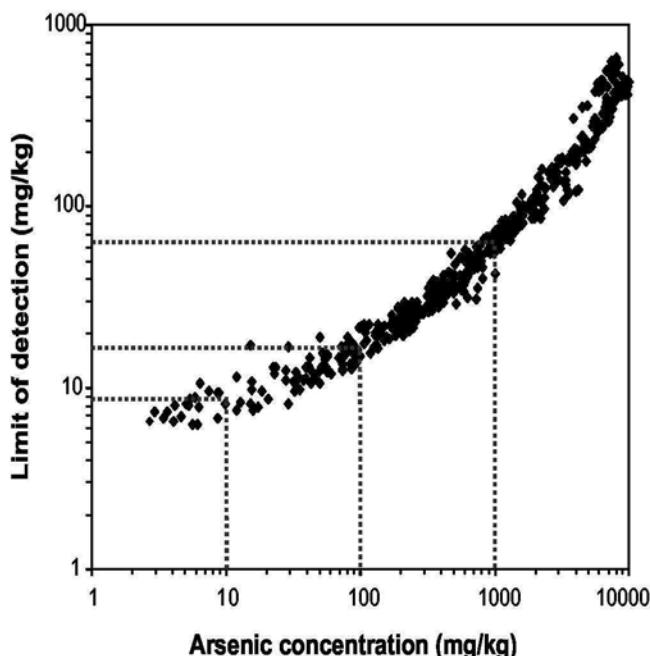


Fig. 6 Detection limits for analyses of samples with As concentrations below 1 wt%. The detection limit is calculated from counting statistics provided by the instrument for each analysis. At concentrations of <10 mg/kg As the instrument no longer produces quantitative results.

error margins to the method and raise the lower limit at which quantitative analyses are possible.

The effect of sample heterogeneity on analysis quality was investigated on c. 30 samples across a range of substrate types and As concentrations. On average, six readings were taken on different surfaces of the same sample. In general, the RSD decreases with increasing concentration. About one-half of the samples exceed the recommended RSD of 20%, thus sample heterogeneity is of serious concern and can lower the

quality of the analysis. To minimise the effect of material heterogeneity, several readings were taken in most cases and readings for the assessment of the instrument's performance were taken on the same sample surface.

Processing of FPXRF data

Moisture content of the analysed materials, especially when exceeding 20%, may be a major source of error when analysing by FPXRF (US-EPA 1998). The Prohibition Mill site is located in a wet climate, and moisture contents above 20% can be expected. To correct for moisture content, each analysed material was classified in the field as dry, damp, moist, or saturated. In the laboratory, the typical moisture content for each moisture class and substrate type of the extracted samples was established. All readings were then corrected using the following equation:

$$\text{As}_{\text{corrected}} = \text{As}_{\text{FPXRF}} \left[\frac{100}{100 - \% \text{moisture}_{\text{inferred}}} \right]$$

where As_{FPXRF} is the immediate reading of an unmodified sample, $\% \text{moisture}_{\text{inferred}}$ is the typical moisture content inferred from substrate type and moisture class, and $\text{As}_{\text{corrected}}$ is the calculated concentration of the material in its dry state. The correlation coefficient between readings on dried and crushed samples and readings on unmodified samples that were corrected for moisture content is 0.94.

DESCRIPTION OF SUBSTRATE TYPES

A wide range of substrate types was encountered at the Prohibition Mill site. To assess the control of the substrate on As concentrations and on the performance of the instrument, each analysed material was classified into one of six categories. Categories were based on material characteristics which were immediately observable, such as texture, colour, and location, for fast field-based classification.

(1) *Tailings* and other unconsolidated material are present among the concrete and timber remains (Fig. 2A) and include dark brown, moderately well sorted, silt-sand sized sediment, consisting mainly of quartz (subangular), muscovite (tabular), hematite (botryoidal), and glass fragments with curved cavities. Arsenolite crystals (c. 0.05 mm) and subordinate scorodite spherules ($< 4 \mu\text{m}$) were also identified. Arsenic concentrations ranged from 2 to 15 wt% with an average As content (FPXRF) of 2.4 wt%.

(2) *Wetland sediments*, at the margin of the upper wetland (Fig. 2A), are light grey and loosely cemented in places. The sediment is bimodal, with a coarser fraction of mainly sub-angular quartz grains and tabular muscovite. Coarse grains are coated by a fine light grey silty fraction. Hematite, glass, and subordinate aggregates of arsenolite crystals ($< 4 \mu\text{m}$) are also present.

Sediment from the lower end of the wetland is less cohesive and lighter in colour. The sediment is also bimodal, consisting of coarse subangular quartz and occasional brown-stained aggregates of arsenolite crystals ($< 4 \mu\text{m}$). The coarse fraction is coated in brown particles ($< 4 \mu\text{m}$) making up at least 30% of the material. Individual arsenolite crystals (c. 0.2 mm) were also identified. Arsenic concentrations can be as high as 10.2 wt%. The fine fraction ($< 2 \mu\text{m}$) is dominated by dark brown silt including some coarse clasts of quartz, hematite,

glass, and subordinate aggregates of arsenolite crystals ($< 4 \mu\text{m}$). Arsenic concentrations average 6.1 wt%.

(3) *Clay-rich subsoil* was found at depth below 20–30 cm and is a natural non-gritty soil with a high percentage of clay minerals. It is cohesive when wet and hardens when dry. It contains little organic material and varies in colour from light grey to yellow. Arsenic concentrations average 2.2 wt%.

(4) The highly *modified substrate* around the condenser tower is composed of poorly sorted sediment. This substrate is not vegetated and the typical O horizon, a layer dominated by organic material, is absent. The material is grey and variably cemented. Clast sizes can be as small as 0.01 mm and generally do not exceed several millimetres. Clasts are composed mainly of quartz (subangular, 0.01–5 mm) and some friable aggregates (0.01–1 mm) of arsenolite crystals ($< 4 \mu\text{m}$). Subordinate muscovite and trace hematite can also be found. All clasts are coated in light brown particles ($< 4 \mu\text{m}$) which consist predominantly of a scorodite precipitate ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). The FPXRF readings for As on this material average 20 wt%.

(5) *Silty natural soil* is composed mainly of silt-sized material. The colour varies from brown to dark brown and can contain significant amounts of organic matter. Even though this substrate type tends to occur at the margin of the processing site, the average As reading is still 2.9 wt%.

(6) *Gravelly natural soil* is the transitional material between the unnatural poorly sorted sediment in the vicinity of the roaster area and the fine brown soil surrounding the site. Silt dominates the finer size fraction and up to 40% is gravel. Arsenic concentrations average 2.3 wt%.

ARSENIC DISTRIBUTION PATTERN

Prohibition Mill site

Most of the substrate on the Prohibition Mill site exceeds the guidelines provided by NEPC (1999) by several orders of magnitude. As expected, the highest As concentrations ($> 10 \text{ wt\%}$, pink in Fig. 7) were found in the substrate between the roaster and the wetland. High As concentrations ($> 1 \text{ wt\%}$, red in Fig. 7) persist to the northwest of the roaster along the wetland but drop abruptly below 1 wt% upstream of the roaster. Elevated As concentrations ($> 0.1 \text{ wt\%}$, orange in Fig. 7 and 8B) prevail to the east of the processing site, whereas westwards concentrations decrease sharply to values below 0.05 wt% (green and blue in Fig. 7 and 8B).

Beyond the boundary of the processing site, high As concentrations persist to the east (Fig. 8B). Other smaller "hot spots" of elevated As concentrations were identified at the northern margin of the elevated plateau adjacent to the processing site and at the foot of the slope descending from the plateau in the northwest (Fig. 8B). Once As concentrations drop below 1 wt% they drop over a comparatively short distance to below 0.05 wt% As.

Extreme As contamination (percentage level) was found in subsurface samples at the Prohibition Mill site. Arsenic concentrations versus depth show a similar trend in all drill-holes (Fig. 9). A rapid decrease in As takes place within the first 30 cm, followed by a comparatively gentle increase at $> 30 \text{ cm}$. At 30 cm depth As concentrations do not exceed 4 wt%. If surface concentrations exceed 1 wt%, As concentrations have generally decreased by 80–95% at a depth of

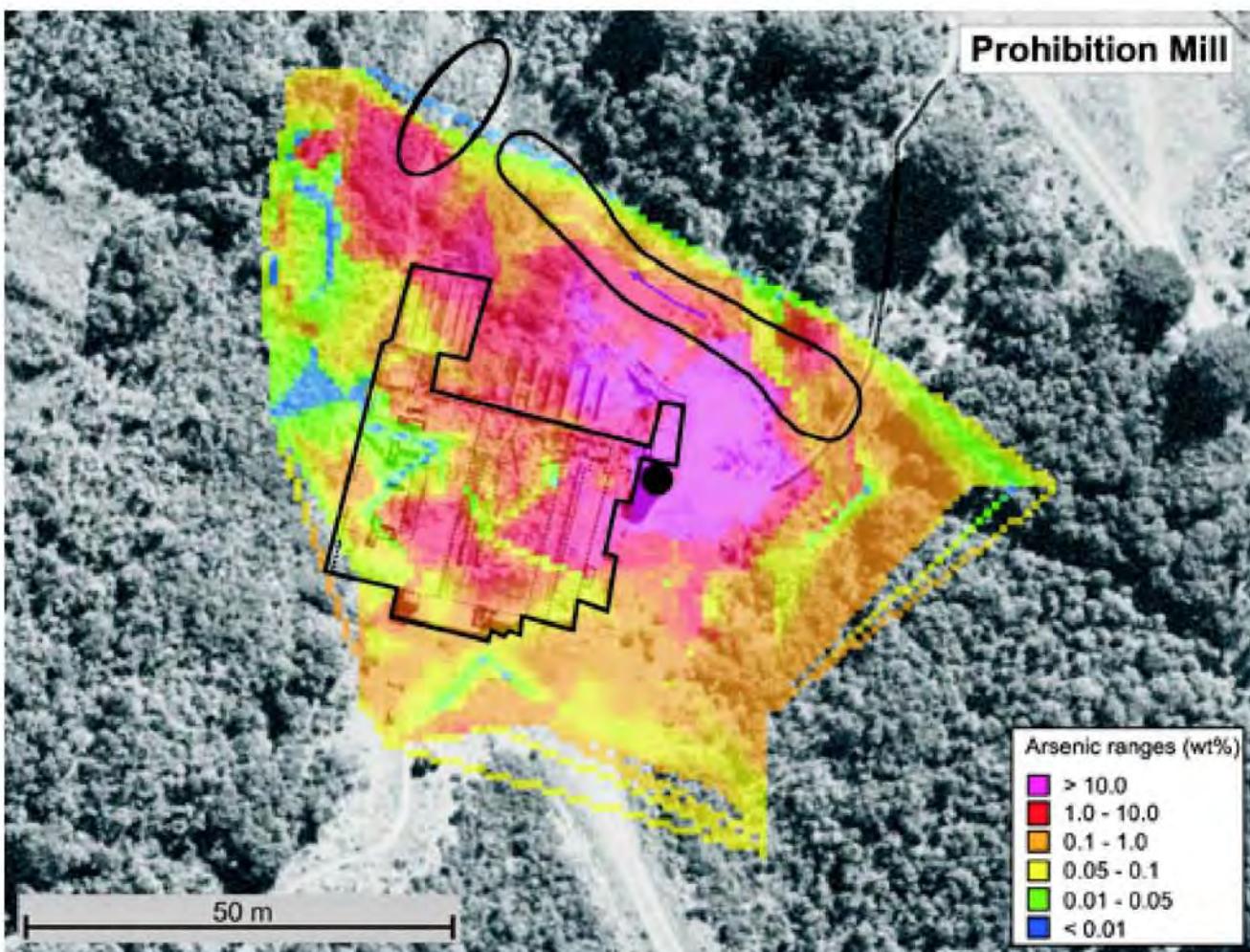


Fig. 7 Arsenic distribution at the Prohibition Mill site based on corrected *in situ* readings from FPXRF.

30 cm. If surface As concentrations are <1 wt%, As decreases only by 40–70% at 30 cm depth. In only two cases As concentrations within the upper 60 cm drop below the NEPC industrial/commercial guideline of 0.05 wt% (NEPC 1999).

Waiuta area

On a regional scale, As concentrations are mostly below the NEPC guideline for commercial/industrial sites of 0.05 wt% (green and blue in Fig. 8A). However, some anomalously high As concentrations (yellow in Fig. 8A) were found in the historic township of Waiuta: first, at the southern foot of the plateau, which supports some mining structures such as a shaft, and is partly composed of mine waste and, secondly, south of the little stream running through Waiuta (Fig. 8A).

Furthermore, the soil immediately beside gravelled roads possesses anomalously high As concentrations (Fig. 10). Within several metres of the road, As concentrations generally exceed 0.01 wt%. At a distance of c. 10 m from the road, concentrations dropped by an order of magnitude, and at a distance of 40 m the effect of the road on surface As concentration ceases and background As concentrations (<0.001 wt%) prevail (Fig. 10).

Transition from site substrate to natural soil

Almost 60% of the natural soil surrounding the site is fine grained (smaller than 4 ϕ , i.e., <63 μm) and clasts larger than

0 ϕ are absent. In between these two size fractions, the material is evenly distributed (Fig. 11A). Towards the condenser tower, the fine fraction is becoming increasingly replaced by larger size fractions (Fig. 11A). This is especially pronounced in the transition substrate, which contains the largest fraction of gravel.

The transition between site substrate and natural soil is accompanied by a drop in As concentrations by three orders of magnitudes from percentage levels (35 wt%) to mg/kg levels (100 mg/kg) over a distance of <20 m (Fig. 11B). In the As-dominated site substrate, As content increases with decreasing particle size. The same trend occurs in the transitional material, which is characterised by a larger scatter of As content among the different size fractions (Fig. 11B). However, with distance from the site there is a shift of As into the larger size fractions, so that towards the naturally derived soil, As is evenly distributed among all size fractions. An exception is the silt fraction in the fine soil, which contains half as much As as the larger size fractions.

Like As, Fe concentrations, which are also at wt% level in the site substrate, decrease with distance from the condenser tower. However, Fe concentrations remain about an order magnitude above the lowest As concentrations (Fig. 11B). Unlike As, Fe content tends to be most concentrated in the larger size fraction throughout the transition.

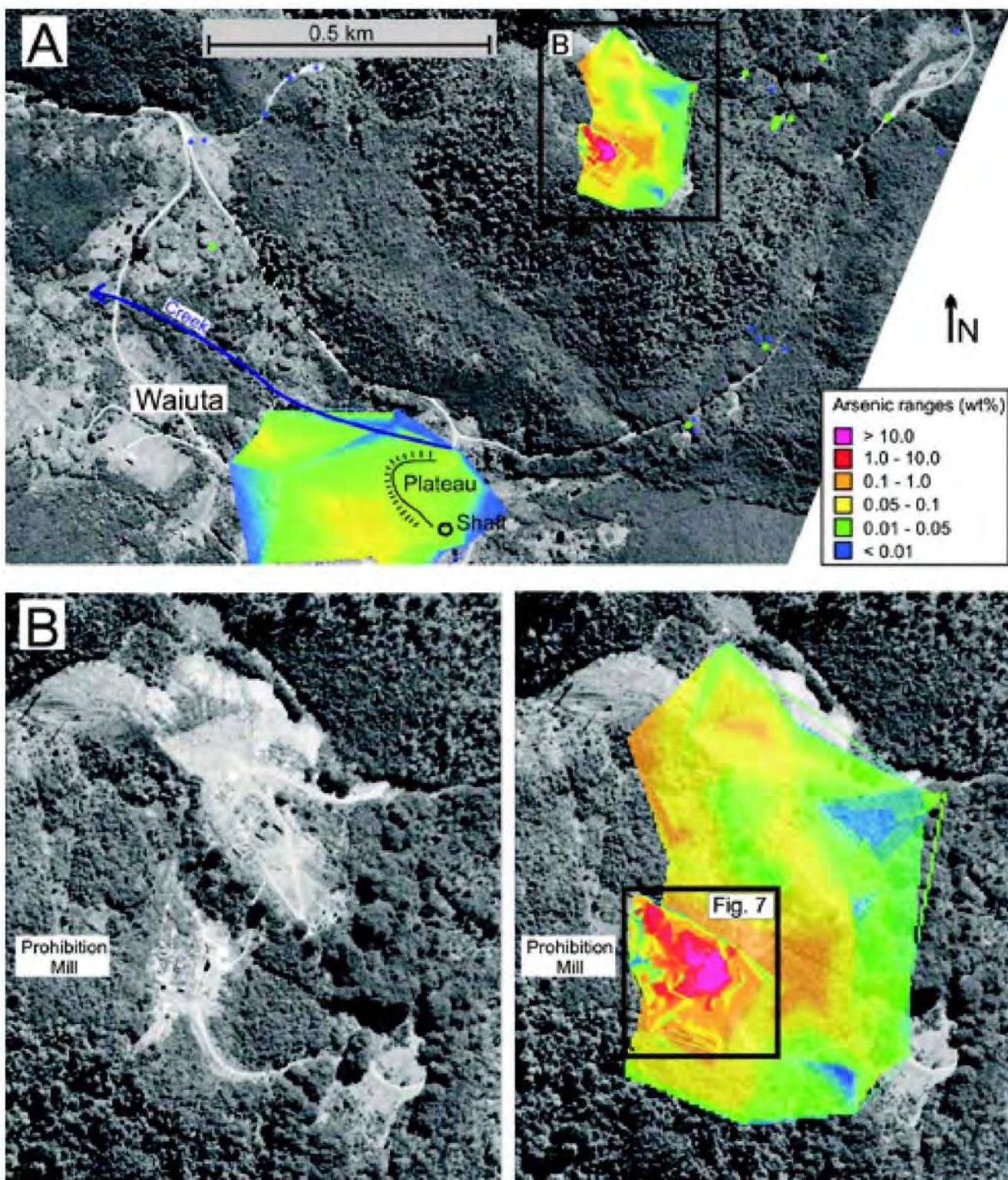


Fig. 8 Arsenic distribution in the greater Waiuta area (A) and around the Prohibition Mill site (B) based on corrected *in situ* readings from FPXRF.

DISCUSSION

Comparison of different analytical and correction methods

FPXRF and acid digestion followed by ICP-MS analysis are fundamentally different methods. XRF measures the bulk concentration of As in a solid sample, whereas acid extractions

are limited to the As that can be removed from a sample using standardised acid extraction procedures (e.g., EPA 200.2). Acid extraction, when following these procedures, produces generally comparable results. In contrast, accurate FPXRF analysis depends on a range of material specific factors, such as particle size, homogeneity, and moisture content, which can significantly lower the reliability of this method. Sample

preparation methods can reduce some of these uncertainties but in turn increase the time spent on each analysis. During this study there were three different methods of preparation before FPXRF analysis: (1) the *in situ* analysis with only minimal preparation; (2) field analysis of extracted material through a plastic bag; and (3) laboratory readings of dried and crushed samples. The analyses of untreated samples were further corrected for moisture content. From Fig. 12 there is an overall good correlation between the different preparation methods ($r = 0.80$) and between FPXRF and ICP-MS analysis of acid digested samples ($r = 0.81$). Thus, FPXRF results are not only applicable relative to each other, but are to a large extent compatible with laboratory methods. The scatter from the ideal 1:1 relationship is acceptable for the purpose of this study, which aims to delineate the scale and distribution of As contamination over a large area. Here, the need for high resolution analysis is outweighed by the need for fast analytical turn around time, for which *in situ* and moisture corrected FPXRF is the optimal method.

Arsenic phases and their properties

Arsenic at and around the Prohibition Mill site is present as three distinct phases: the roaster by-product arsenolite, the secondary mineral scorodite, and As adsorbed onto soil particles following dissolution of the As minerals. Arsenolite is present in the condenser tower, in the wetland sediment, and in the site substrate as a result of spillage or mechanical erosion. Arsenolite contains 75% As, thus more than half of the white precipitate within the condenser tower, which contains 40 wt% As, is composed of arsenolite. Assuming that an intake of 70 mg of As is fatal (Abernathy 1993), 0.17 g of this material is sufficient to be lethal in humans. In the substrate, arsenolite occurs as a friable aggregate (up to 1 mm). Once these are disintegrated during the sieving process, the micrometer-scale arsenolite grains reside in the smallest size fraction (<4 ϕ), which has the highest As concentrations (Fig. 11B). This arsenolite is noticeably raising As concentrations (up to 35 wt%), which would otherwise be similar to Fe concentrations (c. 10 wt%) if scorodite were the only As mineral (Fig. 11B). Arsenolite is unstable in the surficial environment and its dissolution is only constrained by kinetics. Concentrations of As in fresh surface runoff can reach 30 mg/L (Haffert & Craw 2008b).

Scorodite is closely associated with arsenolite, spatially and temporally, because its stability depends on the dissolved As-rich waters produced during arsenolite dissolution.

It occurs mainly as a cement throughout the substrate downstream from the roaster system. Unlike arsenolite, scorodite resides in the larger size fractions due to its cementing nature, and accordingly As concentrations in these fractions approach Fe concentrations. Unstable scorodite is of a lesser environmental concern than arsenolite, because it is, at pH 4, several orders of magnitude less soluble than arsenolite (Krause & Ettel 1988) and it contains half as much As (32% As and 24% Fe).

Towards the fine natural soil surrounding the site, where As concentrations are too low to promote stability of secondary As minerals, As is mainly adsorbed to naturally occurring iron oxyhydroxides. The fact that, more than 50 yr since mine closure, As is still present at elevated levels in the soil upstream from the site, shows that adsorbed As is relatively immobile in this setting.

The site substrate, which is essentially As-cemented mine residues, and the natural siliciclastic soil immediately adjacent to the site are very different in character. The transition between these two materials can occur on the metre-scale and is accompanied by a pronounced change in physio-chemical characteristics. A decrease of As concentrations by several

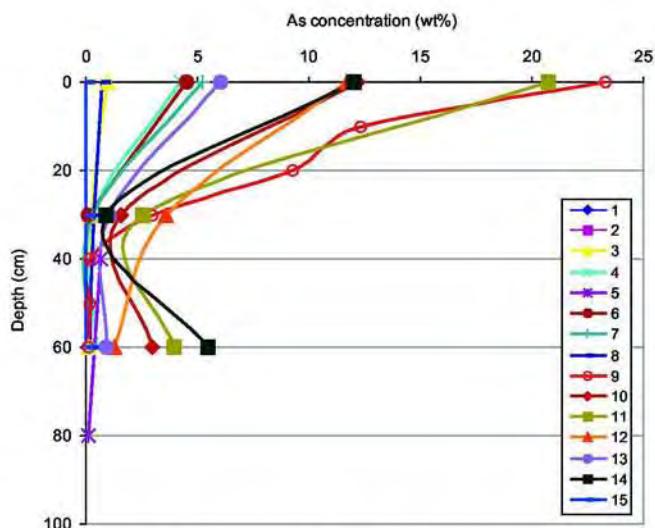
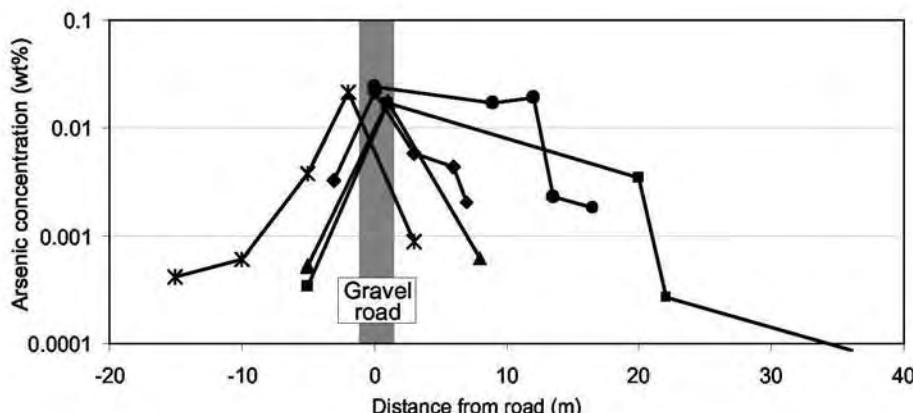


Fig. 9 Arsenic concentration with depth derived from FPXRF analysis of extracted material from drillholes (numbers correspond to those shown in Fig. 3B).

Fig. 10 Arsenic concentration in the vicinity of gravel roads in the Waiuta area.



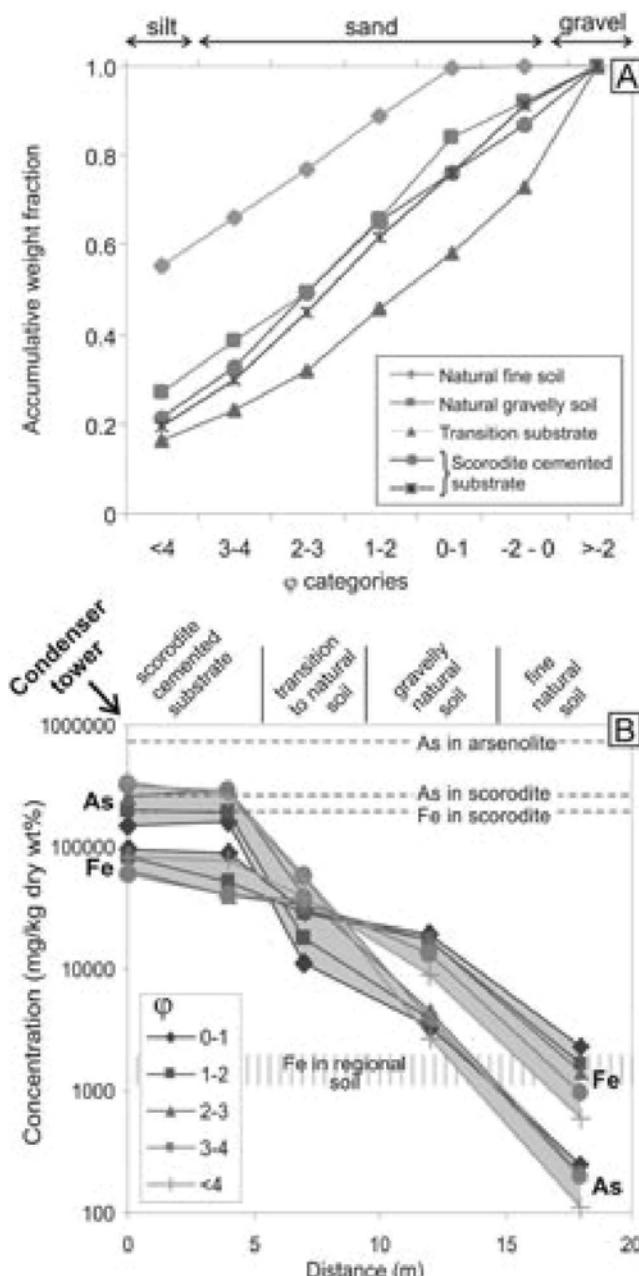


Fig. 11 A, Accumulative weight of the sieved size fractions. B, Changes in As and Fe concentration in five different size fractions (φ) over the transition from scorodite-cemented substrate adjacent to the roaster system to siliciclastic natural soil (transect position shown in Fig. 2A). As and Fe content in arsenolite and scorodite are added. The range of typical Fe concentrations in regional soil is also indicated and is based on regional FPXRF readings with As concentrations below 100 mg/kg.

orders of magnitude occurs, coinciding with the extent of arsenolite dispersion that occurred during processing operation. Consequently, As in the smallest size fraction, in which arsenolite resides, decreases with distance more distinctly than in the other size fractions, which contain scorodite that persists beyond the arsenolite boundary. Consequently, beyond the boundary of arsenolite dispersion, As is closely associated with Fe, either as scorodite or adsorbed onto oxyhydroxide, and the distribution of As among the different size fractions mimics that of Fe.

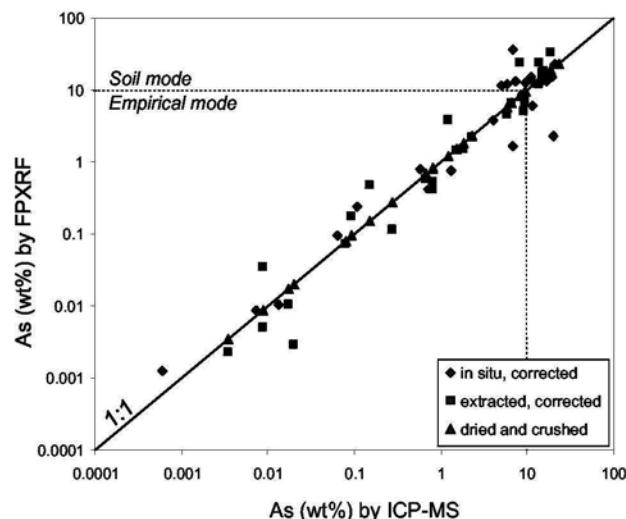


Fig. 12 The effect of preparation method on instrument accuracy. Values on the x-axis remain constant, whereas values for the y-axis vary depending on the applied method.

Like As, Fe concentrations also decrease with distance from the roaster. However, the decrease is less pronounced compared to As because of the persistence of scorodite (Fig. 11B). At a distance of c. 12 m, the decrease in Fe concentrations becomes more pronounced, and this is likely to coincide with the boundary of scorodite distribution and accordingly matches the rate of decrease of As, also controlled by scorodite at this point. Beyond that boundary, Fe concentrations are controlled by the natural weathering of bedrock and fall within the typical range of regional soil (c. 0.1 wt%, Fig. 11B), whereas As is diluted to concentrations of about an order of magnitude below Fe.

Controls on arsenic distribution

At the processing site, As concentrations are at percentage level, especially in the vicinity of the roaster system. These concentrations are induced by the weathering of processing residues, such as arsenolite. The extent of this As mobilisation is spatially defined (e.g., by topography) such that the northern and western slopes which drain the processing site have persistent high As concentrations (Fig. 7, 8).

The extremely high As concentrations found on the surface at the Prohibition Mill site persist at wt% level up to at least 60 cm depth. Some of this As is likely to be present as the original processing residue, arsenolite, and is therefore controlled by the original thickness of this layer. However, the fact that in most drillholes the lowest As concentrations are found at 30–40 cm depth, followed by a downward increase, suggests that stability conditions of secondary As phases, such as arsenolite or adsorbed As to oxyhydroxide, play a significant role in the As distribution with depth.

Outside the boundary of secondary post-mining As mobilisation (i.e., upstream of the roaster system) concentrations may remain above 0.1 wt% As (Fig. 7, 8). Here, atmospheric fall-out of arsenolite dust, which was expelled from the condenser tower during the operation of the mill site, is likely to be responsible for the elevated As content. The persisting high As concentrations (>1 wt%) to the east of the site (Fig. 7, 8) coincide with the prevailing westerly wind direction, explaining the preferred deposition of As in that direction.

Atmospheric fall-out of arsenolite is also likely to have affected the larger Waiuta area. However, As concentrations generally remain below the NEPC guideline for standard residential soil of 0.01 wt% (NEPC 1999). Hence, addition of As has either been initially minimal, or more likely has decreased over the past 50 yr due to leaching by rainfall.

The As "hot spots" in the Waiuta area are created by local As sources. The plateau in the eastern site of the historic township consists of waste rock that was extracted from the nearby shaft (Fig. 8A). This rock is derived from the mineralised zone and contains arsenopyrite, resulting in elevated As concentrations (>0.05 wt%) along the drainage path of the waste material that is the foot of the waste rock slope and the flood plain of the stream draining the waste rock (Fig. 8A).

Other minor sources of environmental As are the gravel roads in the Waiuta area. The road surface can contain up to 0.03 wt% As (Fig. 10). The effect is only noticeable in the immediate vicinity of the road (metre-scale).

Environmental considerations

The Prohibition Mill site has extremely high As concentrations in processing residues, possibly the highest As levels found in New Zealand. Some of these residues contain over 20% As, mostly in the form of scorodite cement. These As levels are more than 1000 times higher than other New Zealand As-contaminated sites such as orchards and sheep-dips. Abernathy (1993) suggested that an oral intake of 70 mg As can be lethal. Thus, accidental ingestion of c. 0.2 g of the arsenolite-rich material exposed around the roaster system could be fatal. Furthermore, some of the As is in the form of arsenolite, which is far more environmentally mobile than most natural forms of As, such as arsenopyrite in original ore. Rainfall readily dissolves arsenolite to form runoff with 30 mg/L As (Haffert & Craw 2008b), which is 3000 times higher than drinking-water guidelines (WHO 2004) and 30 000 times higher than the trigger value for 99% protection of exotic species (ANZECC 2000). Despite effective As attenuation occurring in the artificial dam, dissolved As concentrations leaving the Prohibition Mill site are still unacceptably high, exceeding the drinking-water limit by 200 times. This water affects the local downstream ecology for at least 1 km before it is diluted with background water from larger tributaries.

Management priority at the Prohibition Mill site is the protection of the public visiting this historic site. A high security fence currently surrounds the most contaminated material of the site, ensuring that public entrance is prevented. The positioning of the fence intends to enclose material with As concentration higher than 0.1 wt%. In order to minimise public exposure to material still containing elevated As beyond the fence, the car park at the southwest end of the site has also been covered with gravel.

CONCLUSIONS

FPXRF, in conjunction with selected quality control samples, is a practical method for fast quantification (30 s per analysis) of the lateral extent contaminants, such as heavy metals and metalloids. Its success depends on previously established knowledge about the specific material types encountered at the site and their chemistry.

At and around the Prohibition Mill site a range of processing-related materials (up to 40 wt% As) were identified,

including the unvegetated scorodite-cemented site substrate, tailings, and wetland sediments. Here, the primary control on As distribution is the original extent of dispersion of these processing residues. Post-processing erosion, both chemical and mechanical, controls As distribution downstream of the As-rich residues, and topography exerts a secondary control on As distribution. With depth, As distribution is controlled by the thickness of original As-rich processing residues and the stability of secondary As phases. Consequently, the same pattern of As distribution was found in almost all drillholes (Fig. 9).

The transition from the site substrate to the surrounding natural soil is characterised by marked changes in physicochemical characteristics and can occur over a metre-scale, especially upstream from the mine residues (Fig. 11). Arsenic mineralogy changes from arsenolite and scorodite dominated substrate to diluted scorodite-containing transitional material, and, finally, to natural soil with background Fe levels and elevated amounts of adsorbed As onto iron oxyhydroxides. Changes in mineralogy are also manifested in the distribution of As and Fe among the different size fractions. Micrometre-scale arsenolite grains in the site substrate occupy the smallest size fraction (silt), whereas scorodite and iron oxyhydroxide tend to reside in the larger size fractions (sand to small gravel).

On a regional scale, beyond the boundary of mine residue due erosion, atmospheric fall-out of arsenolite dust from the roasting process is likely to be responsible for elevated As concentrations, especially downwind from the site. Localised As anomalies are also caused by the weathering of arsenopyrite containing waste rock near the shaft in Waiuta and near the gravelled roads, which are built with the same rock (Fig. 8, 10).

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