

# Potential anthropogenic mobilisation of mercury and arsenic from soils on mineralised rocks, Northland, New Zealand

D. Craw\*

*Geology Department and Environmental Science Programme, University of Otago, Leith Street, P.O. Box 56, Dunedin, New Zealand*

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## Abstract

Eroded roots of hot spring systems in Northland, New Zealand consist of mineralised rocks containing sulfide minerals. Marcasite and cinnabar are the dominant sulfides with subordinate pyrite. Deep weathering and leached soil formation has occurred in a warm temperate to subtropical climate with up to 3 m/year rainfall. Decomposition of the iron sulfides in natural and anthropogenic rock exposures yields acid rock drainage with pH typically between 2 and 4, and locally down to pH 1. Soils and weathered rocks developed on basement greywacke have negligible acid neutralisation capacity. Natural rainforest soils have pH between 4 and 5 on unmineralised greywacke, and pH is as low as 3.5 in soils on mineralised rocks. Roads with aggregate made from mineralised rocks have pH near 3, and quarries from which the rock was extracted can have pH down to 1. Mineralised rocks are enriched in arsenic and mercury, both of which are environmentally available as solid solution impurities in iron sulfides and phosphate minerals. Base metals (Cu, Pb, Zn) are present at low levels in soils, at or below typical basement rock background. Decomposition of the iron sulfides releases the solid solution arsenic and mercury into the acid rock drainage solutions. Phosphate minerals release their impurities only under strongly acid conditions ( $\text{pH} < 1$ ). Arsenic and mercury are adsorbed on to iron oxyhydroxides in soils, concentrated in the C horizon, with up to 4000 ppm arsenic and 100 ppm mercury. Waters emanating from acid rock drainage areas have arsenic and mercury below drinking water limits. Leaching experiments and theoretical predictions indicate that both arsenic and mercury are least mobile in acid soils, at pH of c. 3–4. This optimum pH range for fixation of arsenic and mercury on iron oxyhydroxides in soils is similar to natural pH at the field site of this study. However, neutralisation of acid soils developed on mineralised rocks is likely to decrease adsorption and enhance mobility of arsenic and mercury. Hence, development of farmland by clearing forest and adding agricultural lime may mobilise arsenic and mercury from underlying soils on mineralised rocks. In addition, arsenic and mercury release into runoff water will be enhanced where sediment is washed off mineralised road aggregate (pH 3) on to farm land (pH > 6). The naturally acid forest soils, or even lower pH of natural acid rock drainage, are the most desirable environmental conditions to restrict dissolution of arsenic and mercury from soils. This approach is only valid where mineralised soils have low base metal concentrations.

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## 1. Introduction

Acid rock drainage is commonly perceived to have negative environmental effects as acidity inhibits plant growth and encourages mobilisation of base metals such as copper, lead, zinc and cadmium (Ritchie, 1994; Lottermoser, 2003). Consequently, sites with active acid rock drainage are generally treated with limestone (calcite) to neutralise at

least some of the acidity and rise pH (Blowes and Ptacek, 1994; Lottermoser, 2003). The target pH after such treatment is typically 6 or higher, as base metals generally have lower mobility at higher pH (Langmuir, 1997; Plumlee, 1999). In particular, eroded roots of fossil hot spring systems, commonly referred to as epithermal deposits, are notorious for both acid rock drainage and mobilisation of base metals (Plumlee, 1999).

This study examines environmental metal mobility and acid rock drainage in some fossil hot springs systems that contain elevated arsenic and mercury but no elevated base metal concentrations. This combination of metals requires

\* Tel.: +64 3 479 7529; fax: +64 3 479 7527.

E-mail address: dave.craw@stonebow.otago.ac.nz.

a different approach to management from the types of sites described above, as investigated in this study. Natural acidity may be a better means of limiting metal mobility than traditional neutralisation. These issues are examined in the context of changing land use from forest to agriculture, and in the context of distribution of acid generating rock material on roads as aggregate.

## 2. Background description

The studied area is in the north of the North Island of New Zealand, at Puhipuhi, an isolated rural locality (Fig. 1). The area is underlain by lithified weakly metamorphosed greywacke (sandstone) and argillite (mudstone) typical of much of New Zealand basement (Mortimer, 1995). This basement was covered by a veneer (up to 50 m thick) of young (<5 million years old) lake sediments and basalts formed during a period of volcanism that may still be active (Smith et al., 1993). Hot springs associated with the volcanic activity left scattered siliceous sinter deposits at the surface, and siliceous feeder zones for those springs in the underlying rocks (Fig. 1), on the 100 m scale (White, 1986; Grieve et al., 1997). Active uplift and erosion has removed much of the basalt and lake sediment cover, but

small remnants persist on some ridges. Most valleys are cut into the basement greywacke and argillite. Remnants of hot spring surface sinters are preserved locally, and erosion has exposed the deeper levels of some hot spring systems (White, 1986; Craw et al., 2000).

The area has a warm, moist subtropical climate, and receives between 2.5 and 3 m of annual rainfall. Before human habitation, the area was covered in dense indigenous subtropical rainforest. The high rainfall, warm temperatures, and abundant organic matter have facilitated deep weathering and clay alteration of most of the rocks of the Puhipuhi area. This alteration extends for up to 30 m below the surface, and has variably transformed the rocks to clay-rich saprolite. Clay alteration has affected greywacke, argillite, lake sediments and basalts to varying degrees, so that distinctions among these rock types are difficult. Some basalt bodies have resisted this weathering locally due to their dense unfractured nature. Podzolic soils (Gibbs, 1980) on the upper portion of the deeply clay-altered rocks have a well-defined brown or red-brown C horizon enriched in iron oxyhydroxides. The C horizon is typically 30–50 cm below the surface, and is locally up to 50 cm thick.

## 3. Range of environmental pH

Unweathered greywacke, argillite and basalt commonly contain calcium carbonate (calcite) which helps to maintain groundwater pH near-neutral or weakly alkaline (Fig. 2). Weathering of these rocks rapidly removes this calcite, and the rock's pH buffering capacity is diminished. Consequently, pore waters in these weathered rocks have pH between 4 and 6, and groundwater derived from these weathered rocks also has pH between 4 and 6. Likewise, forest soils developed on deeply weathered greywacke, argillite, and basalt commonly have pH between 4 and 6 (Fig. 2). This low pH persists in small streams draining these rocks, but larger (regional) streams and rivers have near-neutral pH (Fig. 2) because of their large components of rainwater and deeper groundwater from less weathered greywacke and argillite.

Hot spring deposits and their siliceous feeder zones contain marcasite (above) which rapidly decomposes in contact with atmospheric oxygen. Decomposition of marcasite generates sulfuric acid and results in localised acidification of runoff waters from these natural mineralised outcrops (Fig. 2). These naturally acidified waters occur on the 100m scale, controlled by the location of the fossil hot spring deposits. Beyond these deposits, the acid waters mix with waters draining normal forest soil waters, and pH rises.

Human occupation of the Puhipuhi area over the past 150 years has resulted in >80% deforestation and cultivation of exotic grassland for agricultural purposes (Fig. 1). Grassland development was facilitated by addition of agricultural lime which has neutralised soil pH on a regional scale (Fig. 2) to maximise grass growing efficiency. Some of

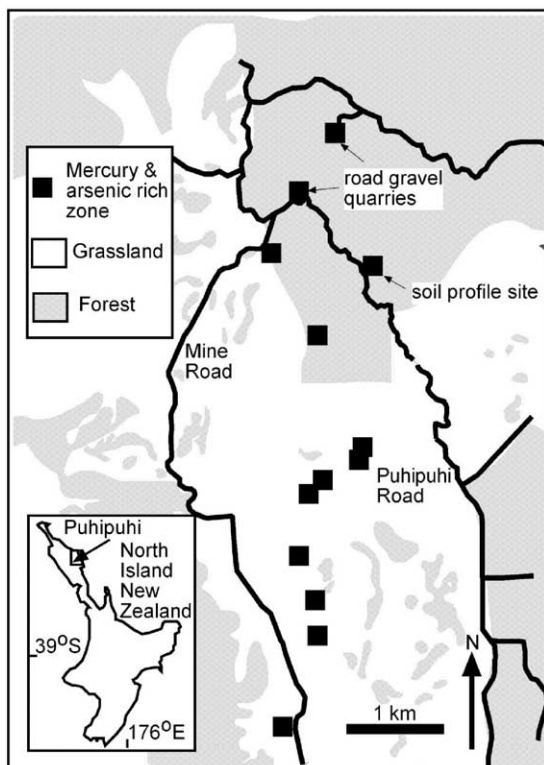


Fig. 1. Location map of the Puhipuhi area in the North Island of New Zealand (inset), showing mineralised zones and general land use. Roads marked with heavy black lines have been surfaced with aggregate made from mineralised rocks. Additional roads (not shown) in some forested areas also have this surface aggregate.

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