

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

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Received 23 March 2004; revised 11 August 2004; accepted 15 October 2004

## 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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*Keywords:* Arsenic; Mercury; Marcasite; Cinnabar; Neutralization; Acid rock drainage; Metals; Soil; Phosphate

## 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

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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

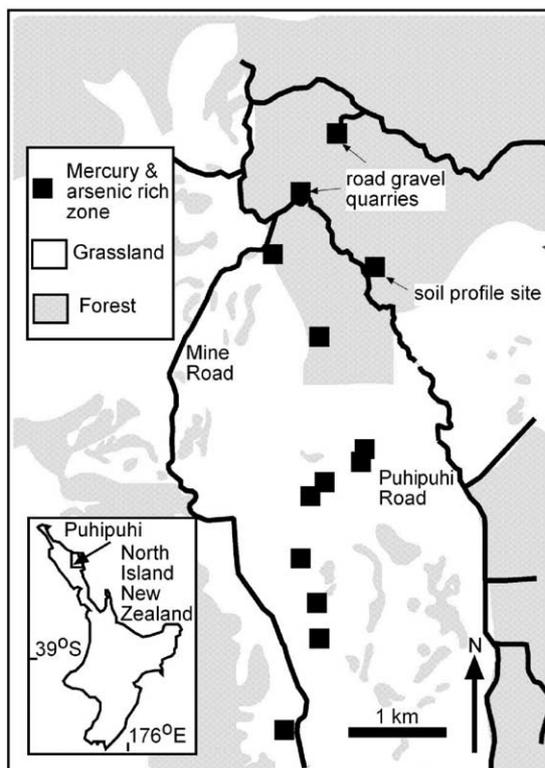


Fig. 1. Location map of the Puhipuhi area in the North Island of New Zealand (inset), showing mineralised zones and general land use. Roads marked with heavy black lines have been surfaced with aggregate made from mineralised rocks. Additional roads (not shown) in some forested areas also have this surface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

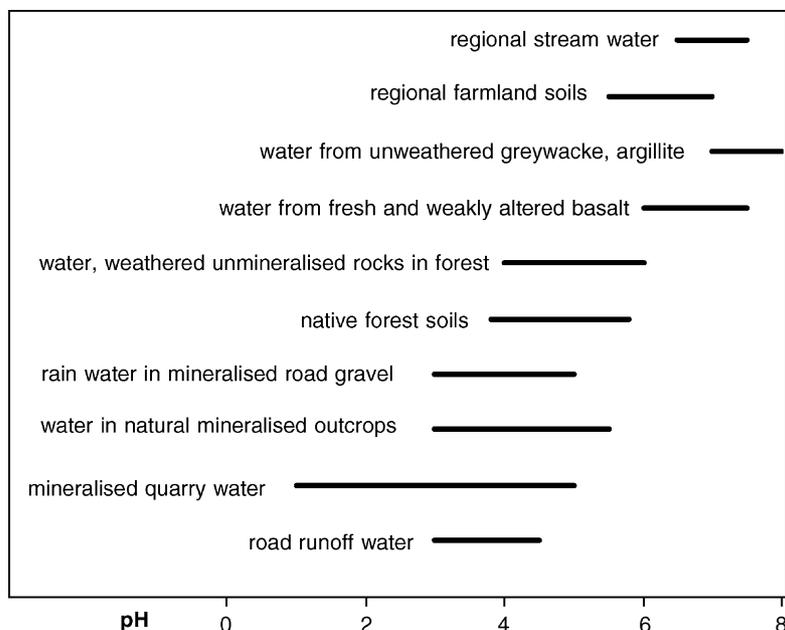


Fig. 2. Summary of the pH ranges in various settings relevant to this study (see text).

this grassland has since been replaced by exotic forest that now contains a dense understorey of regenerating native vegetation. Soil pH in these reforested areas is returning to original acidic levels (pH 4–6).

Road aggregate has been extracted from siliceous hot spring zones (Fig. 1) because these siliceous zones have resisted the deep clay weathering that has affected surrounding rocks. The road aggregate was produced by excavation and crushing of siliceous material and the resulting material was spread around the roads depicted in Fig. 1 (Craw et al., 2002). Additional roads in the area, constructed for management of exotic forests, have also been surfaced with aggregate derived from siliceous hot spring zones (Fig. 1). Typical distribution of pH in pore waters in variably oxidised rock exposed in a quarry, and road aggregate derived from that quarry, is shown in Fig. 3. Fresh rock exposed on quarry margins is mostly unsaturated with water, but rainwater runoff from these rocks has pH as low as 1 locally.

#### 4. Metal content of Puhipuhi rocks and soils

Background levels of mercury and arsenic in unweathered basement rocks are low (5–20 mg/kg As; 0.1–0.6 mg/kg Hg; Craw et al., 2002). In contrast, rocks from the hot spring zones can have 100–1000 times higher mercury and arsenic contents than background rocks. Arsenic contents of mineralised rocks range from 5 to 2100 mg/kg, with an average (120 samples; Craw et al., 2002) of 370 mg/kg, and mercury ranges from 0.1 to 220 mg/kg, with an average of 12 mg/kg in the same rocks. These mineralised rocks contain elevated concentrations of

mercury, principally as cinnabar (HgS) that was mined sporadically early in the 20th Century. These rocks also commonly contain marcasite and pyrite (both FeS<sub>2</sub>) with mercury and arsenic as impurities (up to c. 1 wt%) in marcasite (Craw et al., 2000). Scattered phosphate minerals with mercury and arsenic impurities occur also (Craw et al., 2000). Base metal concentrations are similar to those of background basement greywacke, with ca. 20 mg/kg Cu and Pb and ca. 100 mg/kg Zn (Craw et al., 2002).

Background soil Hg and As contents are even lower than the background rock levels, due to extensive leaching of metals from the rocks during long-term weathering. However, soils developed on the hot spring zones have strongly elevated Hg and As contents, especially in the iron oxyhydroxide-rich C horizon where these metals are present at similar or slightly lower concentrations than the parent mineralised rocks. Soil (C horizon) arsenic contents range from 1 to 4350 mg/kg, with an average of 197 mg/kg (340 samples; Craw et al., 2002), and mercury contents range from 0.1 to 69 mg/kg with an average of 5 mg/kg in the same samples. An example of soil on mineralised rock exposed in a road cut (Fig. 1) demonstrates that the Hg and As contents are highest in the middle of the soil profile (C horizon; Fig. 4). This example also demonstrates the low base metal concentrations of these soils. Copper and lead concentrations are similar to background in the C horizon but have been leached elsewhere in the profile, and zinc has been strongly leached from all the profile compared to background levels.

Most of the metallic minerals associated with hot spring mineralization have decomposed in weathered rocks, and are found only in anthropogenic exposures such as quarries. Cinnabar is resistant to weathering and survives in some

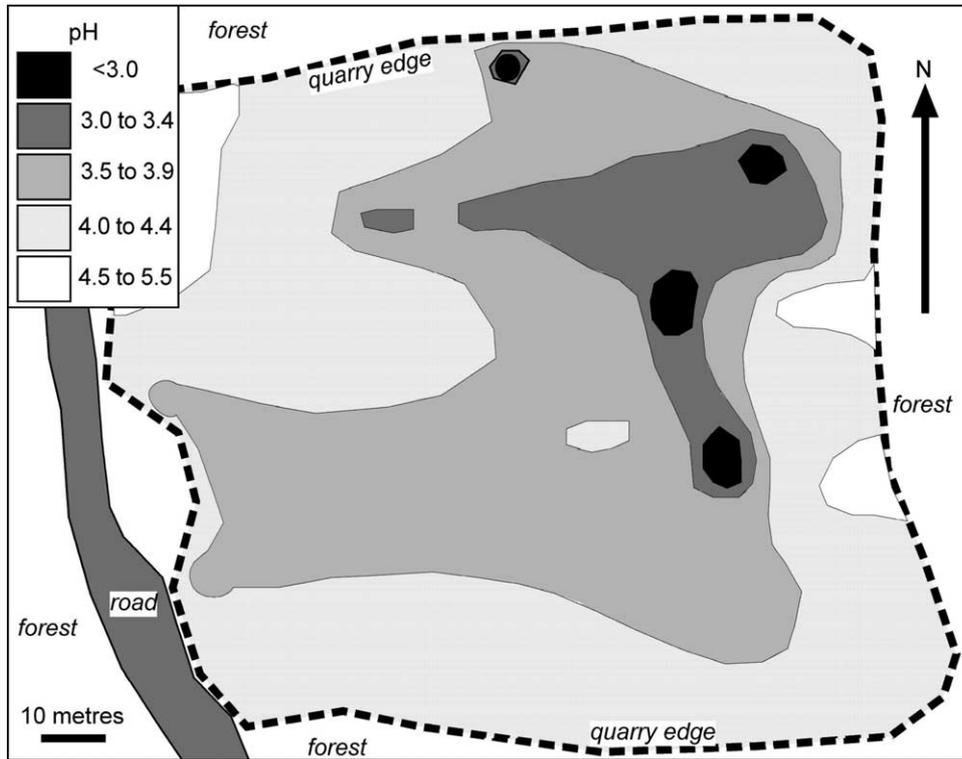


Fig. 3. Contour map of substrate pH in a quarry developed in mineralised rocks at Puhipuhi, showing wide acid pH variation. Data for the map (60 points) were obtained when the substrate was wet after rainfall. The adjacent road is surfaced with aggregate made from mineralised rock from the quarry.

outcrops and as a detrital mineral in streams (Ferrar, 1925). The iron sulfides readily oxidise to yield iron oxyhydroxide which coats joint surfaces, cements brecciated rocks and soils, and coats exposed surfaces in streams. This oxidation

process releases As and Hg from the sulfide structures, particularly from marcasite. Associated acid waters facilitate dissolution of arsenic and mercury from primary phosphate minerals. However, the As and Hg released by

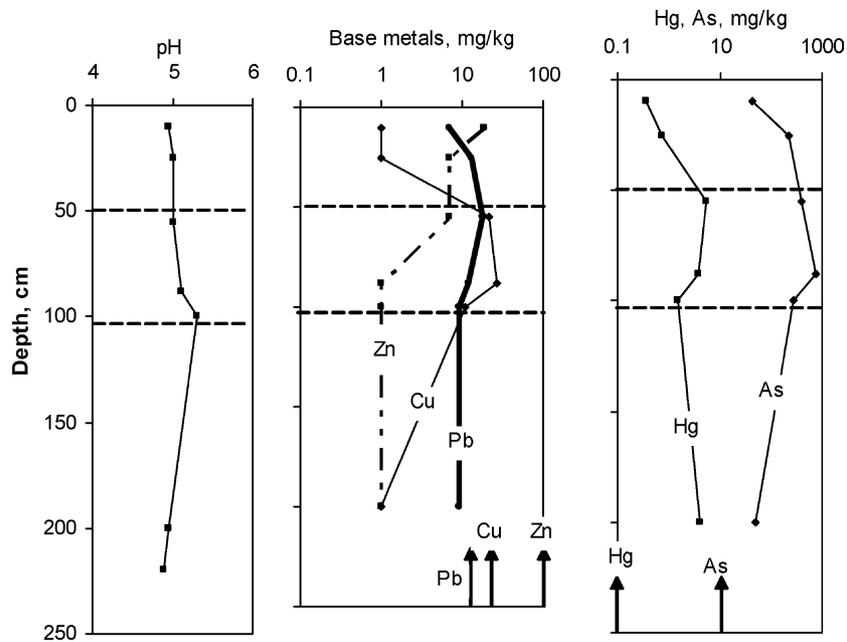


Fig. 4. Geochemical profiles through soil developed on a mineralised zone at Puhipuhi, showing variations with depth of paste-pH, Cu, Pb, Zn, Hg, and As. The iron oxyhydroxide rich C horizon is indicated between dashed lines. Unmineralised greywacke background values for the various elements are shown with arrows at the base of the diagram.

these reactions are largely adsorbed on to the iron oxyhydroxides and the rocks remain elevated in these elements (Craw et al., 2000). Likewise, the C horizons of soils are readily identifiable by their strong enrichment in brown iron oxyhydroxides compared to paler-coloured clay-dominated zones above and below. These C horizons in mineralised rocks also contain elevated levels of As and Hg adsorbed on to the iron oxyhydroxides (Fig. 4). Fresh mineralised aggregate on roads yields iron oxyhydroxide weathering products on a time scale of weeks to years (Craw et al., 2002). Some of this weathering product remains in situ, and some is washed off the roads with storm runoff waters (Craw et al., 2002). As and Hg released by the weathering processes remain largely adsorbed on to these iron oxyhydroxides in the field (Craw et al., 2000).

## 5. Mercury and arsenic in water

Despite the high concentrations of Hg and As in rocks at Puhipuhi, dissolved As and Hg concentrations are low. Dissolved Hg and As are below 0.001 mg/L in side streams draining eroded hot spring deposits. Road runoff water during rain storms carries sediment with variably elevated Hg and As contents, but dissolved Hg and As remain below 0.001 mg/L. Detectable levels of dissolved As (up to 0.13 mg/L) occur in slow-moving groundwaters pooling in road aggregate quarries, but dissolved Hg remains below detection (Craw et al., 2002). River waters in contact with mercury-rich sediments draining from the Puhipuhi area have mercury concentrations below 0.0005 mg/L (Hoggins and Brooks, 1973). Hence, with few exceptions, most Puhipuhi waters have Hg and As concentrations below New Zealand drinking water guidelines (0.01 mg/kg As; 0.002 mg/kg Hg; Ministry of Health, 2000).

## 6. Analytical methods

Measurements of pH in this study (summarised in Fig. 2) were determined in the field with an Oakton WD35615 portable meter calibrated with standard pH buffers. These measurements are reproducible to within 0.1 pH unit. Measurements on surface and shallow ground waters (streams and rainfall water runoff) were made by placing the electrode directly into the water. The pH of wet substrates was determined by placing the electrode into a small hole pushed into the substrate, packing substrate material around the electrode, and vibrating the substrate gently to ensure water saturation of the immediate electrode area. The pH of dry substrates was determined as paste-pH, a standard minesoil technique (Sobek et al., 1978), in which substrate is mixed with distilled water in a small plastic container and the pH is measured in the container as for wet substrates (above). Likewise, some soil pH measurements, such as at a road cut soil profile (Fig. 1), were conducted on

pastures. The paste-pH method gives a less accurate estimate of pH than direct measurement of wet material, but sites at which pH was measured both on wet substrate and as paste-pH of originally dry material yielded results within 0.4 pH units of each other.

Compositions of As and base metals in soils were obtained by acid digestion, solvent preconcentration, and ICP-MS analysis by Australian Laboratory Services, Brisbane. Mercury was analysed by low temperature aqua regia digest with ICP-MS analysis at the same laboratory. Detection limits are 1 mg/kg for base metals, 0.2 mg/kg for As, and 0.1 mg/kg for Hg. Analyses of natural waters were done on filtered (0.45 µm) and acidified samples at Hill Laboratories, Hamilton, New Zealand. Analyses were by ICP-MS for As with a detection limit of 0.001 mg/L, and by AAS (hydride method) for Hg with a 0.0001 mg/L detection limit.

## 7. Experimental leaching of Hg and As

Direct observations (above) show that, despite the abundance of As and Hg in solids at Puhipuhi, only minor amounts of Hg and As are mobilised at pH of 3–5. Even in the widespread natural occurrences of oxidised mineralised rocks, where As and Hg are merely adsorbed on to iron oxyhydroxides, these metals are sparingly mobilised into surface and ground waters. However, human activities in the area have resulted in localised evolution of pH to higher and lower than natural levels, on farmland (pH > 6) and some fresh rock exposures (pH < 3). In order to simulate environmental change for mineralised material from its natural occurrences, some leaching experiments were carried out in a range of different pH solutions.

### 7.1. Acid mobilisation of mercury and phosphorus

Some of the mineralised rocks contain hydrothermal barium–aluminium phosphate minerals with mercury and arsenic in solid solution (up to 0.5 wt%), whereas scandium-bearing phosphates do not contain these impurities (Craw et al., 2000). These phosphate minerals survive essentially intact in oxidised surficial rock in acid waters, and can be expected to persist in soils as well. When these minerals decompose, they will release mercury and arsenic. A set of leaching experiments was set up to estimate the proportion of mercury that could be mobilised by decomposition of phosphates, compared to decomposition of other minerals such as marcasite and pyrite, or desorption of mercury from iron oxyhydroxides. Arsenic was not included in this evaluation because the phosphate-rich material used, from an old mercury mine, is rich in mercury but contains relatively little arsenic. The material is minesoil; that is, it is fine grained waste rock from the floor of an historic mercury mine. The material consists of 1–5 mm particles with a silt and clay matrix, including abundant iron oxyhydroxide.

The material is inhomogeneous, and is mostly highly oxidised, but rare relict sulfides are discernible in some fragments.

Twelve different samples, each in triplicate, were crushed to fine powder, and weighed amounts (ca. 10 g) were placed in glass jars with lids. Solutions acidified with sulfuric acid to pH 3 and 1, and a 50% sulfuric acid solution, were added to the jars (50 ml/jar) and left to leach the sediment for up to 18 days. Aliquots of solutions (0.2–0.5 ml) were extracted at various times during leaching, diluted to provide manageable analytical volumes, and analysed to monitor leaching progress. Mercury was analysed on these extracted solutions by AAS (hydride method), and phosphorus was analysed by ICP. There was no consistent trend of results for different times of leaching, so results are plotted in Fig. 5 distinguished by pH only. Amounts of mercury and phosphorus leached were calculated as mg/kg, or milligrams of extracted Hg or P recalculated for constant weight of 1 kg of sample in a litre of water, to correct for minor differences in weights of powder added to the experiments. This is physically representative of near-stationary pore water saturating mineralised soil or rock. The results show that little mercury or phosphate is leached at pH 3, while more mercury but still only minor phosphate are leached at pH 1. The strong acid solution leached substantial amounts of mercury and phosphorus from many samples.

7.2. Broad pH spectrum leaching

These experiments were intended to evaluate the maximum amount of arsenic and mercury that could be mobilised from weathered rock debris, minesoil, and soil from Puhipuhi mineralised zones over a broad range of pH. Two different sets of experiments, over a range of acid and circumneutral pH, have been carried out at different times,

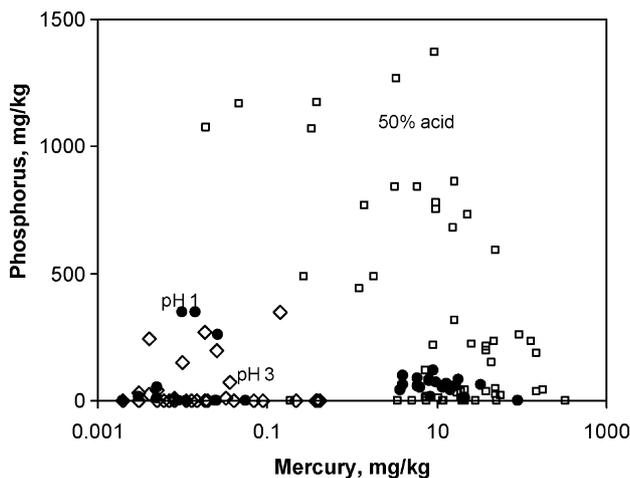


Fig. 5. Results of acid leaching experiments on Hg-bearing Puhipuhi minesoils that contain phosphate minerals. Amounts of mercury and phosphorus released are shown for experiments at pH 3 (open diamonds), pH 1 (black circles), and 50% sulfuric acid (open squares).

and results are combined here. All leached samples had elevated Hg and As, although distribution of those metals through the samples was irregular. Acid leaching of 13 weathered mineralised samples by sulfuric acid was carried out using solutions acidified with sulfuric acid to pH 3 and 1, and a 50% sulfuric acid solution, as for the phosphorus leach experiments above. Aliquots were analysed at various times over 18 days. Mercury was analysed on these extracted solutions by AAS (hydride method), and arsenic was analysed by ICP. Circumneutral leaching of 14 samples (10 g charges) was carried out with 100 ml of a pH 6 solution (acidified with HCl) and pH 8 solution (added NaOH) for up to 12 days, with aliquots removed periodically as for the acid solutions.

There was no consistent trend of amounts of metals leached with differing times, so results are plotted in terms of solution pH only (Figs. 6A and 7A). Amounts of As and Hg

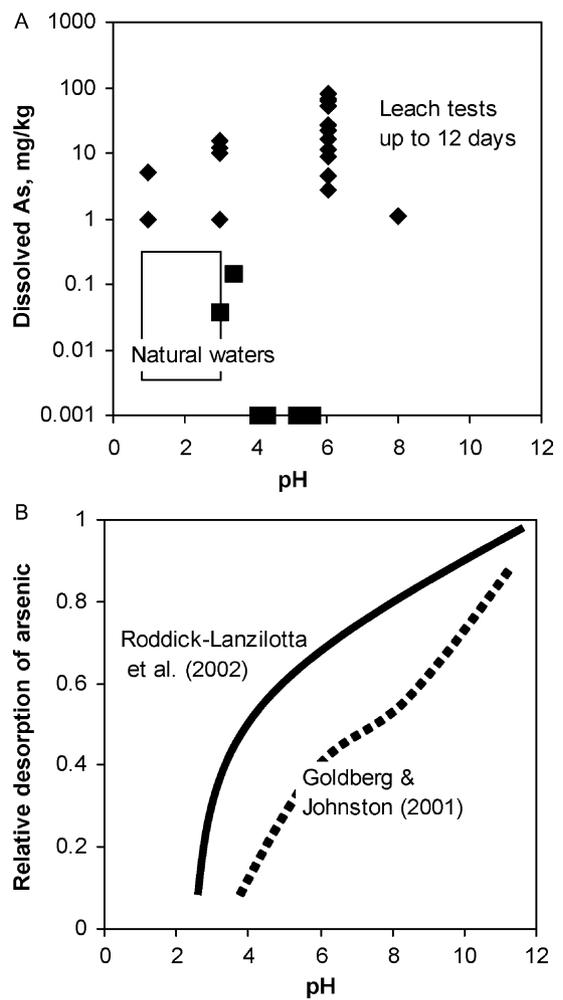


Fig. 6. (A) Results of leaching experiments on Puhipuhi soils at a range of pH, showing resultant amounts of arsenic extracted, as mg/kg of sample (see text). The compositional range of natural waters associated with mineralised rocks at Puhipuhi is shown with a box, and some waters associated with quarries are shown as black squares. (B) Experimentally-determined pH control on dissolved arsenic desorption from iron oxyhydroxide.

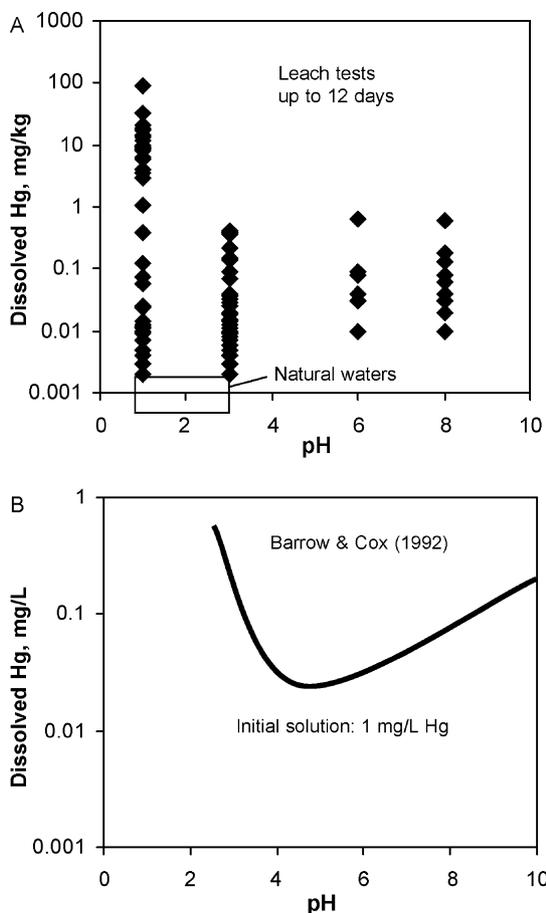


Fig. 7. (A) Results of leaching experiments on Puhipuhi soils at a range of pH, showing resultant amounts of mercury extracted, as mg/kg of sample (see text). The compositional range of natural waters associated with mineralised rocks at Puhipuhi is shown with a box. (B) Theoretically-predicted and experimentally-determined pH control on dissolved mercury adsorption to iron oxyhydroxide.

leached are determined as milligrams of extracted As or Hg recalculated for constant mass of 1 kg of sample in a litre of water, as above. The 50% sulfuric acid solution leach results have been omitted from these diagrams to enable better comparison to theoretical and experimental results (Figs. 6B and 7B; below). Up to 166 mg/kg As and 333 mg/kg Hg were leached by the 50% sulphuric acid solutions. Data plotted for each pH include all results which were above practical detection limits of 1 mg/kg for As and 0.001 mg/kg for Hg, irrespective of the leaching time. The leach results presented in Figs. 7A and 8A show that appreciable amounts of As and Hg (10s–100s of mg/kg) can be leached from the Puhipuhi rocks in a short time. In general, the higher leach values resulted from longer leach times, but some samples and some aliquots from several samples did not follow this trend.

### 7.3. Leaching of a soil profile

More specific leach results for the soil profile (Fig. 4) at pH 6 are summarised in Fig. 8. These results have been recalculated as proportions of original As and Hg that were

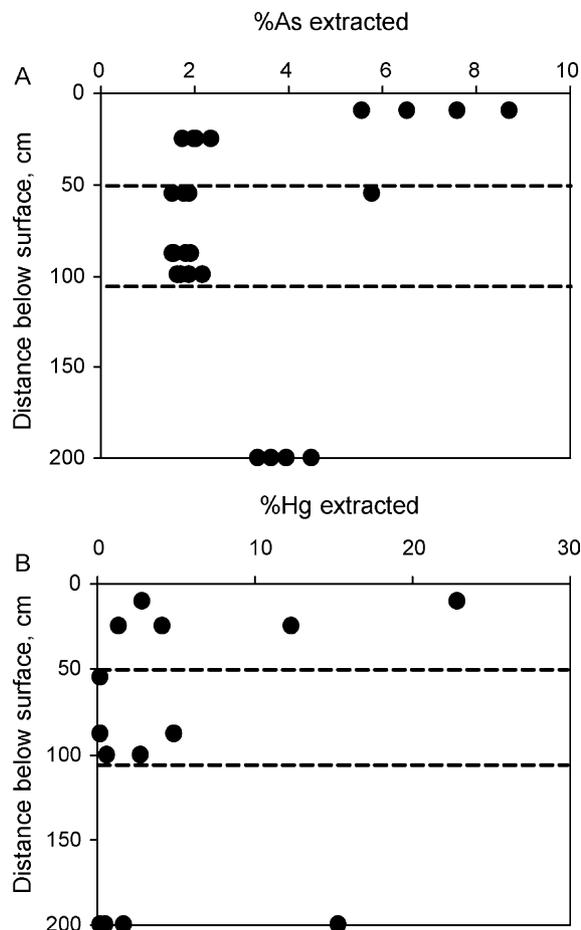


Fig. 8. Results of leaching experiments at pH 6 on soil developed on mineralised rock at Puhipuhi (Fig. 5), showing the proportions of arsenic (A) and mercury (B) extracted from different levels in the soil. The iron oxyhydroxide rich C horizon is indicated between dashed lines.

leached in the experiments (Fig. 8). The highest proportions of both As and Hg were leached from the shallowest part of the soil profile where total As and Hg were low due to weathering processes (Fig. 4). Conversely, low proportions of both As and Hg were leached from the middle of the soil profile where total As and Hg are relatively high (Fig. 5). Nevertheless, some experiments mobilised more arsenic from the middle portions of the profile than from other portions, despite being low proportions of the total amount present. There is a general but irregular decrease in amount of arsenic leached with increasing leach time, but the mercury data are too low and variable to detect a similar pattern.

## 8. Discussion

### 8.1. Theoretical dissolved Hg and As

Adsorption of As and Hg on to iron oxyhydroxides is the most common solid form of these metals in the Puhipuhi environment, especially the natural environment (above).

Adsorption of arsenic on to iron oxyhydroxides chemically resembles formation of scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$  (Roddick-Lanzilotta et al., 2002). Dissolution of scorodite increases with increasing pH (Krause and Ettel, 1988), and adsorption of As decreases as well. This reflects the increasing ease of removal of adsorbed As under alkaline conditions as arsenate anions are replaced by hydroxyl ions (Goldberg and Johnston, 2001; Roddick-Lanzilotta et al., 2002). The gradient of this change is not constant, but is nearly constant over the pH range of interest in the Puhipuhi environment except at very low pH (Fig. 6B). Hence, adsorption of As is expected to decrease as pH rises above the natural range of pH 3–5, and increased mobilisation of As is expected under rising pH (Fig. 6B).

These theoretical predictions are supported by the leaching experiments in this study (above) for pH between 1 and 6 (Fig. 6A). Minimum leaching of As occurred at pH 1, and the amount of As mobilised increased by an order of magnitude at pH 6. Leaching of As in the strongest acid solution was higher (Fig. 6A) than expected from the theory (Fig. 6B). This high As mobilisation may be due to acid attack of more than just adsorption sites, releasing all As from the material. Experiments at pH 8 showed a much lower degree of leaching which is not predicted by theoretical considerations. There is no clear explanation for this discrepancy. Since pH 8 and  $<0$  are beyond the likely reach of the Puhipuhi environment, these issues are not pursued further here.

The above adsorption behaviour of arsenic applies principally to the As(V) oxidation state, the main form of dissolved As in the surface environment (Langmuir, 1997; Smedley and Kinniburgh, 2002). However, pore waters in the deeper parts of soils and underlying clay-altered rocks are relatively less oxidised, and such low-redox waters can readily release adsorbed arsenic as complexes with the As(III) oxidation state (Smedley and Kinniburgh, 2002). Hence, some of the As leached from the lower part of the mineralised soil profile (Figs. 4 and 8), for example, may be As(III) complexes.

Dissolved mercury is readily adsorbed on to iron oxyhydroxides, but to a lesser degree than arsenic. Formation of the  $\text{HgOH}^+$  complex is the principal pathway for Hg adsorption at typical Puhipuhi pH (Barrow and Cox, 1992). This complex is adsorbed in decreasing amounts as pH rises, and the complex is less stable under acid conditions (Barrow and Cox, 1992). Consequently, dissolved Hg in contact with iron oxyhydroxides should be highest under acid conditions, pass through a minimum near pH 4–5, and then rise at higher pH (Fig. 7B). Experimental and field observations support the decrease in adsorption at higher pH (Barrow and Cox, 1992; Rytuba, 2000).

Leaching experiments in the present study support the theoretical prediction that dissolved Hg is highest under acid conditions, decreasing to ca. pH 3 (Fig. 7A). At higher pH, the maximum amount of leached Hg is slightly higher than

at pH 3, although the difference is smaller than theoretically expected (Fig. 7B). Nevertheless, the pattern of maximum leached Hg from Puhipuhi mineralised material at different pH is sufficiently similar to the theoretical curve (Fig. 7A and B) to give confidence that the theory has some application to natural situations. The mercury–phosphorus leaching experiment (Fig. 5) shows that only minor decomposition of phosphate minerals occurs in solutions with pH of 3 or 1, and it is inferred that mercury released from these samples comes from adsorbed sites, not phosphates. Phosphates contributed a larger amount of dissolved Hg in the 50% sulfuric acid solution (Fig. 5).

The leaching experiments conducted on samples from the soil profile on mineralised rocks (Fig. 8) confirms that elevated arsenic and mercury contents in soils can be readily leached at pH 6, as expected from the above discussion. These experiments show that on time scales of days only, arsenic can be readily mobilised from all levels in these soils at pH 6. Mercury mobilisation occurred also, but at lower levels.

## 8.2. Land management implications

Acid rock drainage can have a negative impact on the environment, especially if the pH falls below about 4.3 (Gray, 1998). Consequently, some remediation of highly acid sites is generally required. Remediation has been initiated at the Puhipuhi quarry shown in Fig. 3, with some soil capping and revegetation. The desirable end pH of such remediation remains debatable. For areas of forest at Puhipuhi, with localised mineralised zones, the ambient pH is between 3.5 and 5, which is little different from many anthropogenic acid rock drainage zones in the area (Fig. 2). Because the Puhipuhi mineralised rocks are enriched in arsenic and mercury but not base metals, the optimum pH for limiting metal mobility is acid, probably around 3–4 (Figs. 6 and 7). At lower pH, mercury and possibly arsenic may be more readily leached from the soils, and at higher pH, arsenic and possibly mercury can be more readily leached from the soils. Hence, the most common soil pH that results from acid rock drainage in this area turns out to be the most desirable for limiting metal mobility.

Farmland has relatively high pH (typically  $>6$ ; Fig. 2) and is actively maintained at that level with agricultural lime. This high pH has metal mobility consequences in the Puhipuhi area that are different from most acid rock drainage sites. Because of the lack of base metals, high pH is not a desirable soil chemical condition for limiting metal mobility, even if it is desirable for economic reasons. Addition of lime to soils overlying mineralised zones will encourage mobility of arsenic, and probably mercury, from these naturally-elevated metal-rich soils. Further, where mineralised rocks have been used as road aggregate, sediment carried from the roads in rainfall runoff water will more readily release arsenic and mercury in

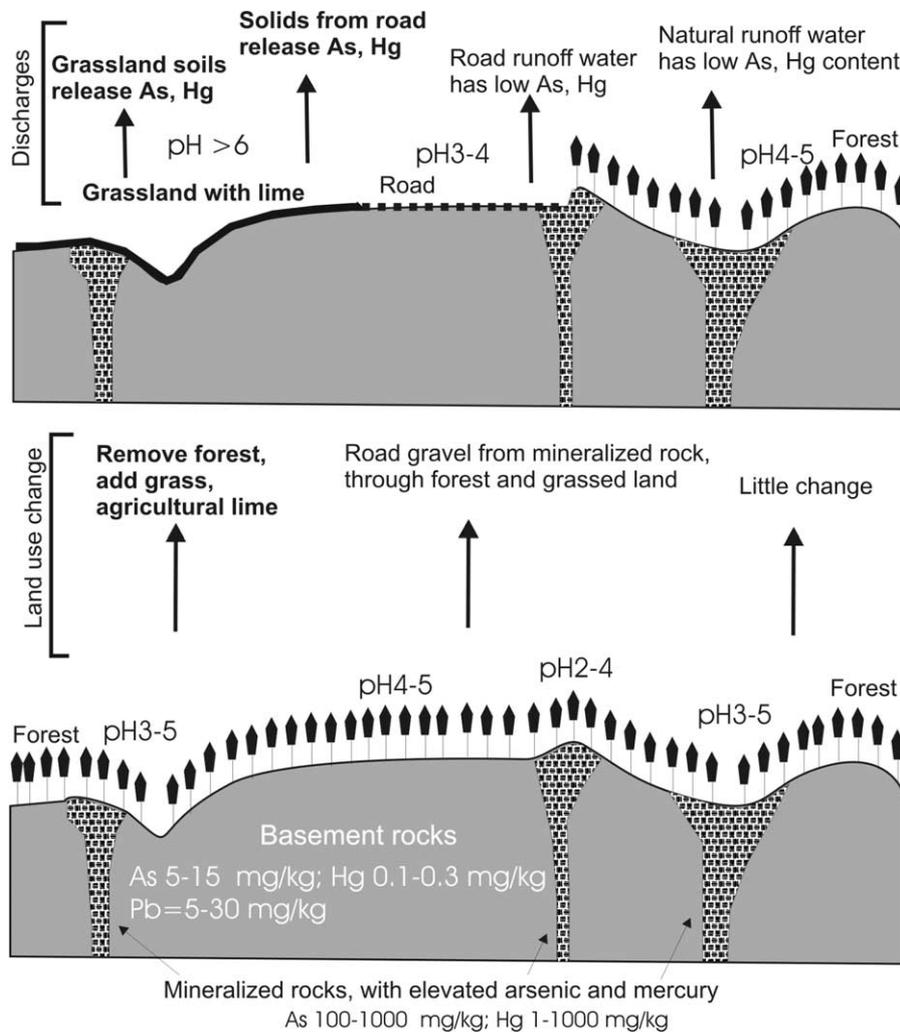


Fig. 9. Sequential cartoons (vertical cross sections) for the Puhipuhi area, summarising the effects of land use changes on arsenic and mercury mobility in soils. The lower diagram shows the original fully-forested state. Arrows from this show evolution to the present land use situation, depicted in the upper diagram. Land use changes involving agricultural lime addition and pH rise are highlighted on the left. Resultant metal discharges in water are shown with arrows at the top.

the artificially high-pH farm soils. It is notable that one anthropogenic activity (agricultural liming) can exacerbate the effects of another anthropogenic activity (distribution of mineralised rock as road aggregate).

The above observations are summarised in cartoon form in Fig. 9. The bottom diagram shows the pre-human situation, with full forest cover on typical basement rocks (soil pH 4–5), and localised mineralised zones with natural acid rock drainage (soil pH 3–4). The upper diagram shows the present situation after human settlement and development. The two principal land use changes that have occurred during recent human settlement are: (a) clearing and liming of farmland (left side of upper diagram) and (b) quarrying and distribution of mineralised aggregate on roads (centre of upper diagram). Natural rainwater runoff and road runoff water have low As and Hg contents (top right of cartoon). Mineralised rock and soil in the elevated pH environment of agricultural grassland, including sediment washed from

the roads, can release As and Hg in runoff water (top left of cartoon).

## 9. Conclusions

The Puhipuhi area has greywacke basement with localised (100 m scale) eroded hydrothermal zones with sulfide-bearing mineralised rocks. The sulfides become oxidised during weathering, generating acid waters and soils (typically pH near 3). Rainforest is the natural vegetation of the area, and forest soils developed during subtropical weathering of unmineralised greywacke commonly have pH between 4 and 5. Soils on mineralised rocks contain elevated arsenic and mercury (100–1000 times background levels) that are released during oxidation of sulfides, mainly marcasite, and phosphate minerals. Arsenic and mercury become adsorbed on to iron oxyhydroxides in soils,

principally in the C horizon, and the arsenic and mercury are fixed in situ. Consequently, waters emanating from these sites have dissolved arsenic and mercury below drinking water limits. This fixation of arsenic and mercury is most effective at pH of 3–4, as determined by leaching experiments and theoretical studies. At lower pH, mercury is desorbed and under strong acid conditions, additional mercury is released from primary phosphate minerals. Likewise, arsenic can be leached from primary minerals at very low pH. At higher (circumneutral) pH, arsenic is strongly desorbed and mercury may be desorbed as well.

These observations have some implications for land management. Some parts of the area have been deforested for agriculture, and the soil pH has been raised with lime to enhance grass growth. Farm soils with pH > 6 developed on mineralised arsenic and metal bearing zones have higher potential for mobilisation of arsenic and mercury than the naturally lower-pH soils. Mineralised rocks have been used on the surfaces of roads in the area. These roads have pH near 3, and runoff waters have negligible dissolved arsenic and mercury. However, runoff waters can transport arsenic and mercury bearing sediments on to farm land with higher pH, and mobility of arsenic and mercury is likely to increase from these transported sediments. The most prudent management regime for these soils is to maintain them at weakly acid pH, similar to their natural conditions. This approach is suitable for the Puhipuhi area because of the low base metal content of the mineralised zones. The presence of high Cu, Pb and Zn concentrations would negate this management approach.

### Acknowledgements

This research was supported financially by the University of Otago and the New Zealand Foundation for Research, Science and Technology. GRD Macraes Co. Ltd, and particularly Paul Angus, provided access to some mineral exploration geochemical data. Discussions with Rob Lieffering of Northland Regional Council were stimulating and valuable. Expert field assistance and laboratory help from Debra Chappell and Amanda Black facilitated the study. Frank Ho ably conducted the leaching experiments and compiled analytical results. Stephen Read provided much-needed assistance in diagram preparation. Two anonymous referees provided constructive and helpful reviews that substantially improved the presentation.

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