ARSENIC IN GROUND WATER

edited by

Alan H. Welch
U.S. Geological Survey

Kenneth G. Stollenwerk
U.S. Geological Survey

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Chapter 4

Geothermal Arsenic

The source, transport and fate of arsenic in geothermal systems

Jenny G. Webster[1] and D. Kirk Nordstrom[2]
[1] *University of Auckland, Auckland, New Zealand*
[2] *US Geological Survey, Boulder, CO, USA*

The release of arsenic from geothermal systems into surface and ground waters compromises the use of these waters as drinking water resources. In surface waters, As contamination can also adversely affect aquatic ecosystems, accumulating in sediments and plants. This review examines the source of arsenic in geothermal areas, its transport and speciation in geothermal fluids and receiving waters, as well as the deposition and removal mechanisms occurring in both natural environments and waste or water treatment systems. The effect of microorganisms on As mobility, and the opportunities that exist for further research in this field, are discussed. The review focuses on two geothermally active regions which have been intensively studied: Yellowstone National Park in the USA, and the Taupo Volcanic Zone in New Zealand, and their associated catchments.

1. INTRODUCTION

Arsenic (As) is a ubiquitous component of active and fossil geothermal systems. It occurs together with other environmental contaminants such as mercury (Hg), antimony (Sb), selenium (Se), thallium (Tl), boron (B), lithium (Li), fluoride (F) and hydrogen sulfide (H_2S). These elements are now recognised as being a typical "geothermal suite" of contaminants (Webster-Brown, 2000). High temperature geothermal systems occur throughout the world, generally in one of three tectonic settings. One such setting is on or close to tectonic plate boundaries. The edge of the Pacific Plate, for example, is defined by geothermal fields in New Zealand, Papua New Guinea, Philippines, Indonesia, Japan, Kamchatka, Alaska, western USA, Mexico, central America and Chile. Another setting is the Earth's "hot spots", where local magma chambers rise from near the mantle to shallow depths in the earth's crust, such as in Hawaii, Yellowstone and the Azores.

Although surface expression of recent volcanism is often associated with geothermal activity, it is not a prerequisite. The Larderello (Italy) and the Geysers (USA) geothermal steam fields, for example, are associated with instrusive activity in areas of fissured sedimentary and metamorphic rocks (Ellis and Mahon, 1967). The third setting is in rift zones where the tectonic plates diverge, such as the Gregory Rift Valley in Ethiopia, Kenya and Tanzania, the Rio Grande Rift valley in Colorado and New Mexico, and in the rift system in Iceland. Ellis and Mahon (1977) provide a more comprehensive description of geothermal settings.

Many geothermal fields have been developed, or are targeted for development, to generate energy from the steam and hot water reservoirs beneath the earth's surface.

1.1 Geothermal arsenic toxicity

The acute and chronic toxic effects of As are well documented. Recently As has also been declared a human carcinogen, contributing to a high incidence of skin and other cancers in populations exposed to high levels of As in drinking water (WHO, 1993). The WHO drinking water guideline for As was lowered from 0.05 mg/L to 0.01 mg/L in 1993, and the new value has since been adopted by many countries as a drinking water standard. In January 2001 the USEPA lowered the USA drinking water limit from 0.05 to 0.01 mg/L (Federal Register, 2001). However, this new standard was challenged by the new federal administration and further review was mandated. The results from three new scientific reports conclude that the new standard should be less than 0.01 mg/L.

Arsenic concentrations in natural surface drainage systems frequently exceed 0.01 mg/L in areas of geothermal activity. The Madison River, which drains part of Yellowstone National Park (Fig. 1), for example, contains ~ 2mg/L As near West Yellowstone (Thomson, 1979). Symptoms of chronic As poisoning such as skin lesions and high As concentrations in hair and nails have been reported from geothermal areas (Chen et al., 1999), but this may not always be as a direct consequence of drinking water contamination. At the Mt. Apo geothermal field in the Philippines, for example, the two rivers draining the field carry elevated As concentrations due to hot spring activity in the river beds. During development of the field, alternative clean drinking water supplies were provided and used by local residents, but the symptoms of high As exposure appeared to persist (Webster, 1999). The accumulation of As in edible aquatic plants is likely to have been to blame, as high levels of As have been reported in aquatic weeds in other river systems receiving geothermal fluids (e.g., Reay, 1972).

This chapter reviews what is currently known of the source and mobility of As in geothermal systems, as well as its fate and toxicity in the near-surface environment. The discussion focuses on two of the most thoroughly studied geothermally active regions: Yellowstone National Park in the US, which is mainly drained by the Madison and Yellowstone Rivers, and the Taupo Volcanic Zone in New Zealand, which is drained by the Waikato River (Fig. 1).

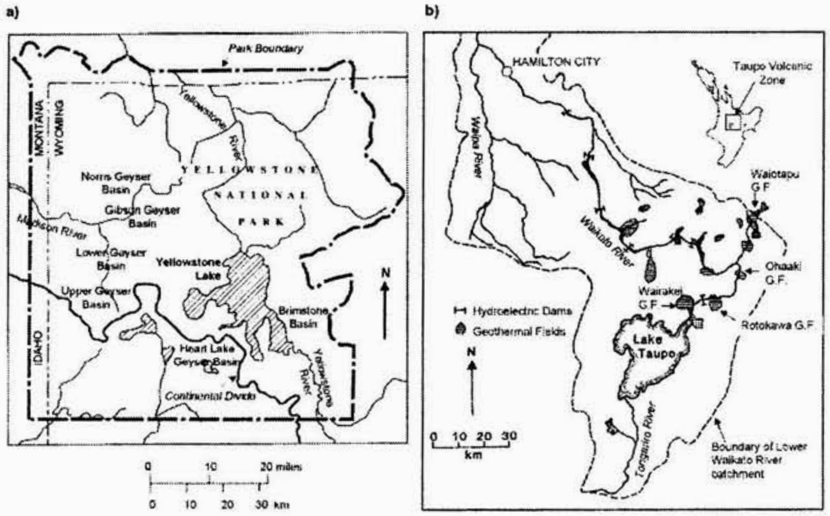

Figure 1. a) Yellowstone National Park (USA) and b) Taupo Volcanic Zone (NZ) and their surface drainage systems.

2. THE SOURCE OF ARSENIC IN GEOTHERMAL SYSTEMS

2.1 The source and nature of geothermal fluids

Geothermally active areas occur where an unusually high geothermal gradient allows hot water or steam to emerge at the earth's surface. The temperature of geothermal fluids may be elevated by only a few degrees, or by hundreds of degrees, above ambient (e.g., Ellis, 1967; White et al., 1971). Heat sources may be related to volcanic or magmatic activity, metamorphism, faulting and radioactivity.

Although geothermal fluids were initially thought to be of magmatic origin, isotopic analyses over the last 50 yrs (e.g., Craig et al., 1956; Giggenbach, 1971) have indicated that they are most commonly derived from meteoric waters. Deuterium-hydrogen and oxygen-isotope ratios are typically similar to those of local surface waters, although a minor contribution from magmatic fluids is a possibility at some fields (e.g., White, 1974). Irrespective of the heat source, deeply circulating ground waters are conductively heated in the crust. The hot fluids are of lower density than surrounding waters, and rise through the host rock, to complete the circulation system (Fig. 2).

The chemical composition of this fluid, which effectively constitutes the "geothermal reservoir", is a function of fluid temperature and host rock composition. As a solvent, hot water has a high dielectric constant, enabling it to dissolve ionic crystalline minerals in the host rock, forming new hydrated minerals, and transporting solutes away from the reaction site. A series of high temperature water-rock interaction experiments were undertaken in the 1960s to characterise the interactions between thermal waters and a variety of rock types including basalts, andesites, rhyolites and greywackes. The experiments were conducted at temperatures of 150 – 600°C and at various pressures (Ellis and Mahon, 1977; Ellis and Mahon, 1964) and confirmed that Cl, B and F could be rapidly leached into solution, even before significant alteration of the host rock had occurred. Other elements such as Li, Rb and Cs, which had previously been assumed to derive *only* from magmatic fluids, were also released into the hot water leachate during mineral alteration.

Such experiments under conditions of controlled gas fugacities and/or leachate chemistry, confirmed the importance of hot water-mineral equilibria in determining geothermal fluid compositions. Together with detailed analysis of mineral alteration assemblages in geothermal host rocks, they led to the development and refinement of a variety of geothermometers. The most applicable of these are the Na/K, Na/K/Ca and SiO_2 geothermometers, which are based on the temperature dependent solution equilibria with feldspars and micas, and with quartz respectively (e.g., Fournier and Potter, 1982; Fournier and Truesdell, 1973; Giggenbach, 1988). The concentrations of dissolved CO_2 and H_2S are also a function of mineral solubility, controlled mainly by equilibria with carbonate and sulfide minerals.

As geothermal fluids rise through the crust, the pressure decrease allows the single-phase fluid to separate into two phases: steam and water. This "boiling" process usually occurs at a shallow depth, but can occur wherever there is a sudden decrease in pressure due to rock fracture or fissure. The surface features in areas of geothermal activity can be grouped into two main

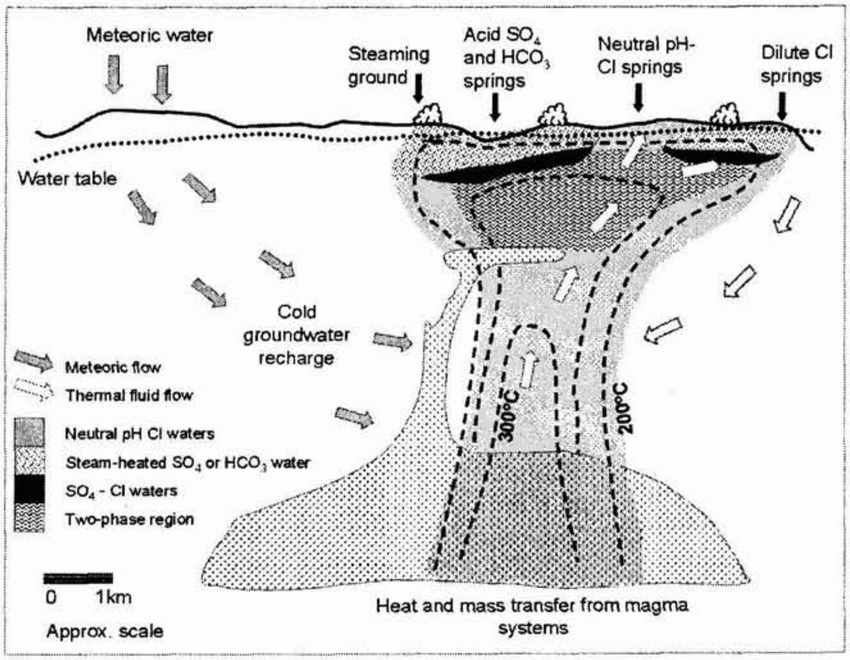

Figure 2. Generalized structure of a geothermal system (modified from Henley, 1985a, b).

types, on the basis of their relationship to the rising geothermal fluids (Fig. 2).

Hot water springs, rich in chloride and silica and with a near-neutral pH, represent direct discharge of the hot water phase. Steam vents and features such as acidic, sulfate-rich springs are formed by the interaction of the steam phase with shallow aquifer waters, which leads to precipitation and sublimation of elemental sulfur, and subsequent microbial oxidation to sulfuric acid. The intense argillic alteration of the host rock associated with these more corrosive fluids can lead to an unstable ground surface, and the formation of bubbling "mudpools" where alteration has rendered the host rock down to a slurry of clay minerals (e.g., Shoen et al., 1974). Surface features of intermediate chemistry can also occur. Geysers and carbonate-rich springs are also hot water discharges, for example, but include steam-heating and steam- phase mixing respectively.

Development of a geothermal field for power generations tends to increase the rate and volume of geothermal fluids reaching the surface. The reservoir fluid is intercepted by drilling and brought to the surface under pressure where it is "flashed" to a desirable temperature to generate the steam to run steam turbines. The extent of steam and water separation (boiling) can be artificially manipulated to maximise plant efficiency. The water phase formed at this separation becomes a waste product, although further heat can sometimes be extracted. This wastewater often has higher contaminant concentrations than analogous natural hot spring water because the processes that remove or immobilise contaminants in natural geothermal features, such as the precipitation of mineral-rich sinters, have been bypassed. Disposal of these wastewaters can be problematic. At most modern geothermal power stations, they are re-injected into the field. However, at some older fields such as the Wairakei Geothermal Field in New Zealand (Fig. 1b), these waters are still discharged into surface drainage systems.

2.2 The source of As in geothermal fluids

The presence of As in geothermal fluids has been known since the mid-19th century. Lefort reported traces of As in acid waters in the crater of Popocatepetl volcano in Mexico in 1863 (Clarke, 1924). The first measurements of As in hot springs and geysers of Yellowstone National Park were reported by Gooch and Whitfield (1888). Yellowstone National Park constitutes one of the largest geothermal systems in the world and has been intensely studied, particularly over the last 40 years. Arsenic concentrations in the thermal features of this field generally range from <0.1 mg/kg to 10 mg/kg, a range that is observed in most active geothermal fields (Table 1). Notable exceptions include the geothermal fields in Iceland and Hawaii where As concentrations of <0.10 mg/kg are consistently reported (Arnorsson and Linvall, 2001; Gudmundsson and Arnorsson, in press; D. Thomas, pers. comm.). These low As levels are attributed to the prevalence of fresh basaltic host rocks, low in arsenic, in the reservoirs of the respective geothermal fields. At the other extreme, As concentrations of >20 mg/kg are not uncommon in geothermal well fluids (Table 1). Geothermal fluid As concentrations are therefore usually three orders of magnitude greater than those in uncontaminated surface and ground waters.

2.2.1 Arsenic from host rock leaching

In the hot water-rock leaching experiments of Ellis and Mahon (1964; 1967), appreciable quantities of As were leached from unmineralised andesite yielding As concentrations of 1.3 mg/kg in the leachate. Subsequent experimental leaching of greywacke with hot water also indicated significant leaching of As, together with Sb, Se and S, at temperatures less than those in many geothermal fields (Ewers and Keays, 1977). On this basis, it can be assumed that neither magmatic fluid input, nor

Table 1. Arsenic (mg/kg) in hot springs and in production or exploration well brines at various geothermal fields.

Field	**As, mg/kg**	**Reference**
Hot springs:		
Yellowstone Nat. Park, US	0.16 – 10	Stauffer and Thomson (1984); Unpublished data, USGS
Wairakei, NZ	0.23 - 3.0	Ritchie (1961)
Waiotapu, NZ	0.71 - 6.5	Webster (1990)
Ohaaki/Broadlands, NZ	1.0	Ellis and Mahon(1977)
Valles Caldera, New Mexico	0.021 - 2.4	Criaud and Fouillac (1989)
Los Azufres, Mexico	0.001 – 4.0	Birkle andMerkel (2000)
Mt Apo, Philippines	3.1 - 6.2	Webster (1999)
Tamagawa, Japan	2.3 - 2.6	Noguchi and Nakagawa (1969
Japan (national survey)	0.001 - 9.5	Sakamoto et al. (1988)
Salton Sea, USA	0.03 - 12	White (1968)
Kamchatka, Russia	2.0 - 3.6	Karpov and Naboko (1990)
Phlegraean Fields, Italy	0.012 - 5.6	Celico et al. (1992)
Iceland	0.001 - 0.048	Arnorsson and Linvall (2001)
Well fluids:		
Wairakei, NZ	1.0 - 5.2	Ritche (1961)
Waiotapu, NZ	2.1 - 3.9	Ellis and Mahon (1977)
Ohaaki/Broadlands, NZ	5.7 -9.0	Ewers and Keays (1977)
Tongonan, Philippines	28 (mean)	Darby (1980)
Hawaii	<0.01 – 0.07	D. Thomas (pers. comm.)
Los Azufres, Mexico	5.1 - 24	Birkle and Merkel (2000)
Lassen Nat Park, US	2 -19	Thompson (1985)
El Tatio, Chile	45 - 50	Ellis and Mahon (1977)
Kamchatka/Kuriles	2 - 30	Goleva (1974)
Ebeko volcano, Siberia	0.19-28	Khramova (1974)

As mineralisation at depth, is a prerequisite for high As concentrations in geothermal fluids. Most reservoir fluids are undersaturated with respect to arsenopyrite and other arsenic minerals (Ballantyne and Moore, 1988) and hence As leaching, rather than As precipitation, is predicted to occur in the reservoir.

Early analyses of As in hot springs of the Taupo Volcanic Zone in New Zealand by Ritchie (1961) revealed a positive correlation between As and Cl which has since been confirmed for most geothermal fields. However, the interpretation of trends in the As/Cl ratio requires caution (Ballantyne and Moore, 1988), as the association is more a function of common behaviour, than of a common source or direct chemical association. The source of the Cl ion may be gaseous HCl associated with magma intrusion, host rock leaching or seawater, whereas As is derived mainly by host rock leaching. However, both elements remain in the fluid phase during sub-surface boiling and phase separation. Consequently, As concentrations are invariably higher in the neutral pH-chloride hot springs than in the acid-sulfate features. Likewise during the separation of steam and bore water in geothermal power generation, As is retained in the waste bore water. This high As content is one of the main problems in the disposal of this water.

The As/Cl ratio can be used as a tool to trace the effects of geothermal fluid dilution, concentration or mixing within a geothermal field. In Yellowstone National Park, for example, Stauffer and Thompson (1984) showed that the ratio could be used to identify simple mixing trends in different geyser basins. Many thermal waters mix with cool meteoric ground waters on their way to the surface and show linear trends of As vs Cl with a dilute end-member having As and Cl concentrations of ~0. A more recent study of As vs Cl concentrations in Yellowstone National Park thermal waters is shown in Figure 3a-c (Nordstrom et al., 2001). Linear mixing trends were identified in at least two pools; Cinder Pool and Cistern Spring in Norris Geyser Basin (Fig. 3a). Cistern Spring was recognised by Fournier et al. (1986; 1992) as a spring that was very sensitive to mixing. The mixing behaviour is caused by changes in subsurface flow patterns following climatic or seasonal changes in weather.

Other thermal waters from around Norris and Upper Geyser Basin tend to lie along the mixing trends defined by extensions of the Cinder Pool and Cistern Spring mixing lines (Fig. 3b). This suggests that the solutes had a similar source but that the Norris waters had undergone adiabatic cooling (boiling) which effectively increased the solute concentrations along sub-horizontal flow paths. Fournier et al. (1986) estimated that the Cl content of the deep thermal reservoir(s) at Yellowstone is about 400 mg/L, so that concentrations greater than this must reflect a concentration mechanism such as boiling. Other conservative solutes also follow this trend. These waters have subsequently mixed with dilute shallow ground waters as they made their way to the surface.

A more general survey of Yellowstone thermal waters (Fig. 3c) shows that many springs are enriched in As relative to Cl. Stauffer and Thompson (1984) showed a direct relationship between high CO_2 concentrations and a high As/Cl ratio. A fluid with high concentrations of oxyanions at depth, especially carbonate ions, will tend to react more rapidly with the host rocks, hydrolysing and solubilising other oxyanions such as arsenite. Nordstrom et al. (2001) also provide evidence for localized enrichment of As relative to Cl through accumulation of arsenic in precipitates near the surface or through dynamic geyser activity.

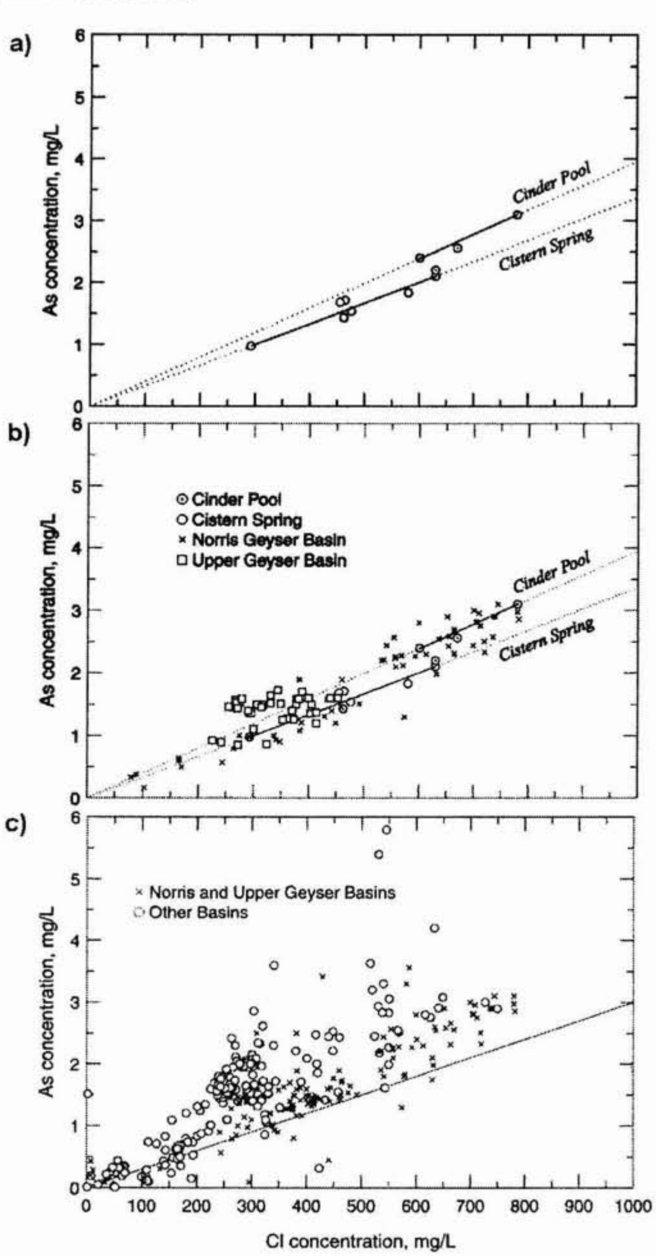

Figure 3. Variations in As and Cl in: a) Cistern Spring and Cinder pool in Yellowstone National Park. b) Springs of Norris and Upper Geyser Basin, together with the linear trends defined by seasonal variations in Cistern Spring and Cinder Pool (solid lines). c) A more general survey of Yellowstone National Park thermal waters, where "x" represents samples mainly from Upper Geyser Basin and Norris Geyser Basin (Nordstrom et al., 2001).

3. SPECIATION OF ARSENIC IN GEOTHERMAL FLUIDS

3.1 Dissolved As

The chemical behaviour of As in sulfide-rich fluids has been the subject of considerable, and ongoing, debate as there are several major obstacles to the accurate prediction of As speciation. In part, this reflects the lack of a complete thermodynamic database for As species. Stability constants for ion pairs and complexes between the As oxyanions and polyvalent cations are few and limited in applicability (Nordstrom, 2000). Also, polymerisation of arsenite, arsenate and thioarsenite complexes in high As or high sulphur solutions appears likely, but is largely unconfirmed. These reactions could significantly complicate As speciation. However, reliable thermodynamic data are available for some As species, and these can be used to interpret As behaviour in many geothermal systems and surface water environments, as long as the limitations are recognized.

3.1.1 Low sulfide, reduced fluids

Heinrich and Eadington (1986) and Ballantyne and Moore (1988) noted that, from thermodynamic considerations, As was more likely to be transported in most hydrothermal solutions as arsenious acid ($H_3As^{III}O_3^{o}$), rather than as a thio complex. H_3AsO_3 is considered to be the product of both As oxide (As_4O_6) and orpiment (As_2S_3) dissolution in reduced fluids at acid to neutral pH, over a wide range of temperature conditions (Eary, 1992; Ivakin et al., 1979; Mironova et al., 1984; Pokrovski et al., 1996). Orpiment solubility, as given by the following reaction:

$$0.5As_2S_3 + 3H_2O = H_3AsO_3 + 1.5H_2S$$

increases with temperature, to at least 300°C (Pokrovski et al., 1996; Webster, 1990; see Figure 4a). The solubility of orpiment is independent of pH under acidic, or acid-neutral pH conditions, but increases with further increase in pH. Note that the orpiment solubilities shown in Figure 4 assume a constant sulfide concentration, and do not take into account additional sulfide released from the orpiment. Once this additional contribution becomes significant, orpiment solubility will decrease (refer Section 3.1.2). Polymerisation has been observed using Raman spectroscopy (Pokrovski et al., 1996), and polymer configuration and stability has been calculated (Tossell, 1997). However, polymerisation is predicted to occur only at very high As concentrations (>1mol/kg; Pokrovski et al., 1996) and these conditions are unlikely to exist in geothermal fluids .

3.1.2 High sulfide, reduced fluids

In sulfide-rich hydrothermal solutions, orpiment solubility as H_3AsO_3 is inhibited but solubility as thioarsenite complexes increases. The thioarsenites are a group of covalently bonded arsenic-sulfide complexes that may or may not include oxygen. Reactions between arsenate ions and dissolved sulfide, for example, can result in the successive replacement of oxygen with sulfide (Pauling, 1970). However, the exact nature of the thio-complexes remains controversial (Helz et al., 1995; Wood et al., 1998). It was evident 40 yrs ago that a simple AsS_2^- stoichiometry and structure was likely to be unrealistic (Angeli and Souchay, 1960). A trimeric configuration ($As_3S_6^{-3}$) was proposed at that time and has since attracted support (Eary, 1992; Helz et al., 1995; Spycher and Reed, 1989a; Vorobeva et al., 1977; Webster, 1990). Dimer species have also been proposed (Mironova and Zotov, 1980; Mironova et al., 1990), but there has been little recent support for other earlier proposed species such as AsS_3^{-3}, $As_4S_7^{-2}$, AsS_4^{-5}, and $As_2S_5^{-4}$. Helz et al. (1995) suggest that the monomer may occur in undersaturated solutions, while the trimer is formed in the saturated solutions present in most experimental solubility studies and As-precipitating geothermal systems. Wood et al. (1998) provided Raman spectroscopic evidence for the simultaneous existence of more than one species.

Assuming a trimer structure occurs in a saturated geothermal fluid, orpiment solubility via the following reaction:

$$1.5As_2S_3 + 1.5HS^- + 0.5H^+ = H_2As_3S_6^-$$

increases with pH and sulfide concentration (Fig. 4b), but is not greatly affected by temperature changes below 200°C (Spycher and Reed, 1989a; Webster, 1990; Weissberg et al., 1966).

3.1.3 Redox state

The oxidation of arsenious acid to arsenate ($H_2As^VO_4^-$ or $HAs^VO_4^{-2}$) is thermodynamically favoured when the redox conditions in low sulfide fluids become sufficiently oxidizing. Oxidation occurs when a rising geothermal

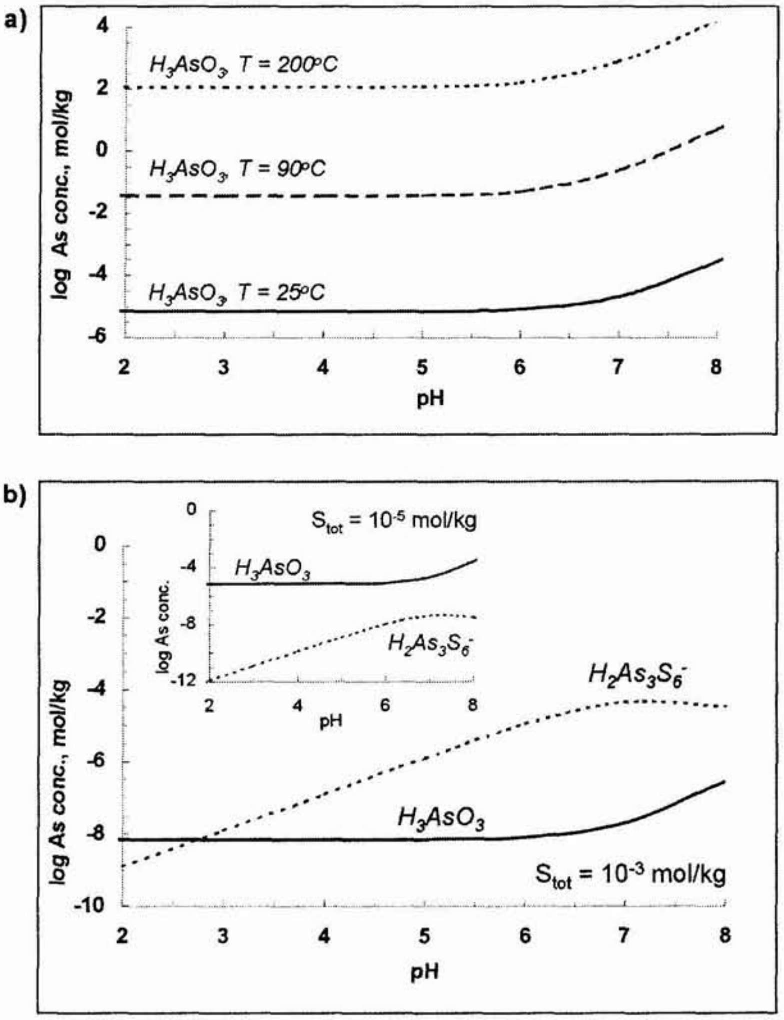

Figure 4. a) Orpiment solubility as a function of pH and temperature in low sulfide fluids, using stability constants for H_3AsO_3 from Webster (1990) and Pokrovski et al (1996). B) Orpiment solubility as a function of pH at 25°C, in a high sulfide fluids using stability constants for $H_2As_3S_6^-$ from Webster (1990).

fluid is exposed to atmospheric oxygen or mixed with another oxidizing fluid, such as a shallow ground water. Arsenate ions appear to be rapidly formed *in situ* in hot springs and their surface drainage systems. Of the many geothermal features in Yellowstone National Park, As^{III} predominates in most hot springs and geysers discharging directly from the reservoir (Ball et al., 1998; Nordstrom et al., 2001). The geothermal reservoir fluids are reduced with respect to the As^{III}/As^{V} redox couple as expected. Oxidation to As^{V}, however, occurs very rapidly in hot spring overflows and receiving streams and rivers. A few hot springs at Yellowstone contain mostly As^{V}, which is likely to be related to fluid flow rates and/or mixing with oxygenated ground waters. Very few Yellowstone geothermal waters have been found with similar proportions of As^{III} and As^{V}, unless they are overflow drainages in the process of oxidizing.

These results are similar to As^{III}/As^{V} distributions reported for hot springs on the island of Dominica (Carribean), in the Valles Caldera (New Mexico) and from the Massive Central in France (Criaud and Fouillac, 1989). In each case, hot springs formed from reservoir fluids contained mainly As^{III}, whereas acid-sulfate and bicarbonate features were more enriched in As^{V}. It is worth noting here that reported As^{III} concentrations may be underestimated if the sample has not been appropriately preserved prior to analysis. On site sample filtration through a 0.45μm (or finer) membrane to remove bacteria and cold storage in an air-tight container are recommended (Hall et al., 1999). Acidification with HNO_3 or HCl to pH 1.5- 2.0 is often recommended, as this inhibits oxidation of As^{III} by chemical oxidants such as Fe^{III}. However, in some waters, acidification has been observed to change As speciation slightly, reducing As^{V} to As^{III} (Hall et al., 1999, Webster unpublished data.) Arsenic oxidation in the stream draining Champagne Pool at Waiotapu geothermal field in the Taupo Volcanic Zone, and in an open, concrete drain conducting geothermal waste water across the Wairakei geothermal field suggests a short half-life of ≤5 minutes for *in situ* oxidation (Finlayson and Webster, 1989). More importantly, however, geothermal water collected immediately after steam separation, and before entering the drain, does *not* show a similar rate of As oxidation. Instead there is no appreciable As^{III} oxidation in the wastewater (collected directly into a sterile glass bottle), even if bubbled with air for several hours.

Such rapid As^{III}/As^{V} oxidation kinetics appear likely to be catalysed by microbial activity, although the mechanisms by which bacteria could facilitate arsenite oxidation at temperatures >50°C are not well studied. However, as bacteria are clearly implicated in As^{III} oxidation in geothermal systems, progress is being made in the identification of the thermophilic bacteria that can oxidise As^{III} (e.g., Gihring et al., 2001; Langner et al., 2001; Mielke et al., 2000). The ability of H_2S and thiosulphate (S_2O_3) to reduce As^{V} to As^{III} is well known (e.g., Cherry et al., 1979; DeKonnick, 1909; Forbes et al., 1922; Rochette et al., 2000), hence geothermal waters containing sulfide or thiosulphate will preserve arsenic as As^{III}, until the reduced sulfur is oxidised or volatilised (Nordstrom et al., 2001).

Further evidence of a microbiological influence on As chemistry may exist in the recent, intriguing observation of slight diurnal variations in the (total) As concentrations of various hot springs at the Waiotapu geothermal field (James Pope, pers. comm).

3.2 Arsenic deposition from geothermal fluids

Arsenic enrichment in geothermal systems occurs predominantly near the surface, along with other "epithermal" elements such as Sb, Au and Hg (White, 1981). In contrast, base metals such as Ag, Cu, Pb, Zn will be deposited at greater depth. A typical example of this type of zoning occurs in the Ohaaki geothermal system (formerly known as Broadlands) in the Taupo Volcanic Zone of New Zealand (Simmons and Browne, 2000). Here, As concentrations in drill core from BR 16 increased from 1.2-1.9 mg/kg at 1.5 km depth, to 19-22 mg/kg near the surface (Ewers and Keays, 1977). At depth, As was mainly concentrated in the pyrite, as has been noted at other fields (Ballantyne and Moore, 1988). Arsenic minerals such as arsenopyrite (FeAsS) appear to be uncommon in the rocks of the geothermal reservoir itself. However, a range of As minerals is precipitated from geothermal surface features such as hot springs (refer Section 3.2).

It has been suggested that the observed metal zoning may simply reflect different precipitation mechanisms for the base metals complexed by chloride and the epithermal metals complexed by sulfide (Drummond and Ohmoto, 1985; Weissberg, 1969; White, 1981). If transported as a thio-complex, As would be expected to precipitate in response to decreasing temperature and boiling (H_2S loss) in permeable zones (Ewers, 1977). However, as noted above, As is more probably transported as H_3AsO_3 in hydrothermal solutions (Ballantyne and Moore, 1988; Heinrich and Eadington, 1986; Spycher and Reed, 1989a). Spycher and Reed (1989b) argue that metal zonation is due to a three-step process of fluid boiling, gas-phase transport and acid reactions with metal-bearing waters. Base metal precipitation occurs in response to boiling and the pH increase which occurs when CO_2 gas is driven off. During boiling, As remains soluble as an oxyanion under the higher pH and lower sulfide concentrations present in the fluid. Precipitation of orpiment then occurs in response to the acidification of hot spring waters with acid-sulfate waters (Spycher and Reed, 1989b), subaerial cooling of the fluid or increased H_2S concentrations (Webster, 1990).

This scenario is consistent with the relationships discussed in Section 3.1.1 and shown in Figure 4, as rapid oxidation of As^{III} or H_2S would reduce the concentrations of these components and thereby increase orpiment solubility. Note that only if the fluids boiled dry would As be taken into the gas phase. Vapour deposition of realgar could occur when the temperature decreases below 130°C (Spycher and Reed, 1989b).

3.3 Arsenic in hot spring deposits and scales

The As contents of coloured precipitates forming at the periphery of hot springs, hot pool and geysers can be very high (Table 2). Analyses of red precipitates around the periphery of Champagne Pool in the Waiotapu geothermal field (Fig. 5a), for example, revealed an amorphous deposit containing up to 2wt% As, as well as sulfides of Hg, Sb, Tl and ore-grade Au and Ag concentrations (Weissberg, 1969). Similar red As-rich precipitates have been reported from Steamboat Springs in Colorado (White, 1967), Roosevelt Hot Springs in Utah (J. Moore, pers. comm.), and Beppu hot pool in Japan (Koga, 1961) .

The mineralogy of these coloured precipitates can be difficult to determine, given the amorphous nature of most recent deposits. Useful As:S ratios are obscured by other sulphide-bearing minerals and sometimes by native sulphur if there is a steam component to the hot spring. Nor is colour always a definitive indicator. For example, amorphous realgar is a bright red colour, but so is stibnite (Sb_2S_3) and cinnabar (HgS). Orpiment is a yellow-green colour, reminiscent of native sulfur. However, in the absence of high levels of antimony and mercury, As–rich precipitates in hot springs are commonly yellow orpiment (Fig. 5b). Thermodynamic calculations provide support for orpiment precipitation in hot spring environments. Hot springs on the Waiotapu and Rotokawa geothermal fields in New Zealand, for example, are saturated or slightly over-saturated with respect to orpiment (Webster, 1990). Also, orpiment precipitation has been observed where small H_2S-rich steam vents occur in the bed of hot spring-fed streams at these fields.

Realgar does not appear to be actively depositing in hot springs at Waiotapu but does occur as coatings and veins in the altered rocks of the geothermal field. This supports the hypothesis of different deposition mechanisms for realgar and orpiment, as proposed by Spycher and Reed (1989b). It has also been proposed that a transient As disulfide solid phase occurs in hot spring environments (Noguchi and Nakagawa, 1969), but it has not been isolated. Scorodite ($FeAsO_4.2H_2O$) has been reported from the Osorezan geothermal area in Japan (Aoki and Yui, 1981). Native As has been reported from low temperature hydrothermal deposits (eg., Sergeyeva et al., 1969) but is rare. Other As sulfides, such as dimorphite (As_4S_3) and duranusite (As_4S), have not been reported from geothermal systems.

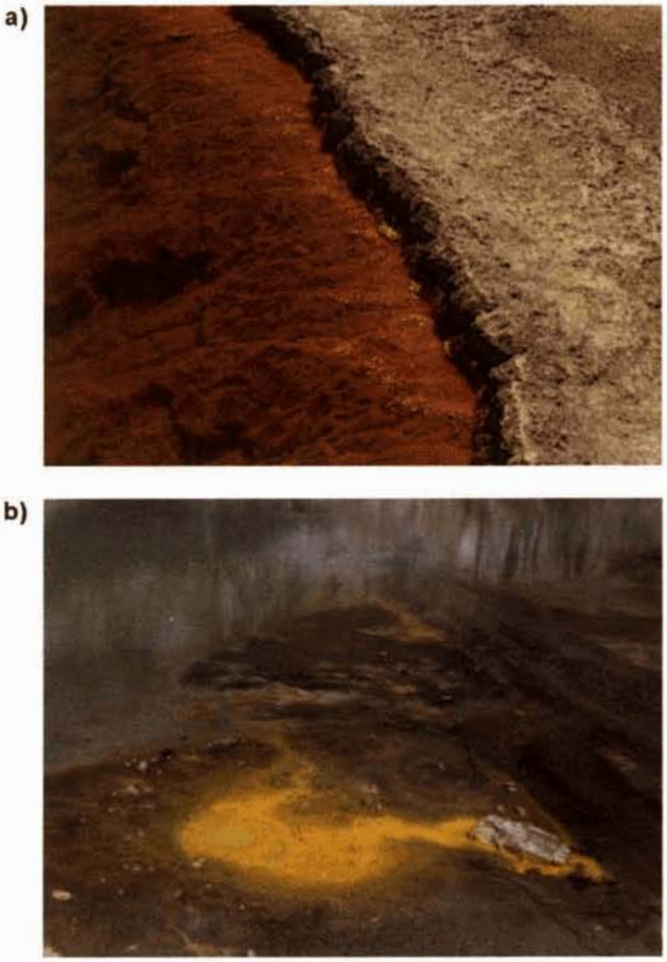

Figure 5. Arsenic mineral precipitates at the Waiotapu geothermal field, Taupo Volcanic Zone, NZ: a) An As- and Sb-rich sulphide precipitate in Champagne Pool. b) Yellow orpiment in a small hot spring.

The scales which form in pipes and drains of a developed field can also be rich in As (Table 2). Scales rich in As and Au deposit on back pressure plates at the Ohaaki geothermal field, for example, due to the sudden drop in pressure and consequent boiling of the fluid (Simmons and Browne, 2000). The subaerial scale forming in the Wairakei borefield drain demonstrates a close positive correlation between As and Fe content, with As deposition mainly due to adsorption on Fe-oxide (Finlayson and Webster, 1989).

Table 2. The As content (mg/kg or wt%) of various hot spring and scale deposits

Field	**As**, mg/kg or wt%	**Reference**
Hot Spring Precipitates:		
Yellowstone Nat. Park, US	<2 mg/kg - >5%	White et al. (1992)
Steamboat Springs, US	50 – 700 mg/kg	White (1981)
Tamagawa, Japan	6 - 56%	Noguchi and Nakagawa (1969)
Waiotapu, NZ	1.0 - 25%	Weissberg (1969); Webster (1990)
Rotokawa, NZ	0.4 - 3.4%	Weissberg (1969);Krupp and Seward (1990)
Ohaaki, NZ	300-400 mg/kg	Weissberg 1969)
Kamchatka, Russia	0 - 0.67%	Karpov and Naboko (1990)
Power Station Scales:		
Wairakei waste water drain, NZ	1.6 mg/kg- 9.4%	Finlayson and Webster (1989); McKenzie et al. (2001)
Ohaaki back-pressure plate scale, NZ	10 mg/kg - 0.1%	Simmons and Browne (2000)

3.3.1 The role of bacteria in arsenic deposition

Thermophilic bacteria and cyanobacteria in hot spring biofilms facilitate the extracellular and intracellular formation of silica, silicates, carbonates and oxide minerals in sinter deposits (e.g., Konhauser and Ferris, 1996; Tazaki, 1995). Microbial activity can also influence the macrotexture of sinters, resulting in the formation of columnar and laminated stromatolites, coccoids and oncoids (Hinman and Linstrom, 1996; Jones et al., 1997; Renaut et al., 1996). Microbial biofacies identified in sinter deposits include cyanobacteria (eg. *Phormidium* and *Anabaena* sp., *Oscillatoria* sp., *Nostoc* sp., and *Calthrix* sp.; Tazaki, 1995; Jones et al., 1997). However, recent developments in molecular microbiology suggest that the biodiversity of hot spring microbial communities is considerably more complex than previously reported based on microscopic examination and cultivation (Ward et al., 1998).

An analysis of microbial mats in mudpools at the Rotokawa and Waimaungu geothermal fields (Taupo Volcanic Zone) indicated enrichment of As, along with Sb, P and Zn, in the organic matrix relative to the bulk samples (Hirner et al., 1990). However, this was not confirmed in a more recent investigation (McKenzie et al., 2001). Consequently the role of thermophilic bacteria in As precipitation, adsorption or other uptake into the sinter remains uncertain.

4. THE FATE OF ARSENIC FROM GEOTHERMAL SOURCES

The contamination of natural drainage systems by As is one of the most significant environmental effects of geothermal activity. Although a degree of soil contamination will occur in the vicinity of a geothermal field, this is a local effect and one which is generally regarded as acceptable. However, water flow through the surface and subsurface catchments has the potential to transport As beyond the boundary of the geothermal field. In the vicinity of geothermal systems, it is chemical contamination of surface waters, rather than ground waters, which is the most commonly detected and reported. In surface waters, As enters a cycle of chemical and biochemical reactions (review by Ferguson and Gavis, 1972).

4.1 Surface waters

Hot springs, geysers and steam features all produce an excess of fluid at the surface; fluid that usually drains unimpeded into the nearest catchment system. Even after orpiment precipitation, many hot springs fluids will still contain >1 mg/kg As (Table 1) because orpiment is a relatively soluble salt. Consequently, water to be used for drinking, stock watering, irrigation or simply to support aquatic life, may have unacceptably high As concentrations downstream of a geothermal system. The WHO (1993) drinking water limit is 0.01 mg/L, compared to higher limits for the protection of aquatic life of 0.19 mg/L (USEPA, 1986) and for stockwatering and irrigation of 0.2 and 0.1mg/L respectively (USEPA, 1972). Consequently, the use of a water body for a drinking supply is the use most likely to be compromised by As contamination. Arsenic contamination of water for drinking or domestic use has therefore received considerable attention (e.g., Kneebone and Hering, 2000; McLaren and Kim, 1995; Webster, 1999; Wilke and Hering, 1998).

Arsenic speciation is important in surface waters because acute toxicity of As^{III} is greater than that of As^{V} or the organic forms of As (e.g., Jain and Ali, (2000). For human chronic toxicity the redox form of arsenic may not matter because arsenic is largely reduced to As(III) and methylated (National Research Council, 1999). Another issue is the processes by which As interacts with sediments, organic and biotic substrates in freshwaters, as this affects both As concentration and speciation. Studies of As in the rivers draining the two geothermal systems specifically featured in this review: Yellowstone National Park and the Taupo Volcanic Zone, have shown that As is principally transported in dissolved form (Nimick et al., 1998; Webster-Brown, 2000). "Dissolved" in this case is defined as passing through a 0.45μm filter membrane. On a macro-scale, As also appears to behave conservatively downstream of these geothermal systems, with little change in As mass flux down the river (Nimick et al., 1998) or in lakes and estuaries (Timperley and Huser, 1996; Webster-Brown, 2000). Studies of geothermal-derived As in other freshwater systems support this observation (e.g., Deely and Sheppard, 1996; Kneebone and Hering, 2000).

4.1.1 Dissolved Arsenic Speciation

Assuming thermodynamic equilibria prevail, As released into an oxygenated surface water as H_3AsO_3 should undergo immediate oxidation to arsenate ions: $H_2AsO_4^-$, or at pH > 6.9, $HAsO_4^{-2}$. Arsenate certainly predominates in the Waikato River (Aggett and Aspell, 1978; McLaren and Kim, 1995) and in streams and rivers receiving hot spring discharge from Yellowstone National Park (Ball et al., 1998; Nimick et al., 1998; Nordstrom et al., 2001). This is also the case in rivers draining the Mt. Apo geothermal field in the Philippines (Webster, 1999), and in Hot Creek which drains geothermal activity in the Owens River catchment, Sierra Nevada, US (Wilke and Hering, 1998).

A half-life of ~20 mins for As^{III} oxidation to As^{V} was calculated for As in Hot Creek and attributed to microbial catalysis (Wilke and Hering, 1998). Langner et al. (2001) derived a similar half-life for As oxidation in an acid hot spring in Yellowstone National Park. Gihring et al. (2001) found *Thermus aquaticus* and *Thermus thermophilus* in a high pH (8.8) hot spring in Yellowstone Park that effectively oxidize arsenite at about the same rate as in acid hot springs. Tantalus Creek, which drains most of the thermal waters from Norris Geyser Basin and empties them into the Gibbon River in Yellowstone National Park, contains about 1.7 mg/L arsenic of which at least 97% is As^{V} (USGS, unpublished data). These results attest to the efficiency of microbial arsenic oxidation in thermal overflow waters.

In river waters, as in geothermal features, the role of bacteria in the oxidation process may be very important. Wilkie and Hering (1998) noted that As oxidation in Hot Creek did not occur if the river water was filtered under sterile conditions or after an antibiotic had been added. They surmised that bacteria attached to submerged plants were mediating As^{III} oxidation. Bacteria capable of As^{III} oxidation have been isolated, and some of the most common are *Pseudomonas* sp. (Cullen and Reimer, 1989). Other bacteria genera that have been found to oxidize As^{III} include *Xanthomonas* and *Acromobacter* (Ehrlich, 1996). As^{V} may be predominant, but it is not exclusive. In the Waikato River, for example, high concentrations of As^{III} do appear periodically. Sudden, short-lived pulses of As^{III}, and associated higher concentrations of total As, have been attributed to the annual, but unpredictable, overturn of the deep, stratified hydroelectric lakes (Aggett and Kreigman, 1988). Interstitial sediment waters in the anoxic depths of the lakes are rich in As^{III}, and when thermally-driven overturn occurs, these waters are released downstream. However, a broader seasonal variation in As in the Waikato has also been identified (McLaren and Kim, 1995; see Fig. 6) and attributed to seasonal activity of arsenate-reducing bacteria. Various bacteria and strains capable of As^{V} reduction have been identified (e.g., Macy et al., 2000; Stolz and Oremland, 1999; Switzer et al., 1998) including *Anabaena oscillaroides* which has been isolated from the Waikato River (Freeman, 1985).

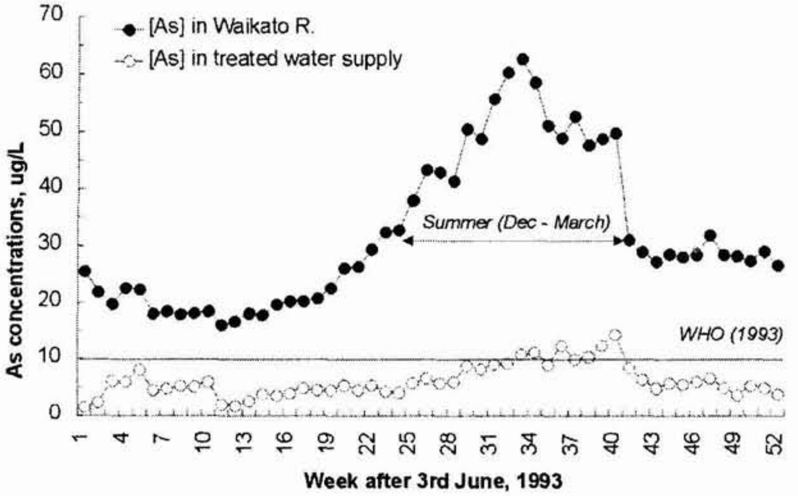

Figure 6. Seasonal variation in As concentrations in the Waikato River, and after passage through a conventional (alum floc) water treatment plant in Hamilton city, New Zealand. Residual As in the reticulated drinking water supply is indicative of As^{III} concentrations in the river water, as As^{III} is not removed alum floc treatment (modified from McLaren and Kim (1995); data courtesy of Nick Kim).

The third group of As species in natural freshwaters are the methylated arsenic species. Arsenic can be methylated by bacteria, algae and fungi to form gaseous mono-, di- and tri-methyl arsine $(CH_3)_nAs)$ (Baker et al., 1983; Cullen and Reimer, 1989; Maeda et al., 1987), which dissolve in water forming the methylarsenic oxyacids, monomethylarsonic acid (MMAA) and dimethyldarsenic acid (DMAA). Organic As complexes are estimated to make up <20% of the As in the Madison River draining Yellowstone National Park (Nimick et al., 1998), which is consistent with an estimate of 10-20% of total As for freshwater environments in general (Cullen and Reimer, 1989). DMAA has been reported as the dominant form of As in summer in a eutrophic lake in Japan (Sohrin et al., 1997), although the source of this As is unclear. Unlike methyl-mercury compounds, methylated arsenic does not appear to biomagnify in the food chain (Isensee et al., 1973; Maeda et al., 1992).

4.1.2 Transport & removal from the water column

A small portion of the As released into a river from a geothermal system will become part of the biochemical cycle, interacting with plants, biota, suspended material and bed sediments. In the Waikato River, for example, 7-8% of the As entering the river is being adsorbed onto the sediments, and sediment As concentrations as high as 1000 mg/kg have previously been reported from the deeper hydroelectric lakes (Aggett and Aspell, 1980). Suspended sediment As concentrations provide a better indication of the direct association between As and sediments. Concentrations of 0-60 mg/kg As in suspended sediments are reported from the Missouri River draining Yellowstone National Park (Nimick et al., 1998), while higher concentrations of 61-1790 mg/kg are found in the Waikato River draining Taupo Volcanic Zone (Webster-Brown et al., 2000). The higher As concentrations in suspended sediments of the Waikato River are a function of their proximity to geothermal activity. Where the Waikato River passes through the area of geothermal activity (Fig. 1b), As concentrations in the silica-rich suspended sediment are limited only by the adsorption capacity of the suspended sediment, which is ~1500-1800 mg/kg As (Webster-Brown, 2000).

A strong association between As and Fe-oxides in river and lake sediments has been reported (eg., Aggett and Roberts, 1986; Belzile and Tessier, 1990; Brannon and Patrick, 1987). This association is attributed to the adsorption of arsenate onto the Fe-oxide coatings on sediment particles. Arsenite ion, although also adsorbed, is not as rapidly or completely adsorbed onto Fe-oxide as arsenate (Belzile and Tessier, 1990; Pierce and Moore, 1982; Swedlund and Webster, 1999). This observation has important implications for the re-release of adsorbed As under anoxic conditions. Microbial reduction of arsenate can occur even when As is bound to Fe-oxide (Langner and Inskeep, 2000), and reduction or methylation of sedimentary arsenate under anoxic conditions is the principal mechanism for re-release of As into the water column (Aggett and

Kreigman, 1988; Brannon and Patrick, 1987; Dowdle et al., 1996). The seasonal variation in total As concentration in the Waikato River (Fig. 6) has been attributed to the seasonal activity of As^V-reducing bacteria (McLaren and Kim, 1995), as there is no evidence that seasonal changes in water temperature affects As^V adsorption onto sediments (Webster-Brown, 2000).

The life-cycle of aquatic plants may also affect the concentrations of As in the water column (Kuwabara et al., 1990). The uptake of As by aquatic macrophytes (plants) has been reported in rivers contaminated by geothermal waters. There is often a significant degree of As enrichment relative to the water column. Concentration factors of up to 20,000 times, depending on the plant species, have been reported for the Waikato River where the plants are estimated to take up 3-4% of the As available (Aggett and Aspell, 1980; Reay, 1972). Plant uptake of As is generally considered to be due to the chemical and behavioural similarity of arsenate and phosphate ions, the latter being an important nutrient for plant growth. High phosphate concentrations can inhibit As uptake by plants, as well as As adsorption on Fe- oxide surfaces (Kuwabara et al., 1990; Reuther, 1992).

Finally, As interacts with macrobiota either directly or via the food chain. As well as the issue of toxicity, there is the potential problem of As accumulation in animal flesh. Freshwater snails in the Waikato River, for example, were found to have 20 times the As content of snails in a control site (Golding et al., 1997). However, there has been little evidence that animals further up the food chain, such as trout, accumulate As from the Waikato River (Robinson et al., 1995).

4.2 Ground waters

Although As-rich ground waters appear to occur with alarming frequency (e.g., Del Razo et al., 1990; Frost et al., 1993; other chapters in this volume) other contributions in this volume), there are relatively few examples where the As is clearly related to geothermal activity. Geothermal fluids are themselves effectively deeply circulating ground waters. The thermally driven ascension to the surface limits opportunities of lateral spreading of these As-rich fluids at depth. Near the surface, however, contamination of shallow aquifer systems can and does occur.

High As concentrations in ground waters of the upper Missouri River catchment have been attributed to As in the thermal waters of Yellowstone National Park (Nimick, 1994; Welch et al., 2000). Arsenic-enriched ground waters of southwest Idaho and in the Intermontane Plateaus province are also considered to be influenced by thermal waters (Welch et al., 2000). Geothermal contamination of ground water has not yet been reported from the major geothermal fields of the Taupo Volcanic Zone, but it has been observed in a shallow ground water outflow to a wetland area at the southern end of Lake Taupo (Chague-Goff et al., 1999).

Elsewhere As contamination of drinking water wells in Taiwan, and the consequent toxic effects on the human population (Chen et al., 1994), is considered likely to be due to mixing with geothermal fluids. High pH ground waters of the Vulcano Porto field on Vulcano Island, near Sicily, have As concentrations ranging 0.6 to 134 μg/L (Aiuppa et al., 2000).

Ground water contamination is a concern for geothermal developers because there are several potential pathways for aquifer contamination. These include:

i) Unintentional reinjection of spent geothermal waste water into an aquifer. This will normally occur only if the integrity of the casing around a well is breached.

ii) Seepage from poorly-lined, or unlined, holding ponds for the retention of geothermal fluids and from pipelines, as reported from Los Azufres in Mexico for example (Birkle and Merkel, 1998).

iii) Burial of As-rich sludge from an As-removal waste treatment process or scale from drains and pipes (e.g., Peralta et al., 1996).

The speciation and solubility controls on As in ground water are similar to the abiotic processes influencing As behaviour in surface water. Arsenic may occur as both As^{III} and As^{V}, with solubility controlled by adsorption onto sediment surfaces (Welch et al., 2000). Under the higher rock:water ratio present in aquifers, clays and other silicate surfaces, as well as Fe- and Mn-oxides, may act to regulate As concentrations through adsorption under appropriate pH conditions (e.g., Goldberg and Glaubig, 1988a; Manning and Goldberg, 1997). It should be noted that high sulfide concentrations may accompany As of geothermal origin when it enters a ground water aquifer, and this will limit As solubility through the formation of orpiment.

5. ARSENIC REMOVAL FROM GEOTHERMAL FLUIDS

Clearly it is preferable to avoid the release of As from geothermal systems into surface or ground water systems. In developed geothermal fields, reinjection of waste water into the field is commonly used to avoid environmental pollution and maintain reservoir pressure. In many countries, including the US, reinjection is required by law. However, where this is not the case, reinjection is viewed as an expensive option and one which can reduce field productivity if the cooler waters find their way back into the reservoir too quickly (Brown and Bacon, 2000). Effective removal of As, and other contaminants of the "geothermal suite" from waste water prior to discharge, would enable the bore waters to be discharged or re-used without environmental damage. It may also allow valuable elements or minerals to be extracted, offsetting the cost of treatment, which may still be economically viable when compared to the costs of reinjection (Brown and Bacon, 2000).

Various methods for the removal of As from geothermal waste waters have been investigated at theoretical, laboratory, pilot plant and full plant scales. These include adsorption onto Fe-oxide floc and subsequent separation by dissolved air flotation (De Carlo and Thomas, 1985; Shannon et al., 1982) and co-precipitation with lime to form an As-rich calcium silicate (Rothbaum and Anderton, 1976). In both cases, effective removal was achieved only after oxidation of As^{III} to As^{V}. For Fe-oxide floc treatment, competitive adsorption of silica inhibits As adsorption, particularly that of As^{III} (Swedlund and Webster, 1999), suggesting that prior removal of silica would help optimise As removal efficiency. The use of ion selective chelating resins for As^{III} removal from geothermal waters has also been successfully tried (Egawa et al., 1985).

Arsenic contamination of surface or ground waters is, however, rarely a "point source" event, given the complex plumbing of most geothermal systems and the variety of opportunities this presents for thermal and ambient fluid mixing. While As removal prior to a point source waste water discharge will help to minimise impacts on aquatic ecosystems, particularly As accumulation in aquatic plants and sediments, it is unlikely to reduce As concentrations to a drinking water standard in regions of natural geothermal activity. Consequently, the ability of conventional water treatment plants to remove As from drinking water supplies continues to be important. Both alum- and Fe-oxide-based treatment systems effectively remove As^{V} if optimised to favour As adsorption and particulate removal, but alum-based systems are less effective in their removal of As^{III} (Hering et al., 1997; McNeill and Edwards, 1995). Figure 6 shows As removal from the Waikato River using a conventional alum-floc treatment station at Hamilton City, New Zealand (McLaren and Kim, 1995). Effective removal of As is achieved, except during the summer when As^{III} is also present in the water column. Reverse osmosis and nanofiltration membranes have greater potential for efficient As^{III} removal, as they do not discriminate between As^{V} and As^{III} (Waypa et al., 1997).

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