Characterization of Three Water Types in a Fractured Schist, High Arsenic, Watershed in Maine

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This study is part of a larger investigation of the controls on the distribution and transport of the As in a small watershed in coastal Maine. Investigation of the geochemistry reveals three distinct water types, a CaHCO3 type, a NaHCO3 type, and a HighAs type (a Na and HCO3 water with considerably less Na and HCO3 than the NaHCO3 type that coincides with the highest As concentrations). The identification of these water types is helpful in determining flow paths, secondary weathering processes, and in illuminating circumstances responsible for the high As concentrations.

Arsenic concentrations of up to 2.3 mg/L are found in the ground water of this watershed. The wells with the highest As concentrations are spatially clustered in the center of the discharge area. The bedrock in the watershed is composed of by interbedded sulfidic pelite and quartzite that has been intruded by various granitic and dioritic plutons and has been covered by glacial deposits of dense till, marine clay, and gravel. Most of the watershed has been inundated by the sea after the retreat of the last glaciers. The down gradient coastal area is covered with up to 40 m of overburden, whereas the hilltop has exposed bedrock. There is no evidence for trapped seawater, but remnant Na and K from the seawater intrusion likely remains on the aquifer surfaces. Electron microprobe investigation of the fracture surfaces shows clays containing Na and K.

Stiff diagrams are used to distinguish the water types. Box and whisker plots and rank sum tests confirm that the three water types are distinct from each other. The three water types cluster together in three separate areas. The CaHCO3 type wells are found primarily in the hilltop region to the SW and represent recharge water that has had little interaction with the bedrock and whose chemistry is controlled by the dissolution of calcite. The NaHCO3 and the HighAs waters are found down gradient (NE) of the CaHCO3 wells near the shore. The NaHCO3 wells are adjacent and SE of the HighAs wells. Piper plots and x-y plots indicate that considerable cation exchange has occurred in the NaHCO3 and HighAs waters. The Ca-rich recharge water exchanges Ca for Na and K, producing the NaHCO3 and HighAs type waters. The problem, then is to explain the distinct difference between the NaHCO3 and the adjacent HighAs wells.

There are three possible explanations for the differences in the NaHCO3 and the HighAs wells: (1) Greater seawater influence in the NaHCO3 area, (2) Differences in bedrock and secondary mineral composition, (3) Different flow paths. Undoubtedly, inundation of the bedrock aquifer by seawater impacted both areas, and there is no physical or chemical reason for the NaHCO3 area releasing more Na and K (having retaining more Na and K during inundation). Greater cation exchange in the NaHCO3 type wells and their higher pH, alkalinity and specific conductance indicate that the NaHCO3 type wells are more evolved than the HighAs waters. Differences in mineralogy may explain some of the differences, but they do not explain the evidence for the greater evolution of the NaHCO3 waters. The best explanation for the differences between the NaHCO3 and the HighAs waters is that the NaHCO3 and the HighAs waters come from different recharge areas. Inspection of the topography supports this. The HighAs wells receive recharge from the nearby, low elevation, western watershed boundary, whereas the NaHCO3 wells receive recharge from the more distant, greater elevated, CaHCO3 area. The sharp demarcation between the HighAs and the NaHCO3 wells probably results from a streamline separating the two recharge areas. Additional differences between the HighAs and the NaHCO3 water chemistry, such as high Si and Mg in the HighAs wells, probably derive from mineralogical differences. The intrusion of granite near the western watershed boundary is likely the cause of hydrothermal silicification and epidotization of the pelitic rocks to the immediate northeast that are intercepted by the HighAs wells. Secondary mineralization and re-mineralization on the fracture surfaces due to hydrothermal fluids, seawater incursion, and weathering reactions are observed with an electron microprobe and probably contribute to the chemical differences between the NaHCO3 and HighAs water types.

Introduction

Arsenic concentrations greater than the maximum contaminant level (MCL) of 10 µg/L occur in approximately 12-13% of the bedrock wells in Maine (Loiselle et al., 2002) and throughout New England (Marvinney et al., 1994; Peters et al., 1999; Loiselle et al., 2001). Understanding the processes responsible for the distribution and transport of As in the ground water is important for identifying high-risk areas and evaluating mitigation strategies. Basic to understanding these processes is the determination of flow paths and reactions along the flow paths. The purpose of this presentation is to illustrate the usefulness of water chemistry in recognizing flow paths through fractured rock and the changes in the water chemistry as water passes through the fractured bedrock of a small watershed.

The arsenic in the ground water in New England in crystalline bedrock is attributed to natural sources (Peters et al., 1999; Ayotte et al., 1999; Sidle et al., 2001; Hon et al., 2002; Lipfert et al., 2004, in review), although anthropogenic sources cannot be discounted (Ayuso et al., 2004) and probably slightly enhance the natural levels.

The primary controls on As in ground water are thought to be oxidation of sulfides, reductive dissolution or precipitation of ferric oxyhydroxides, and adsorption/desorption of As oxyanions. Many studies have been conducted to determine the importance of these processes to particular ground-water systems (eg. Matisoff et al., 1982; Schreiber et al., 2003). Particularly interesting is a study in New Mexico that finds that hydrologic conditions influence the As concentrations in ground water (Bexfield and Plummer, 2003).

The study area is a small watershed in Northport, Maine, USA that contains well water with As concentrations up to 2.3 mg/L, the highest in the state of Maine. Previous work in this area delineated a spatial cluster of high As wells within this watershed having water with distinctive chemistry (Horesh, 2001). More detailed study of the watershed reveals three different water types identified by Stiff diagrams (Lipfert et al., 2004, in review). Plentiful As-bearing minerals such as arsenopyrite, arenian pyrite, cobaltite, and gersdorfite are found within the bedrock in the area (Horesh, 2001; Lipfert et al., 2004).

Site hydrology

The Northport water shed (Figure 1) has a variable cover of glacial material ranging from a very thin till on the upland recharge area along the southwestern boundary to a ~34 m thick knob of dense till on the southeastern boundary and a ~12 m thick layer of till along the coastal exposure. The elevation of the entire watershed decreases from the southwest to the northeast where it meets the Atlantic Ocean. An ephemeral stream follows a channel that has cut through the overburden exposing the bedrock in several places. A small pond lies in the center of the water shed just above the head of the stream.

The watershed is underlain primarily by the Penobscot Formation (Ordivician), a sulfidic, thinly bedded, alternating pelite and quartzite with rare limestone and calcareous sandstone that has been multiply intruded by small Silurian plutons of the Northport granite (a muscovite-biotite-garnet granite), hornblende-biotite quartz diorite, tonalite, biotite granodiorite, the Shaw Brook diorite (a hornblende diorite) and a diorite porphyry composed primarily of plagioclase with phenocrysts of hornblende (Stewart, 1998). Occasional layers of calc-silicate have been found in the Penobscot Formation, but none is mapped within this watershed (Stewart, 1998). Veins of quartz, carbonate, and tourmaline+quartz±carbonate are found throughout the area. Many of the carbonate and tourmaline veins are planar, but the quartz veins are commonly swirled. Arsenopyrite and arsenian pyrite are found within the bedrock throughout the watershed, primarily associated with the tourmaline veins.

Four boreholes have been drilled in the water shed with 5 and 10 cm diameter core retrieval. The F-core (Figure 1) is composed entirely of a sulfide- and carbonate-rich granite. Both the B-core and the C-core (Figure 1) show evidence for hydrothermal alteration such a silicification, argilization, and epidotization, apparently from the intrusion of the granite in the nearby F-core. Arsenopyrite is found within the F-core and associated with tourmaline veins in the B-core, the C-core, and the Bu-core.

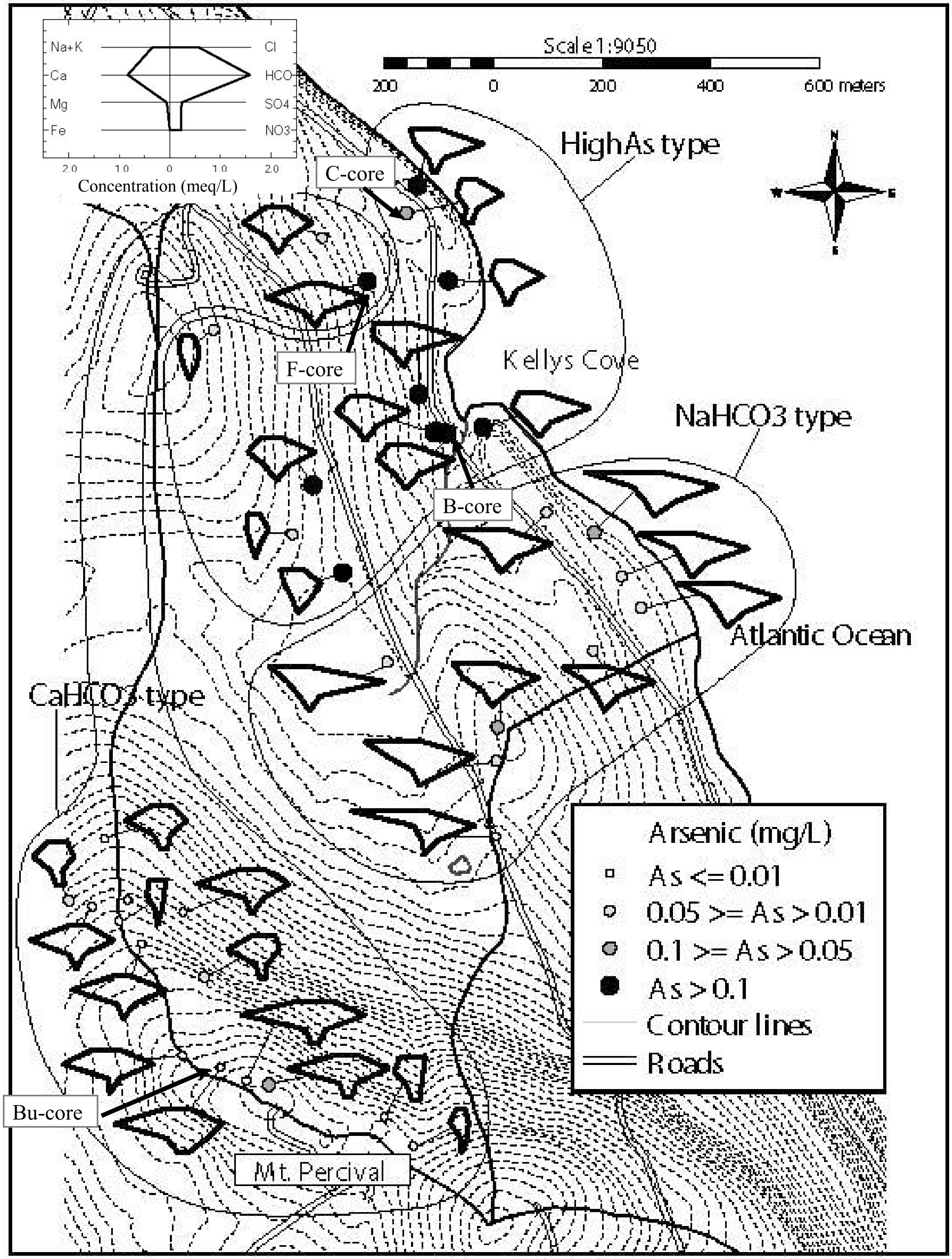

Figure 1. Arsenic concentrations and Stiff diagrams of water samples. The three water types are circled and identified. The dotted lines are contours of surface elevation.

The foliation of the Penobscot Formation has a primarily northeast-southwest orientation. The bedrock is weakly fractured, the granitic and dioritic bodies being the least fractured. Fracturing is common along foliation planes and along planar veins.

Methods

Water sampling

Five rounds of ground-water sampling were performed on 35 bedrock wells, 7 shallow wells, a stream and a pond within the watershed from July, 2002 to October, 2003. Water samples were taken from an outside spigot except for four open boreholes that were sampled with a submersible pump. Wells that have treatment systems were sampled before the treatment system. Conductivity, pH, Eh, and temperature were measured in the field using Hach meters. Vinyl tubing connects the spigot to a closed flow-through chamber that holds pH, temperature, conductivity, and Eh meters. Water was allowed to flow until pH, temperature, conductivity, and Eh stabilized, typically 15 to 30 minutes. Filtered (0.2 um) samples for trace metals and major cations were collected in 60 mL Nalgene LDPE bottles and acidified with nitric acid. Split filtered samples for anion analysis were collected in 60 mL HDPE bottles at the same time. Cation and trace metal concentrations were measured using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) Perkin Elmer model 330X with ultrasonic nebulizer sample introduction. The anion concentrations were measured with ion chromatography using a Dionex model DX500 IC system.

Most of the sites were sampled five times, but some were sampled fewer times because of inaccessibility to the wells. The values that are reported for the concentrations throughout this manuscript are the arithmetic mean of all the sampling rounds for which there are data.

Leach Tests

Sequential leach tests are performed on 15 fracture surfaces that have been cut from the four bedrock cores. The sides and the bottoms of the fracture samples are coated with paraffin wax leaving the fracture surfaces exposed. Two leaching solutions recommended by Daus et al. (1998) are used for the leach tests, a NaOH solution and an oxalate buffer solution. Each fracture is first leached in 100 ml of 1 mol/L NaOH in zip-lock bags for 1 h. The fractures and the bags are rinsed three times with deionized water and each fracture sample is leached in 100 ml of an oxalate buffer solution containing 0.2 mol/L oxalic acid and 0.2 mol/L ammonium oxalate for 24 hours. The leachates are then analyzed in the same way as the ground-water samples.

Data analysis

Stiff diagrams (Stiff, 1951) are constructed from four horizontal axes of concentrations (in meq/L) of the major cations and anions (Figure 1, upper left). Concentrations of the cations, Na+K, Ca, Mg, and Fe (in descending order of horizontal axes) increase to the left and concentrations of the anions Cl, HCO3, SO4, and NO3, increase to the right.

A Piper plot (Piper, 1944) is constructed from two ternary diagrams, one of the major cations on the left and one of the major anions on the right. The points on the two ternary diagrams are projected upward to a diamond diagram.

Results and discussion

Ground-water chemistry

Arsenic concentrations are spatially clustered within the watershed (Figure 1). The As concentrations are typically low (below the MCL) in the upland areas of Mt. Percival and high (above the MCL) in the downgradient areas (Figure 1). A cluster of wells in the northeastern area of the watershed has very high As concentrations (> 0.1 mg/L). A visual examination of the major chemistry in these wells using Stiff diagrams (Stiff, 1951) reveals three water types that can be associated with As concentrations (Figure 1). The water tpes are delineated as such: CaHCO3 water type, calcium bicarbonate-dominated samples found in the Mt Percival recharge area; NaHCO3 water type, sodium bicarbonate-dominated samples in the southeast quadrant; and HighAs, sodium bicarbonate-dominated to the north that are rich in As and lower in sodium bicarbonate. The water types cluster associate with each other within the watershed, with the exception of two CaHCO3 waters that occur near the HighAs waters (Figure 1). Box and whisker plots as well as rank sum tests confirm that the three water types are statistically distinct from one another (Lipfert et al., 2004, in review). A Piper diagram (Piper, 1944) of the water samples shows that the water types cluster together within the diagram (Figure 2). The arcuate trend of the sample chemistry from the $CaHCO_3$ to $NaHCO_3$ waters in the Piper plot suggests an evolution of the waters from Ca-dominance to Na-dominance due to cation exchange along the flow path. Note that the chemistry of the HighAs waters lies between the CaHCO3 and NaHCO3 waters on the Piper plot.

The clustering of the water types and the sharp distinction between the NaHCO3 and HighAs water types can be explained as follows. The CaHCO3 water type is found primarily in the upland, Mt. Percival area and is

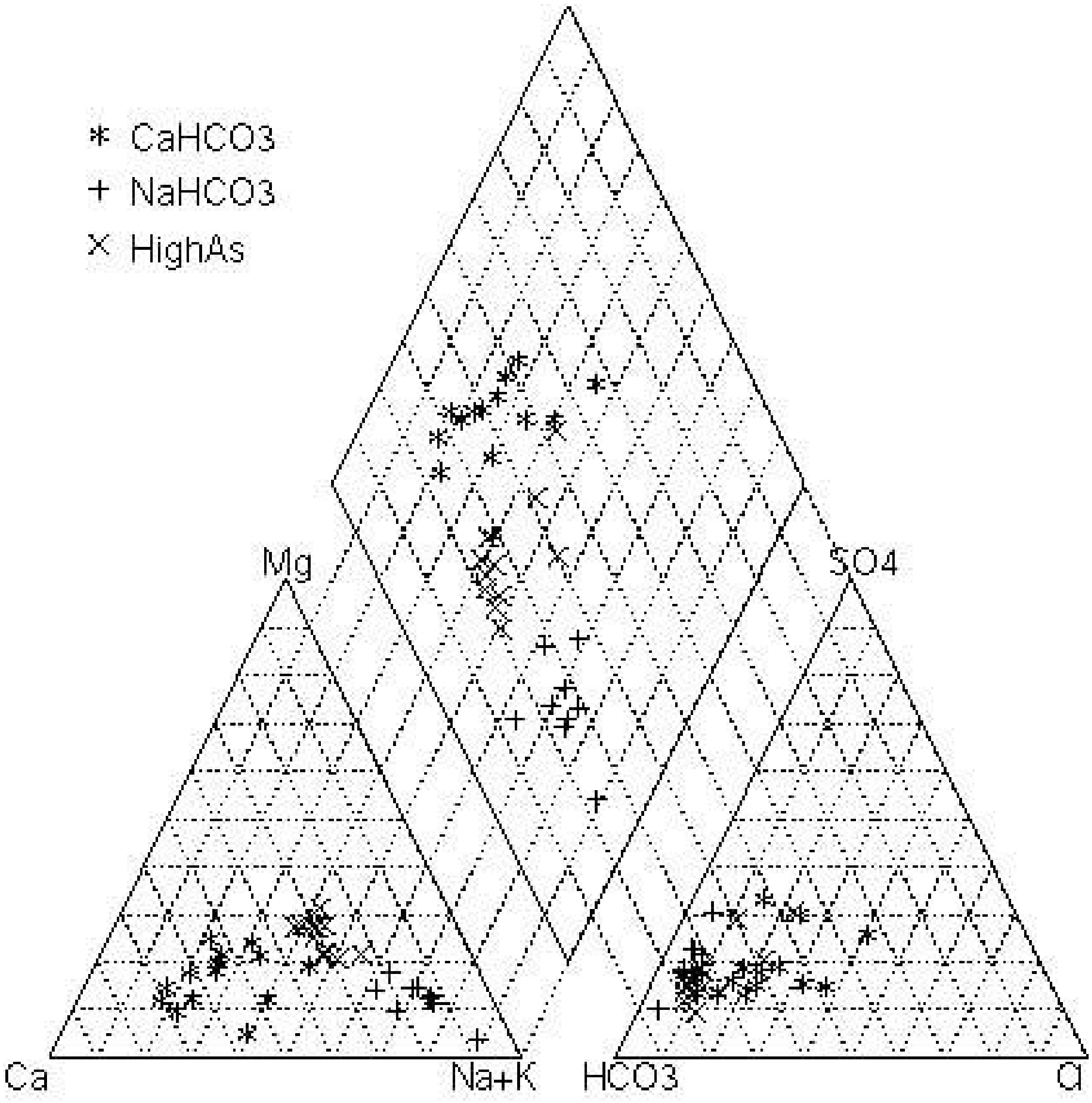

Figure 2. Piper diagram of the major cation and anion chemistry of all the bedrock samples. The trends from the CaHCO3 water to the NaHCO3 water indicates an evolution of the water and cation exchange of Ca for Na.

dominated by Ca^{2+} and HCO_3^- derived from the weathering of minerals in the bedrock, including calcite the most easily weathered mineral in the aquifer. Low concentrations of Na^+ in the CaHCO3 waters indicate that little cation exchange and dissolution of Na-minerals has occurred. The CaHCO3 waters represent recharge waters with short residence times. The NaHCO3 water type is the most evolved of the waters and derives their Na^+ from cation exchange of Ca for Na and K as well as dissolution of plagioclase (Lipfert et al., 2004, in review). The HighAs water type is also $NaHCO_3$-dominated because of cation exchange and plagioclase dissolution, but is less evolved than the NaHCO3 waters and probably has a shorter residence time. The distinct difference between the HighAs waters and the NaHCO3 waters indicates that they are not in chemical connection with each other. Several wells in the Mt. Percival recharge area and the HighAs area have Stiff diagrams with narrow, funnel shapes that indicate little interaction of the ground water with the bedrock and also represent a recharge water. The proximity of these dilute ground waters to the rest of the waters suggests that there is little connectivity among the waters in the recharge areas.

Assuming that ground water equipotential lines mimic topographic contours, it can be seen in Figure 1 that the HighAs and NaHCO3 areas likely receive recharge from different areas. A simple (homogeneous and isotropic) ground-water model constructed with MODFLOW and delineation of flow paths with MODPATH, showed that all the wells in the NaHCO3 area received recharge from Mt. Percival and some of the wells in the HighAs area received recharge from the small hill at the western boundary of the watershed (Figure 3). The clear differences between the HighAs and NaHCO3 well chemistry are more useful at delineating flow paths and recharge areas than the model which has many HighAs wells receiving recharge from Mt Percival.

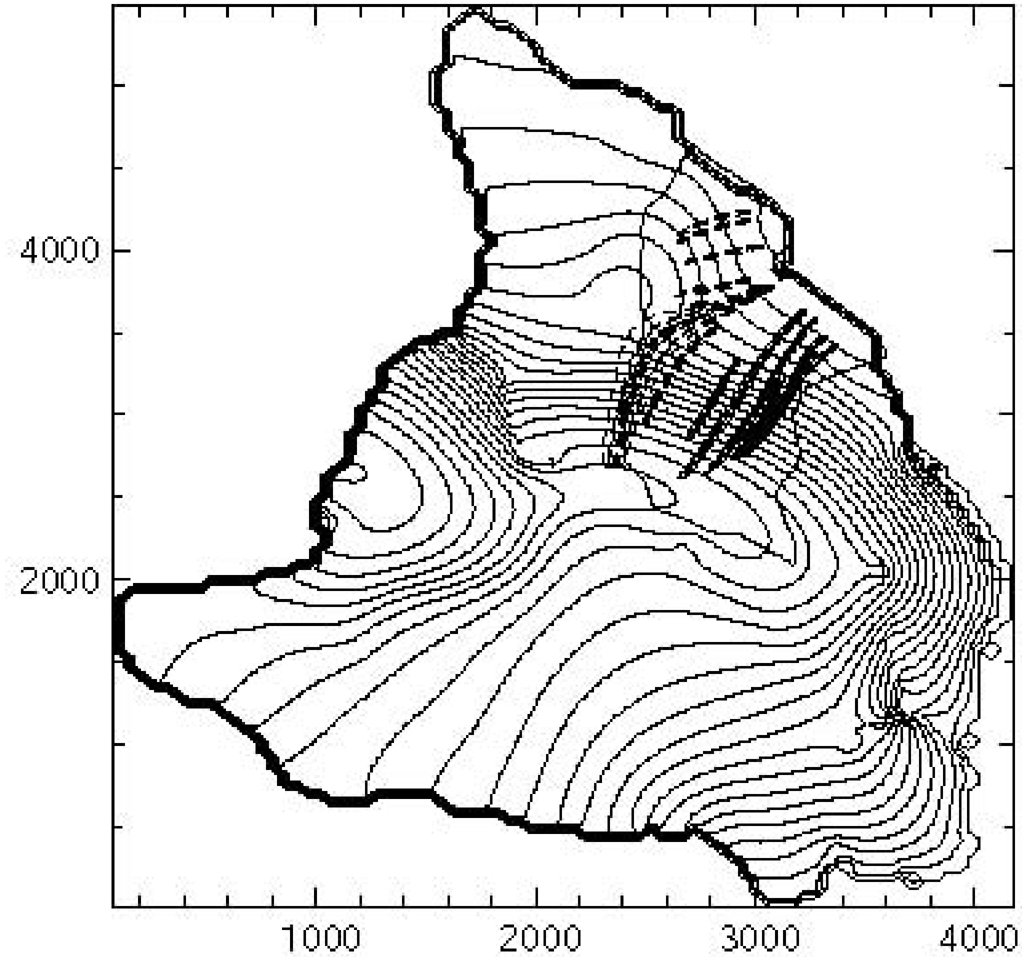

Figure 3. Simple ground-water model of the area including the watershed showing flow paths to the NaHCO3 wells (solid lines) and to the HighAs wells (dashed lines).

Chloride concentrations are useful for elucidating flow paths, recharge waters and residence times. The Cl and NO_3^- concentrations in the CaHCO3 waters are higher than in the other waters indicating anthropogenic contamination of these wells in an area with very little overburden. The fact that the Cl and NO_3^- concentrations are lower in the NaHCO3 wells (that we have interpreted above as receiving recharge from the CaHCO3 area) than in the CaHCO3 wells suggests that either the NaHCO3 wells receive more recharge from other sources or that the recharge from the CaHCO3 area has not yet reached the NaHCO3 wells. Most of the wells in the Mt. Percival area are from recently built homes (last 5-10 years). Because the chemistry of the NaHCO3 waters is interpreted to be the most evolved waters and there is no evidence for dilution of these waters by rain water, it is suggested that the residence time for the NaHCO3 waters is greater than 5-10 years.

Fracture surface analysis

Visual, microscopic, and SEM examination of the fracture surfaces from the four cores shows that the weathering materials have considerable variability and heterogeneity. The degree of weathering on the surfaces varies from undetectable to complete coverage of secondary materials. SEM and EDS analysis reveals kaolinite, pyrite, marcasite, Fe-Mn-Ca-Mg carbonates, Fe and Mn oxides, silica, chlorite and muscovite as well as many unidentifiable phases, possibly smectite, illite or a combination of both, or amorphous mixtures of weathered silicates, oxides and sulfides. Patches of similar weathering material cluster together and are distinguishable at the scale of the surface exposed on the cores (5-10 cm). Fracture surface materials vary from fracture to fracture within a single core and from core to core. It is not uncommon for fractures to occur along veins whose composition is significantly different from the host rock (e.g. carbonate veins crosscutting a granite) and can strongly influence the water chemistry. Given the high degree of variability of materials on fractures within one core (not to mention the unknown materials on surfaces extending from the cores), it is understandable how difficult it is to interpret chemical relationships in ground-water samples throughout a watershed.

The NaOH leach test raises pH and desorbs As from the surfaces while the oxalate buffer leach tests dissolves amorphous and weakly crystalline phases. Thus, As concentrations in the NaOH leachate indicate the amount of As that was adsorbed to the surface and the As concentrations in the oxalate leachate indicate the As that was co-precipitated on the surface. Both leachates of 24 fracture surfaces show that the amount of As that is either adsorbed or co-precipitated on the surfaces is quite variable even within the same core (Figure 4). This lack of consistency indicates heterogeneity of the fracture surfaces intersected by a borehole and possible lack of hydrologic communication among the fractures before the drilling of the borehole, although given the heterogeneity on a single 5 cm surface, lack of hydrologic communication is not necessary to explain the As variability. No correlation of As with Fe is found in either the NaOH or the oxalate buffer leachates (Figure 5), an association that is expected if As, as is commonly assumed, is associated with ferric oxyhydroxides.

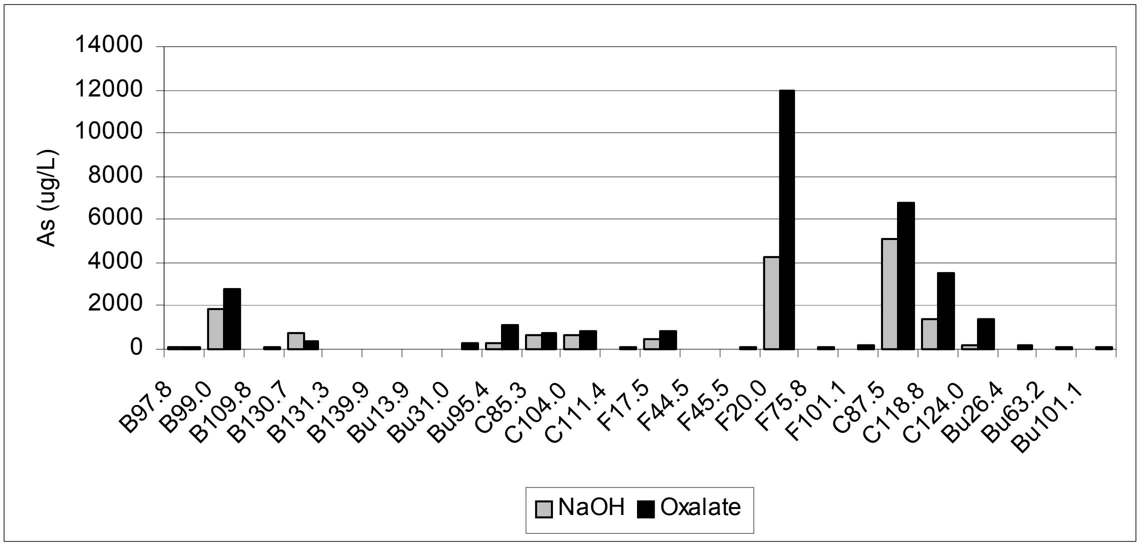

Figure 4. Arsenic concentrations of both leachates of six fracture surfaces from four cores.

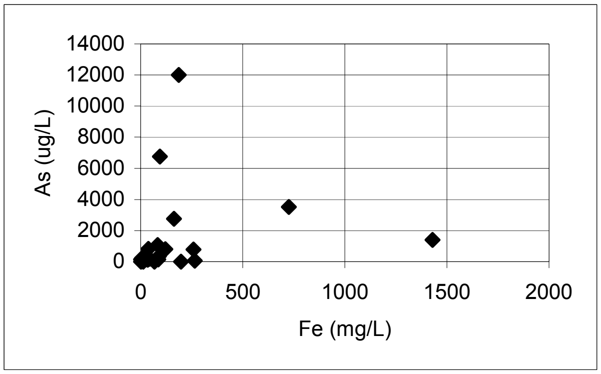

Figure 5. As versus Fe in the oxalate buffer leachates.

Strong correlations of Fe with Si and Fe with Al are found in the oxalate leachates (Figure 6), suggesting that Fe is associated with aluminosilicates such as clays and micas rather than oxihydroxides. Further investigation of the weathering products on fracture surfaces will be useful in determining what phases are responsible for controlling the chemistry of the ground water.

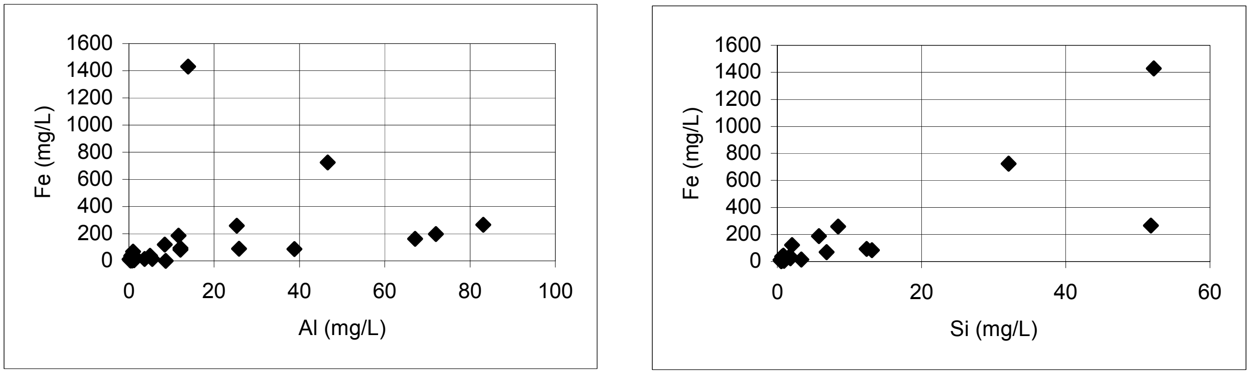

Figure 5. Fe versus Si and Fe versus Al in the oxalate buffer leachate (representing the co-precipitated material).

Conclusions

The delineation of water types using Stiff diagrams is useful in determining flow paths, recharge areas, and communication between fracture networks within a small watershed. Three water types are identified: a CaHCO3 water type that is dominated by Ca^{2+} and HCO_3^- from the dissolution of easily-weathered carbonates and represents a recharge water; a NaHCO3 water type dominated by Na^+ and HCO_3^- from dissolution of plagioclase and cation exchange of Ca for Na and is the most evolved of the waters; and a HighAs water type, a sodium bicarbonate water that is less evolved than the NaHCO3 waters and coincides with the highest As concentrations. The sharp demarcation between the NaHCO3 and the HighAs waters suggests no hydrologic communication exists between them and is useful in interpreting the accuracy of ground-water flow models. The complexity of the weathering materials on the fracture surfaces explains the difficulties encountered sometimes in interpreting geochemistry of bedrock ground-water systems.

References

Ayotte, J.D., M.G. Nielsen, R. Gilpin, J. Robinson, and R.B. Moore, 1999, *Relation of arsenic iron, and manganese in ground water to aquifer type, bedrock lithogeochemistry, and land use in New England coastal basins.* Water-Resources Investigation Report 99-4162, U.S. Geological Survey.

Bexfield, L.M. and L.N. Plummer, 2003, *Occurrence of arsenic in ground water of the Middle Rio Grande Basin, central New Mexico*. In Welch, A.H, and K.G. Stollenwerk (Eds.), Arsenic in Ground Water, Kluwer Academic Publishers, 295-427.

Hon, R., K. Doherty, T. Davidson, W.C. Brandon, C.L. Stien, and D.F. McTigue, 2002, *Arsenic sources and pathways in the overburden of central Massachusetts.* In: Arsenic in New England: A Multidisciplinary Scientific Conference, New Hampshire Consortium on Arsenic, Manchester, New Hampshire.

Horesh, M.Y., 2001, *Geochemical investigation of a high-arsenic cluster, Northport, Maine, U.S.A.* Master's thesis, University of Maine.

Lipfert, G., A.S. Reeve, W. Sidle, and R. Marvinney, 2004, *Geochemical patterns in an arsenic-tainted, fractured-bedrock ground-water system in Northport, Maine USA*. Applied Geochemistry, in review.

Loiselle, M.C., R.G. Marvinney, and A.E. Smith, 2001, *Spatial distribution of arsenic in the ground water in Maine.* In: GSA Annual Meeting, Geological Society of America, Boston, Mass.

Loiselle, M.C., R.G. Marvinney, and A.E. Smith, 2002, *Arsenic in ground water wells in Maine*: In: Arsenic in New England: A Multidisciplinary Scientific Conference, New Hampshire Consortium on Arsenic, Manchester, New Hampshire.

Marvinney, R.G., M.C. Loiselle, J.T. Hopeck, D. Braley, and J.A. Krueger, 1994, *Arsenic in Maine groundwater: an example from Buxton, Maine.* In: Proceedings of the 1994 FOCUS Conference on Eastern Regional Ground Water Issues, the National Ground Water Association, Burlington, Vermont, 701-715.

Matisoff, G. Kourey
Peters, S.C., J.D. Blum, B. Klaue, and M.R. Karagas, 1999, *Arsenic occurrence in New Hampshire drinking water.* Environmental Science & Technology, 33, 9, 1328-1333.

Piper, A.M., 1944, *A graphical procedure in the geochemical interpretation of water analysis.* American Geophysical Union Transactions, 25, 914-923.

Sidle, W.C., B Wotten, and E. Murphy, 2001, *Provenance of geogenic arsenic in the Goose River basin, Maine, USA.* Environmental Geology, 41, 62-73.

Stiff, H.A., 1951, *The interpretation of chemical water analysis by means of patterns*. Journal of Petroleum Technology, 3, 10, 15-16.

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