ARSENIC GEOCHEMISTRY OF STREAM SEDIMENTS ASSOCIATED WITH GEOTHERMAL WATERS AT LA PRIMAVERA GEOTHERMAL FIELD, MEXICO

By

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Submitted to the Faculty in partial fulfillment
of the requirements for the degree of
Master of Science

New Mexico Institute of Mining and Technology
Socorro, New Mexico
February, 1999

ABSTRACT

The purpose of this study is to determine factors controlling the mobility of arsenic under natural conditions and is part of a reconaissance study on arsenic speciation of geothermally impacted stream waters. Stream sediments and algae were collected at 20 sample locations along the Rio Salado Watershed and its tributaries at La Primavera geothermal field near Guadalajara, Mexico. Sediments were analyzed by several partial extractions to determine: 1) the amount of arsenic available to the environment and its partitioning into different size fractions; 2) the species of arsenic present in sediments; 3) the sedimentary phases that are associated with arsenic; and 4) the relationship between arsenic sediment chemistry and water chemistry. In addition, Rio Grande River sediments, collected near Socorro, New Mexico, were analyzed for As, Mn, Fe and percent total organic carbon (%TOC) for comparison with La Primavera sediments. In carrying out these objectives, a modified method of ion-exchange chromatography is used for speciation of As(III), As(V), monomethylarsonate (MMA) and dimethylarsinate (DMA) in sediment extracts.

Total arsenic in sediments available to the environment ranges between 3 and 16 ppm and is highest in the silt-clay fraction. Arsenic is present primarily as inorganic forms that account for over 90% of the total; MMA and DMA are detectable in small amounts. Algae from La Primavera contains between 18 and 68 ppm arsenic (dry weight) with similar proportions of inorganic and organic forms.

The primary sedimentary phases that are associated with arsenic and control its mobility are oxides and hydroxides of iron and manganese, and organic carbon. Arsenic concentration is positively correlated with manganese and %TOC and shows no direct correlation with Fe; however, evidence suggests that iron oxides are also enriched in arsenic. The positive correlation between arsenic and TOC suggests that plants and algae may represent a significant sink in some natural settings.

Sediment arsenic concentrations showed no correlation with surface water concentrations. Though sediment-water heterogeneity may account for this lack of correlation, evidence indicates that sediment arsenic concentrations are determined by the amount of organic matter, iron and manganese oxides and hydroxides present, not the concentration of arsenic in surface waters.

Comparison of sediment-water data from the Rio Grande River to that of La Primavera showed arsenic to be more mobile in La Primavera waters with relatively less being retained in the sediments. This is most likely due to lower concentrations of iron, occurring as iron oxides and hydroxides in La Primavera sediments, but could also occur if the capacity of the sediments to take up arsenic has been exceeded.

ACKNOWLEDGEMENTS

I would like to acknowledge my advisors David Norman, Andrew Cambell, Don and Lynn Brandvold. In particular I would like to recognize David Norman who has provided much input and guidance in my research, and Lynn Brandvold for her valuble assistance and advice in laboratory procedures, instrumentation and sample analysis. I also owe thanks to William Balsam at U.T. Arlington for his input on carbonate analysis and for doing reflected light work on the sediments. I would also like to thank Barbara Popp and Chris McGee at the New Mexico Bureau of Mines and Mineral resources for conducting FLAA and XRF analyses as well as Jill Buckley and Mary Crouch at the Petroleum Recovery Research Center for assistance and permission in using the monosorb BET surface area analyzer. I would also like to thank Gregory Miller at New Mexico Tech for allowing me to use La Primavera water chemistry data he collected. The costs of analyses and materials used in this project was funded by grant money from the Geological Society of America. I am also thankful to the Electric Power Research Institute for seed money that made sample collection possible.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The current maximum contaminant level (MCL) for arsenic in drinking water is set at 50 μg/l, however reduction of this level is currently under consideration by the Environmental Protection Agency (EPA). Changing the current MCL would affect many localities throughout the Western U.S. whose arsenic levels are already close to the present maximum. Small towns, in particular, would be affected by this change, due to the high cost of As removal from drinking water. Understanding the species present and their mobility in natural settings is vital to water treatment and management strategies.

Although there have been several studies on the mobility of arsenic in streams (Baker et al., 1998; Mok and Wai, 1990; Mok and Wai, 1988; Wilson and Hawkins, 1978) most were conducted in contaminated areas that have extremely high concentrations of arsenic. Streams in the La Primavera Geothermal Field, Mexico, provide an opportunity to study arsenic mobility under natural conditions. At La Primavera, natural concentrations of arsenic average about 1 ppm and are discharged by hot thermal waters that exhibit significant changes in pH, Eh and temperature with travel downstream.

Although several studies have been conducted on speciation of As(III) and As(V) in stream and lake sediments (Ficklin, 1990; Manning and Martens, 1997) few include analysis of the organoarsenicals monomethylarsonate (MMA) and dimethylarsinate (DMA) (Maher, 1984; Maher, 1981; Yamamoto, 1975). Also, the extraction and speciation of arsenic from sediments often involves elaborate procedures or specialized equipment that is not accessible to all laboratories. However, a method of ion-exchange chromatography, modified after Grabinski (1981), used in this study is simple and inexpensive enough to be conducted in the field as well as most analytical laboratories.

The objective of this study is to characterize the arsenic geochemistry of stream sediments and to determine controls on the mobility of arsenic in La Primavera waters. To attain this objective, the association between arsenic and sediment components Fe, Mn and total organic carbon (TOC) was investigated in La Primavera sediments to determine secondary phases that control arsenic mobility and to determine whether sediment-water relationships exist. Analysis of Fe, Mn and TOC was also done on Rio Grande sediments for comparison. Speciation of sediment and algae extracts was used to determine relative proportions of As(III), As(V), MMA and DMA present. Also, a new method for determination of very small amounts of carbonate is described.

BACKGROUND

Sources and Occurrences of Arsenic in the Environment

Arsenic is a trace element found in all environments with normal abundances (listed in ppm) of 1.8 (igneous rocks), 1.0 (sandstone), 9.0 (shale), 1.8 (carbonates), 7.5 (soils) and 2.0 ppb (fresh water) (Turekian, 1977; Horn and Adams, 1966). Abnormally high arsenic levels in the environment and waters typically occur in active and fossil geothermal areas.

Early reports on arsenic occurrence in the environment suggest that arsenic in geothermal areas originates primarily from magmatic waters (Onishi and Sandell, 1955). However, later experimental studies have shown that arsenic concentrations found in thermal waters can be accounted for by hot water-rock interaction and do not require magmatic input (Ewers, 1977; Ellis and Mahon, 1964). A more recent field study of the thermal waters at Yellowstone National Park by Stauffer and Thompson (1984) found similar conclusions. Although it is believed that the arsenic occurs primarily within mineral lattices, evidence suggests that some of it also occurs on crystal surfaces and fractures (Ewers, 1977; Ellis and Mahon, 1964).

Arsenic Geochemistry of Waters

The geochemistry of arsenic is complex due to the multiple oxidation states (+5, +3, 0, and -3) occurring in waters under natural conditions and is further complicated by biological, oxidation-reduction, mineral dissolution-precipitation and sediment-water reactions (Welch, et al., 1988). In waters arsenic is present as an oxyanion with stable arsenates (As(V)) (most often as $H_2AsO_4^-$ and $HAsO_4^{2-}$) in oxidizing conditions and arsenites (As(III)) (H_3AsO_3 and $H_2AsO_3^-$) in reducing conditions (Fig. 1). Methylated forms are also found in waters as anionic monomethylarsonate ($CH_3AsO_2OH^-$) and dimethylarsinate ($(CH_3)_2AsOO^-$) (Anderson and Bruland, 1991; Braman and Foreback, 1972).

Biologically mediated reactions are important processes affecting arsenic geochemistry of waters. In some cases bacteria catalyze the oxidation of As(III) to As(V) (Wilkie and Herring, 1998) and may be responsible for the reduction of As(V) to As(III) (Ferguson and Gavis, 1972). Bacteria and phytoplankton also affect the cycling of arsenic by methylation of inorganic As to produce MMA then DMA (Wood, 1974), which in some California lakes has accounted for up to 60% of the total arsenic (Anderson and Bruland, 1991). MMA is considered to be a precursor to DMA and is generally present in smaller amounts (Braman and Foreback, 1973). Because methylation requires a large

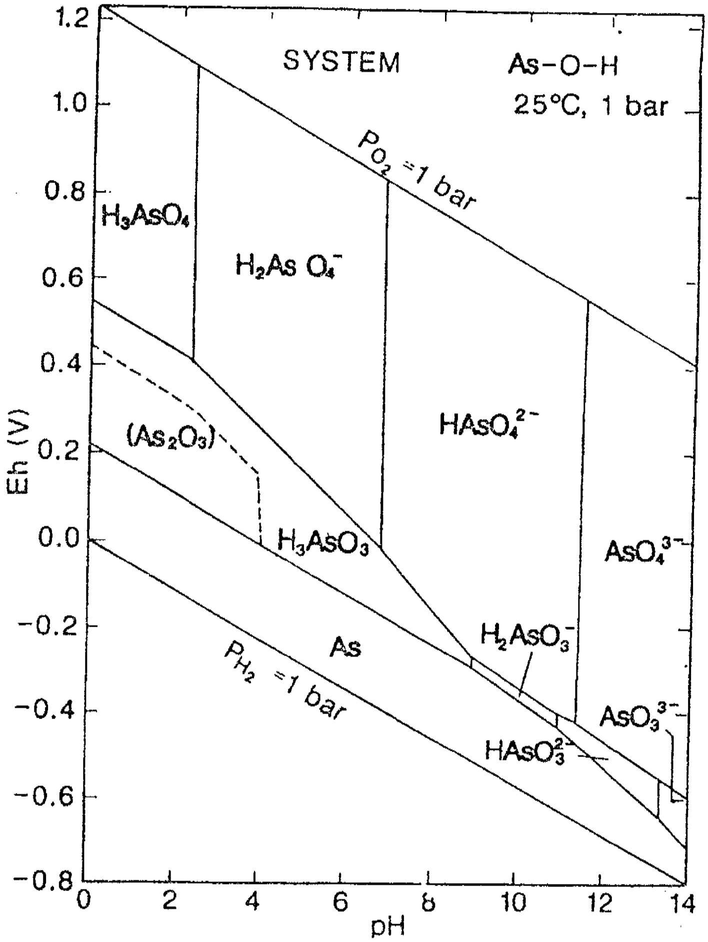

Figure 1. Eh-pH diagram for inorganic arsenic (From Brookins, 1988).

amount of energy it is believed to take place only in the presence of biota (Ferguson and Gavis, 1972). Although the use of arsenic by biota is not well understood, it is hypothesized that uptake occurs due to the similarity between arsenate and phosphate (Aurillo et al., 1994; Sanders, 1980; Andreae 1979). Others have found seasonal variations in the amount of organic forms present that also suggest biological involvement (Anderson and Bruland, 1991; Howard et al., 1982).

Oxidation and reduction reactions involving arsenic can be biologically mediated, as discussed earlier, or take place abiotically on mineral surfaces or due to the presence of other aqueous species. The ability of manganese oxides to oxidize As(III) is well known (Driehaus et al., 1995; Moore et al., 1990; Oscarson et al., 1983; Oscarson et al., 1981; Oscarson et al., 1980). Experimental work shows that manganese oxides rapidly oxidize As(III) to As(V) which then adsorbs to the surface of the oxide (Oscarson, 1980). Iron oxides may also contribute to the oxidation of As(III), but it is believed to be less important due to much slower oxidation kinetics (Oscarson et al., 1981). Arsenic transformations are also brought about abiotically by dissolved Fe, H_2S and O_2. However, knowledge about the kinetics of arsenic oxidation in natural systems is sparse and reports of arsenic transformation rates in surface water and groundwater vary widely.

There are few common arsenic minerals that precipitate out in natural waters and those that do generally occur under extreme conditions of pH and Eh. The iron arsenate mineral scorodite ($FeAsO_4 \bullet 2H_2O$) generally occurs as an oxidation product of arsenopyrite-bearing ores, but has a tendency to break down forming iron hydroxides releasing arsenate into solution. It has also been found to occur in geothermal areas under oxidizing ($Eh>0.4$ V), acid ($pH<2$) conditions where waters have high activities of iron and arsenic. Theoretical calculations show that barium arsenate could also be a mineral phase present in natural waters, but has not yet been found in nature (Wagemann, 1978). Under reducing conditions, arsenic forms arsenic sulfides and can coprecipitate with pyrite and other metal sulfides (Belzile, 1988; Moore et al., 1988).

Arsenic Sediment-Water Interactions

Sediment-water interactions including adsorption and co-precipitation are the primary factors that determine arsenic mobility in surface waters (Baker et al., 1998; Mok and Wai, 1989; Wilson and Hawkins, 1978) and ground waters (Welch and Lico, 1998). These sediment-water interactions are dependent upon many environmental factors and affect arsenic mobility by the removal from or addition to solution. Adsorption and co-precipitation vary with mineral type, pH, Eh, and ionic strength as well as the species of arsenic present.

Adsorption and co-precipitation of arsenic by amorphous iron oxides and oxyhydroxides is one of the primary mechanisms for its removal from waters and is dependent upon pH, Eh, and the presence of competing ions as well as arsenic oxidation state (Bowell, 1994; Pierce and Moore, 1982; Pierce and Moore, 1980). Adsorption occurs due to the oxide's large surface area and net positive surface charge that covers the pH range of most surface waters, with maximum absorbance of As(III) occurring at pH 7 and that of As(V) at pH 4 (Pierce and Moore, 1982). The affinity of the other arsenic species to sorb onto iron oxides also varies with pH as follows: As(V)>DMA=MMA>As(III) below pH 7, and As(V)>As(III)>MMA=DMA above pH 7 (Bowell, 1994). However, aqueous species such as phosphate and organic acids also compete for sorption sites and can reduce the oxides ability to take up arsenic (Bowell, 1994).

Associations between arsenic and manganese oxides are not as common and there are few reports of this occurrence in nature (Peterson and Carpenter, 1986; Takamatsu et al., 1985; Crecelius, 1975). One reason may be that manganese oxides have a net negative charge in waters, pH > 2.5 to 3, making adsorption of oxyanions unlikely. However, a study by Takamatsu et al. (1985) showed that adsorption of divalent cations Mn^{2+}, Sr^{2+}, Ba^{2+} and Ni^{2+} onto the surface of manganese oxides releases H^+ ions resulting in a net positive surface charge able to adsorb anions. Oscarson et al. (1983) also reports adsorption of arsenate by manganese oxides in laboratory experiments. Another mechanism by which manganese oxides may take up anions is by ligand exchange in which surface hydroxyls are exchanged by another ligand.

Other important minerals involved in arsenic adsorption are clays (Frost and Griffin, 1977), highly aluminous minerals, colloids (Huang, 1975; Gupta and Chen, 1978) and carbonates (Goldberg and Glaubig, 1988; Brannon and Patrick, 1987). Adsorption onto these surfaces is also strongly pH dependent with maximum adsorption onto clays and aluminous minerals occurring between pH 4 to 7 (Goldberg and Glaubig, 1988; Gupta and Chen, 1978; Frost and Griffin, 1977). Goldberg and Glaubig (1988) found that sorption of arsenic by carbonates increased between pHs 6 to 11, with maximum adsorption occurring at pH 10.5. Adsorption of arsenic by carbonate may be an important process under alkaline conditions where clays and aluminous minerals are less effective (Goldberg and Glaubig, 1988).

The redox condition within the sediments is important because it determines the oxidation state and species of the arsenic, as well as the stability of secondary oxides and hydroxides present that may remove arsenic from solution. Several studies look at the vertical distribution of arsenic in lake sediments and the changes that occur with changing redox conditions (Aggett and Kriegman, 1988; Belzile, 1988; Moore et al., 1988; Duell and Swoboda, 1972). Arsenic solubility is generally determined by Fe oxides in the oxidized zone and by sulfide minerals, if sulfur is present, in the reduced zone (Moore et al., 1988). With progressive burial and change in the redox interface, arsenic is released by reduction of iron oxides and can diffuse upwards where it re-precipitates in the oxic zone (Belzile, 1988). Arsenic solubility may also be increased by reduction of As(V) to As(III) which is not as tightly bound to the sediments (Aggett and Kriegman, 1988).

Field Areas

Geologic Setting of La Primavera

The La Primavera geothermal field is associated with a Late Pleistocene rhyolitic caldera about 20 Km west of Guadalajara, Mexico. The eruptive units include lava flows and domes, pyroclastic flows, air fall pumice, and caldera lake sediments (Mahood, 1981). These volcanic deposits (Fig. 2) all consist of high-silica rhyolites erupted between 145,000 and 30,000 years ago (Mahood, 1981). The largest deposit is the Tala tuff which erupted 95,000 years ago and consists of 20 km^3 of ash flows (Mahood, 1981). The roof of the magma chamber collapsed after eruption of the Tala tuff forming an 11 km diameter caldera (Mahood, 1981). Afterwards a lake formed in the caldera resulting in lake deposits of reworked volcanics (Mahood, 1981). Later eruptive episodes at 75, 000, 60,000 and 30,000 years ago formed two series of ring domes and brought an end to the lake (Mahood, 1981).

Hot springs that occur at La Primavera are associated with three major fault systems related to caldera collapse and magma insurgence (Mahood et al., 1983). The main field area lies in a valley created by a north-south normal fault with a maximum displacement of 100m at Rio Caliente (Mahood et al., 1993). Four major hot springs

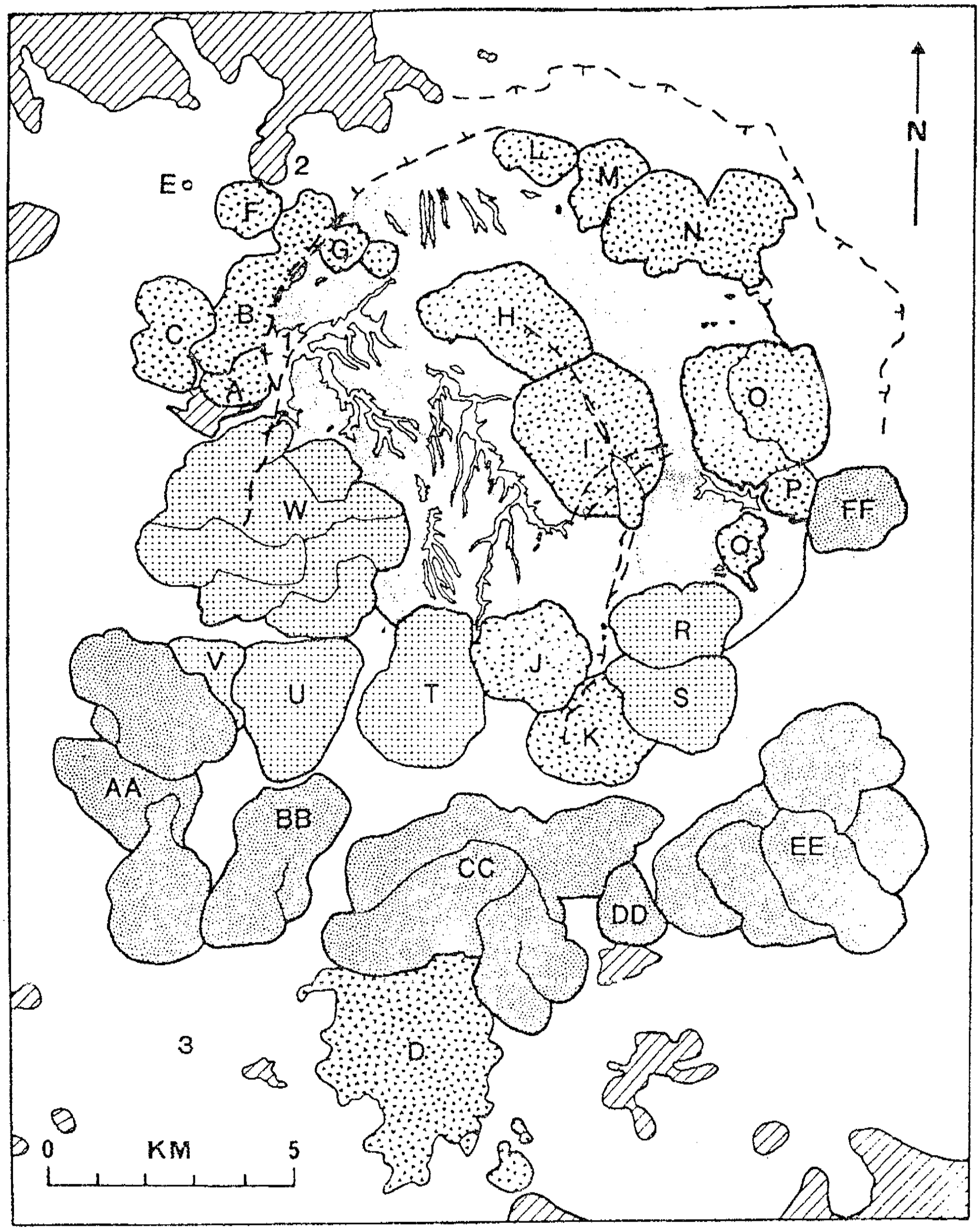

Figure 2. Geologic map of La Primavera volcanic field (From Mahood et al., 1983). Volcanic rock units are labeled on the map as follows: "diagonal ruling: pre-Primavera volcanic rocks; V pattern: pre-caldera lavas; unpatterned: Tala Tuff; light stipple: lake-sediments; double-dash pattern: older ring domes rectilinear dots: younger ring domes; heavy stipple."

discharge near neutral sodium bicarbonate waters (60 to 65 °C) forming Rio Caliente which drains into the Rio Salado. Numerous smaller thermal seeps also occur along much of the stream reach.

The stream banks are vegetated by small willow-like trees, oaks, grasses and reeds. Algae is also abundant, occurring as thick mats that cover the entire stream bottom where waters exceed 45 °C and as thin filamentous forms that attach to rocks and sediments in cooler waters.

Geologic Setting of the Rio Grande Valley, Socorro Region

One of the most prominent features of central New Mexico is the Rio Grande Rift which extends from central Colorado into the Mexican state of Chihuahua. Rifting began about 30 m.y.a. forming a series of basins along its length that have been filled with alluvium and volcanics. Along either side of the rift in the Socorro region are tertiary volcanics, ranging from basaltic to rhyolitic in composition, and thick upper paleozoic sandstones and carbonate sequences. Tertiary sediment sequences of alluvium and river sands that fill the Rio Grande valley make up the Santa Fe Group.

The Rio Grande river flows along the rift valley through central New Mexico, then travels eastward along the Texas-Mexico border until it empties into the Gulf of Mexico. The Rio Grande waters are similar to those at La Primavera with alkaline pHs between 7.5 to 8.5 and measured Eh between +40 to 100 mV. Arsenic concentrations are generally low, between 2 to 5 ppb in waters and 1.5 to 3.5 ppm in the sediments (Chapin and Dunbar, 1995).

ANALYTICAL METHODS

Sample Collection and Preparation

Samples were collected at 20 sample stations separated by approximately 500 meters along Rio Caliente and its tributaries (Fig. 3). Sediments were collected within 20 meters of locations where stream waters were sampled so that direct comparisons could

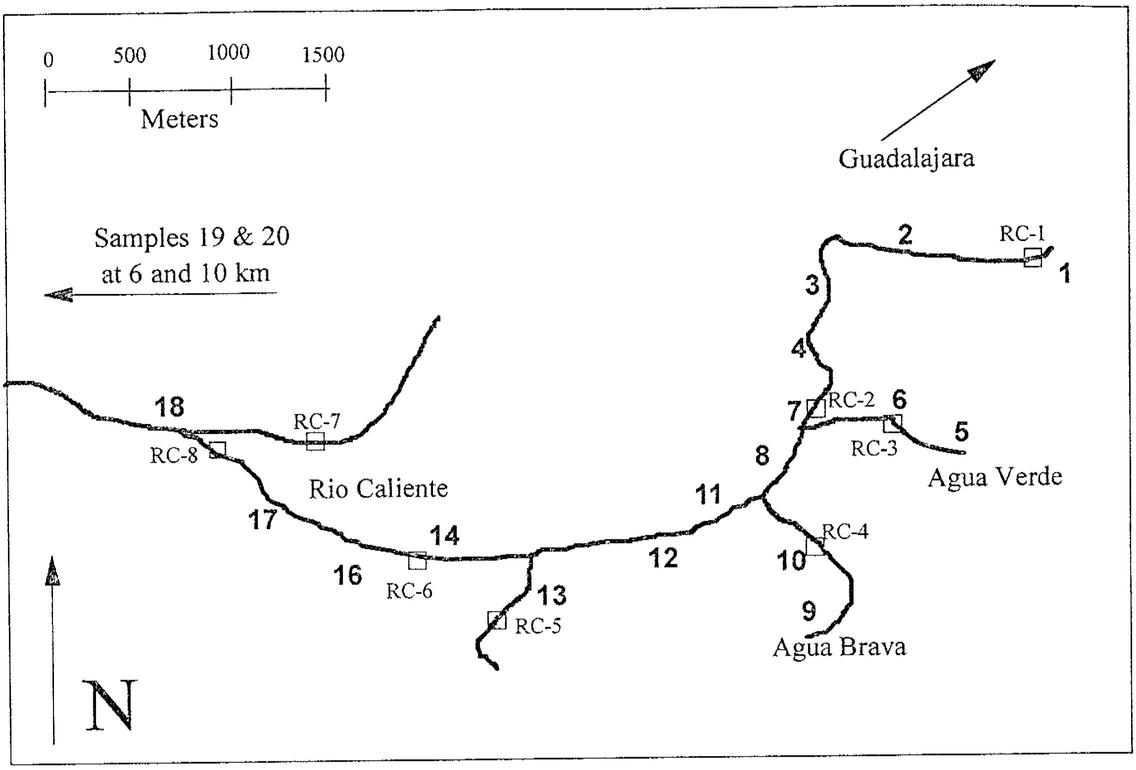

Figure 3. La Primavera sample location map.

be made between water and sediment chemistry. Where possible, sediments were collected midstream by plastic scoop and contained in one-half gallon plastic buckets and one-liter plastic bottles that were refrigerated to 4 ± 2 °C until time of sample preparation. In some locations larger cobbles and algal mats were removed before scooping.

Before sample collection, redox conditions at the sediment-water interface and several inches within the sediments were tested using an OMEGA model PHH-82 meter. Though measured Eh conditions within sediments ranged from -130 to +150 mV (Appendix A) only samples with Ehs greater than 0 were used for direct comparison between sample stations. This was done to reduce heterogeneity of samples resulting from different mineral assemblages stable under differing redox conditions. Also, the procedures involved in preservation of reducing sediments are elaborate and were beyond the scope of what could be accomplished on this sampling trip.

River sediments were also collected from the Rio Grande River at Escondida, Socorro, and San Antonio, New Mexico (Fig. 4). These samples were collected and preserved in the same manner previously described for La Primavera samples. No plants or algae were collected from the Rio Grande.

Algae, plant and rock specimens were also collected at each of the La Primavera sample locations. An attempt was made to collect each type of plant, algae and rock present at sample sites. Algae and plants were stored in separate ziplock bags and refrigerated at 4 ± 2 °C until time of sample preparation.

Sediments were air dried and split into manageable portions using the cone and quartering method. With this method, a cone was initially made by pouring the sediments through a plastic funnel. The sediment cone was then quartered on a sheet of plastic. Two of the opposite quarters were then mixed and quartered again. This procedure was repeated several times until a manageable sample size was obtained. Air-drying of the samples was done because it is believed to have a lower possibility of affecting secondary mineral phases and organic matter than heat-drying or freeze-drying.

Sediments were dry-sieved using U.S. Standard steel sieves to characterize the grain size distribution. Initially, in order to reduce sample heterogeneity, the >2 mm size fraction was sieved out and archived and is not used in the grain size distribution or chemical extractions. About 100 grams of dried sediment was weighed for separation into the size fractions 1.0-2.0 mm (very coarse sand), 0.5-1.0 mm (coarse sand), 0.25-0.5 mm

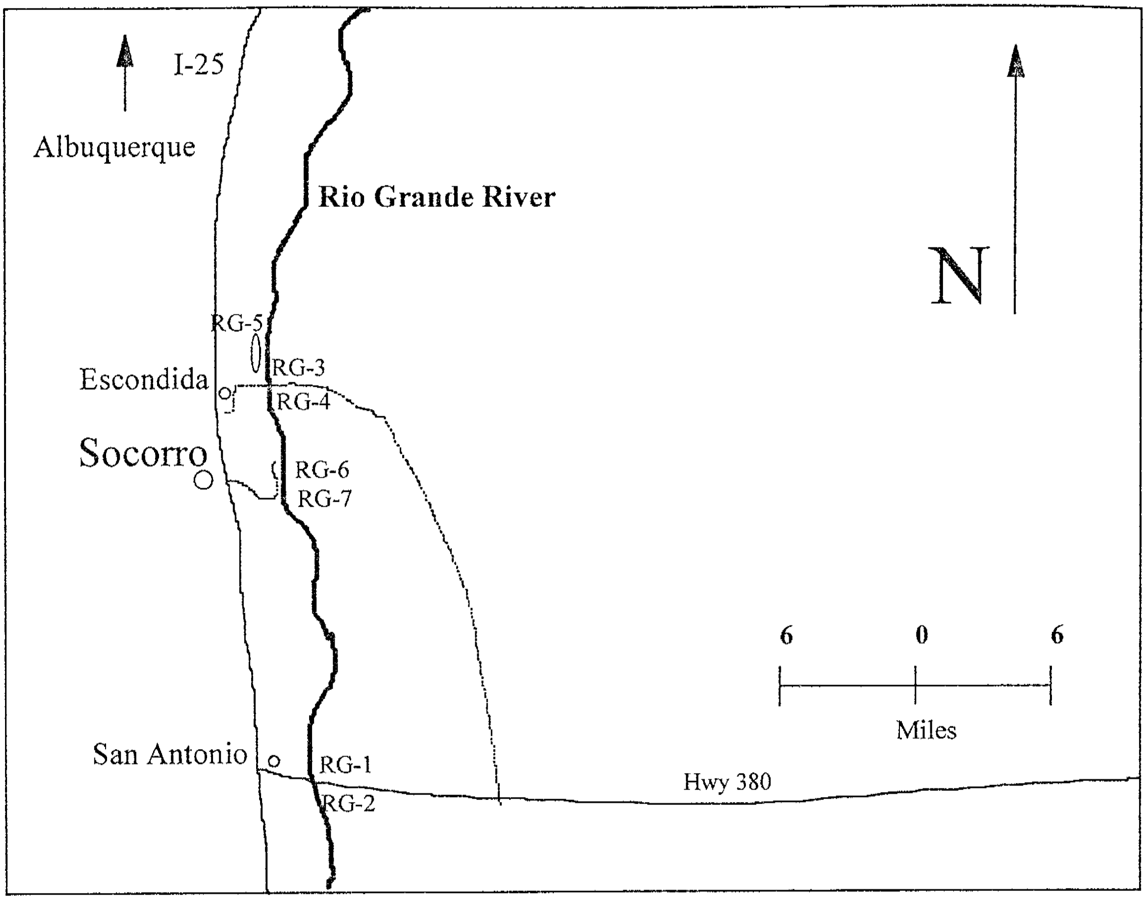

Figure 4. Sample locations along the Rio Grande.

(medium sand), 0.125-0.25 mm (fine sand), 0.0625-0.125 mm (very fine sand) and <0.0625 mm (silt-clay). The different sieves were stacked in sequence with fining mesh sizes towards the bottom and placed on the Ro-Tap machine to be shaken 15 minutes as outlined by Folk (1974). After shaking, sediments from each of the size fractions were weighed to obtain the grain size distribution.

A small portion of split sediments was ground to -80 mesh in a ball crusher to reduce the heterogeneity present in un-sieved material for some of the analyses. A grinding time of only 10 to 20 seconds was used to prevent the sample from heating up as well as to cut down on possible contamination by metal from the grinder itself.

Algae samples were first patted dry with a paper towel to remove excess moisture and weighed to obtain a "wet weight" then dried overnight at 105 °C. The dried algae was re-weighed to obtain a dry weight and ground to a powder in a ceramic mortar for analysis.

Chemical analyses of La Primavera stream waters were provided by Greg Miller of New Mexico Institute of Mining and Technology and are discussed in detail in Miller (1999).

Partial Extractions

Selective Extraction

A combination of partial extraction techniques developed by Tessier et al. (1979) and Chao and Zhou (1983) was performed on the sediments to determine relative proportions of exchangeable arsenic (water soluble and affected by adsorption-desorption processes), arsenic associated with carbonates, amorphous iron and manganese oxides, and organic matter. The procedure used is as follows: about one gram of sediment, ground to -80 mesh, is agitated in 8 ml of 1M NaOAc adjusted to pH 8.2 for 1 h to remove exchangeable arsenic. Next, the residue from the exchangeable extraction is agitated in 8 ml of 1M NaOAc adjusted to pH 5 for 4 hours to remove arsenic associated with carbonates. The resulting residue is then digested in 20 ml of 0.25M NH_2OH-HCl in 0.25M HCl heated to 50 ^{0}C for 30 min to extract arsenic associated with amorphous iron and manganese oxides. Extraction of arsenic bound to organic matter is achieved by adding the residue from the iron-manganese oxide digestion to 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3. This mixture is heated to 85 °C for 2 h after which an additional 3 ml aliquot of 30% H_2O_2 is added with continued heating for an additional 3 h. The use of 0.25M NH_2OH-HCl in 0.25M HCl, described by Chao and Zhou (1983), was used instead of the 0.04M NH_2OH-HCl in 25% v/v HOAc suggested by Tessier et al. (1978) because of its greater selectivity for amorphous Fe and Mn oxides and reduced matrix effects.

All extractions were conducted in plastic centrifuge tubes to avoid loss of sample and cross contamination. Between each successive extraction samples were centrifuged at 10,000 rpm for 30 min and the supernatant pipetted off for analysis. Afterwards, 8 ml of distilled water was added and the residue again centrifuged for 30 min. The second supernatant was removed and discarded before addition of the next extracting reagent.

HNO_3 Digestions

Nitric acid extractions were conducted on each of the size fractions and on un-sieved sediment samples. About 1 gram of sediment was added to 10 ml of 8M HNO_3, (1:1 HNO_3 and distilled water) and microwave-heated under pressure in sealed teflon containers. This mixture was heated 12 min at 50 psi and followed by 30 min at 100 psi, about 180 ° C. After cooling, extracts were filtered and diluted for analysis on a Varian 600 Zeeman graphite furnace atomic absorption spectrophotometer (GFAAS).

The HNO_3 procedure dissolves many of the secondary minerals and organic matter, but not residual minerals and glasses. It also provides an estimate of the "total" acid leachable arsenic in the sediments, and represents arsenic that could be remobilized with changes in environmental conditions such as pH or Eh. Nitric acid was chosen for the extraction because procedures using heated HCl and or HF could result in loss of As as volatile $AsCl_3$ or AsF_3.

H_3PO_4 Digestions and Arsenic Speciation

Speciation of As(III), As(V), MMA and DMA in sediments was achieved by a method using ion exchange chromatography modified after Grabinski (1981). The apparatus consisted of a 10 cm glass column, 1 cm diameter, filled with AG-1X8 anion resin in the chloride form connected by a capillary to a 26 cm glass column, also 1 cm diameter, filled with AG50W-X8 cation resin in the hydrogen form. Resins were 50-100 mesh allowing gravity flow rates of about 3 ml/min. The top and bottom of the anion column and the bottom of the cation column were capped with a porous polymer bed support, and a luer fitting for flow control was used at the base.

Before use, the ion exchange columns were first conditioned and regenerated as described by Grabinski (1981). Initially, resin was packed into the columns with distilled water, then washed twice with successive elutions of 1.5 M NH_4OH (70 ml), 1.0 M HCl (70 ml), 0.48 M HCl (70 ml) and 0.006 M (25 ml) trichloroacetic acid (TCA). After the first sample had been run columns were regenerated by washing with the same successive elutions only once after each additional use.

Validation of the ion-exchange method was done using the sediment extracting reagent (0.1 M H_3PO_4) before running samples. This was carried out with prepared standard solutions of 250 ppb As(III), As(V), MMA and DMA in 0.1 M H_3PO_4. Initially, each arsenic species was run separately to determine sample collection ranges and to validate separation. After sample collection ranges were determined, mixed standards containing known amounts of all 4 arsenic species were run to determine sample recoveries. Average recoveries for each of the species ranged as follows: As(III) (84%), MMA (96%), As(V) (79%) and DMA (79%). This extraction procedure provides semiquantitative results for comparison between arsenic species and for comparison of the same species between different sample stations.

The effect of the H_3PO_4 extractant on arsenic species was also investigated before sample analysis. Three sets of mixed standards in H_3PO_4 were run through the ion-exchange columns immediately after preparation, and an additional 3 sets run 1.5 h after preparation. No significant difference was observed between samples indicating no oxidation of As (III) during the time required for sediment extraction and centrifuging.

Samples were run through the columns by using successive additions of 0.006 M TCA (55 ml), 0.2 M TCA (8 ml), 1.5 M NH4OH (55 ml) and 0.2 M TCA (50 ml). The first 29 ml of sample collected from the column contained As(III), 29 to 60 ml MMA, 60 to 90 ml As(V) and 90 to 140 DMA. A description of the elution process is as follows: during the first elution with 0.006 M TCA (pH~2.5) As(III) is present as a neutral species and travels through the column to be collected in the first 29 ml. MMA is also a neutral species under these conditions and is eluted after the As(III) and collected in the 29 to 60 ml fraction. Although there is no explanation for this behavior in any literature it is possible that MMA is weakly retained by non-polar interactions (Greg Miller personal com.). While As(III) and MMA are being eluted As(V) and DMA retain a charge and stick to the anion and cation resins. Arsenic(V) is converted to its neutral form when the 0.2 M TCA reaches it in the anion resin and is collected in the 60 to 90 ml fraction while DMA is strongly retained on the cation exchange resin. The DMA is converted to its anionic form and moves from the cation resin to the bottom anion resin with the addition of 1.5 M NH_4OH. The final elution with 0.2 M TCA converts the DMA to a positively charged species removing it from the anion resin to be collected in the 90 to 140 ml fraction.

The procedure used in sediment analysis is as follows: about 1 gram of sediment, ground to <80 mesh, was added to 10 ml of 0.1 M H_3PO_4 and shaken for 1 h in a plastic centrifuge tube. Samples were centrifuged for 30 min at 10,000 rpm, then 5 ml of sediment extract was pipetted on to the top of the ion-exchange column. The column was eluted until the sample was level with the resin bed, after which the first elution with 55 ml of 0.006 M TCA was begun. The first 5 ml of eluant, collected while leveling the sample with the resin, was discarded and the As(III) fraction was collected from 5 to 29 ml. The other As species were collected in the ranges described previousely. Analyses were conducted by GFAAS with calibration of the instrument in the same matrix as the sample (H_3PO_4).

Algae Digestions

About 0.5 g of ground, dried algae was added to 10 ml of concentrated HNO_3 in a capped teflon microwave vessel. Samples were microwave heated at 55% power under 40 psi for 10 min allowing 5 min to reach pressure, followed by 55% power at 85 psi for 10 min allowing 5 min to reach pressure and finished with heating at 55% power and 100 psi for 10 min allowing 5 min to reach pressure. After cooling 30% H_2O_2 was added until the effervescence ceased, then an additional 2 ml 30% H_2O_2 was added and allowed to digest overnight. Digestion overnight was done to give the solution time for the H_2O_2 to dissipate, otherwise the 30% H_2O_2 will oxidize the graphite tube in the GFAAS. Samples were then filtered and diluted for analysis by GFAAS.

Speciation of arsenic present in the algae was also done using the same technique as described previously for stream sediments. Digestion by HNO_3 and 30% H_2O_2 gave results for total arsenic in algae, leaving no visible trace of algae afterwards. The digestion procedure for speciation is less destructive and provides qualitative data on relative amounts of each species present, it does not completely digest the algae nor does it liberate all the arsenic present.

HCl+HNO_3 Digestions for Mn and Fe

Concentrations of Fe, Mn, Ca, Mg and Zn were determined using ASTM method D 3974-81 for extraction of trace elements from sediments. About 4 g of sediment, ground to -80 mesh, was added to 10 ml concentrated HCl and 1 ml concentrated HNO_3 which was diluted to 100 ml with distilled water. This solution was heated at 95 °C on a hotplate until 10 to 15 ml remained. The remaining solution was filtered and diluted for analysis on an IL Video Model 12 flame atomic absorption spectrophotometer (FAAS). This procedure dissolves secondary minerals and organic matter, but does not affect primary minerals. Sedimentary Fe and Mn was also measured in HNO_3 and H_3PO_4 extracts by FAA.

Carbonate Analysis

Carbonate was present in very small amounts and was measured by pressure difference, due to acid evolved CO_2, and gas analysis using a quadrupole mass spectrometer. A glass vacuum reaction vessel was used that had a glass partition at the bottom creating two open, but separated chambers. The reaction vessel fit into a glass neck with a teflon valve allowing the vessel to be sealed. This apparatus was fitted to a system of vacuum lines in contact with a capacitance manometer for pressure measurements. The system of vacuum lines is also set up to send a gas sample directly to a Balzers model QMG 125 quadrupole mass spectrometer.

Initially, sediment ground -80 mesh, was oven dried at 105 °C for about 10 min to remove excess moisture. Afterwards, about 1.5 g of sediment was placed in one chamber of the reaction vessel and 4 ml of concentrated H_3PO_4 was pipetted into the other. The apparatus was sealed with vacuum grease and attached to the vacuum lines. Low and hi-vacuum pumps were used to create a vacuum in the reaction vessel and were allowed to pump down overnight to remove adsorbed water and gas from the sample. The following day a downward extension on the vacuum line, filled with glass beads, was emersed in a cold trap of dry-ice in ethanol for removal of water. When the pressure in the vacuum line reached about 0.0000 mbar the initial pressure was recorded and the reaction vessel sealed off and tipped, allowing the acid to react with the sediment. The reaction was allowed to proceed for two hours, during which time the vacuum lines were pumped down to about 0.0000 mbar. Next, the vacuum pumps were sealed off and the reaction vessel opened allowing the evolved gas to fill a known volume of vacuum line connected to a capacitance manometer and cold trap. After two minutes the reaction vessel was sealed off to prevent possible leakage of air into the system. About 30 to 45 minutes were required for the pressure to equilibrate, due to removal of water from the vacuum lines by the cold trap. The final pressure and temperature was then recorded and the sample sent to the quadrupole mass spectrometer for gas analysis.

Before analysis, background intensities of H_2O, N_2, O_2, Ar and CO_2 gasses were measured when the pressure in the mass spectrometer was less than 2E 10^{-7} mbar. Next, a valve was opened allowing the sample to enter the mass spectrometer. A leak valve was used to maintain a pressure in the spectrometer of 2E 10^{-6} mbar. After a few moments, the intensities of H_2O, N_2, O_2, Ar and CO_2 gasses from the sample were recorded. Mole percentages of each of the gasses were calculated and corrected from sample intensities on spreadsheet.

Determination of the time required for reaction was made by recording pressure increases with time after reacting a sample with acid. After two hours, in a sample containing the largest amount of carbonate, 97% of the total gas had been evolved. The largest possible sample size, about 1.5 to 2 g was used to obtain the maximum precision possible. One sample, done in triplicate, was used to provide a detection limit of 0.05% carbonate which was calculated as two times the relative standard deviation. A second sample, containing less carbonate, was also done in duplicate with reproducibility better than 0.05%. Although, the amount of evolved CO_2 could be measured very precisely, the proportions of CO_2 resulting from dissolution of $CaCO_3$, $MnCO_3$, $MgCO_3$ can not be determined. As a result, values are reported as % carbonate not as % $CaCO_3$.

Electron Microprobe Analysis

Polished one-inch round sections were examined by a Comica SX-100 electron microprobe. An accelerating voltage of 15 KV and a probe current of 20 na was used. Iron oxides were visible as grain discrete grains and as oxidized mafic grains that still retained relict textures. No manganese minerals were detected with the microprobe. The distribution of arsenic within iron oxides was examined by conducting line scans on two different grains. Scans began in the center and proceeded in a line towards the outer edge of the grain. Output data from the line scans consisted of the number of counts of Fe and As at points along the traverse. The microprobe was also used to make point-count measurements of arsenic contents in iron-oxides relative to background glasses. Point count measurements do not provide a concentration of arsenic, only the number of counts of arsenic in one phase relative to another allowing comparison between the two.

Reflected Light Spectrophotometry

A method of visible light (VIS) reflectance spectrophotometry, outlined by Barranco et al., (1989), was used to identify the types of iron oxides present in sediments. About 5 drops of water were added to 0.1 to 0.15 g of ground sediment, which was then mixed to make a thin slurry on a petrographic slide and dried. Samples were run on a Perkin-Elmer Lambda 6 spectrophotometer relative to a barium sulfate standard for the wavelength range 250 to 850 nm. Output data consisted of percent total reflectance vs. wavelength. Data was processed and enhanced by taking the first derivative of % reflectance and plotting it against wavelength.

Surface Area Measurements

Surface area measurements were conducted on a monosorb direct-reading surface area analyzer (Quantachrome corp) using 30 mol % N_2 with 70 mol % H_2 carrier gas. Before analysis, un-sieved sediments were heated overnight in a muffle furnace at 430 °C for removal of organic matter. The monosorb was calibrated following factory recommended procedures. About 1 to 1.5 g of sample was placed in a u-shaped glass sample tube with holder, leaving space above the sample so that gas flow was not impeded. The sample tube was then placed in an "out-gassing" station and heated with a heat gun for about 2 min to drive off excess moisture. After cooling the sample tube and holder is moved to a "sample" receptacle and immersed in a liquid nitrogen bath, during which time the monosorb records an adsorption signal. When the adsorption signal is completed the sample tube is removed from the bath and the desorption signal begins. When the desorption signal is completed the monosorb displays the surface area in square meters. This number is divided by the sample weight to determine m^2/gm of sediment.

Though no standard reference material was available for determination of accuracy, triplicate measurements were made on 60-100 mesh Silicar silica gel produced by Mallinckrodt, which reported a surface area of 480 m^2/g. Triplicate measurements conducted on the silica gel were 598 m^2/g ± 7.8. Triplicate measurements were also made on samples from the Rio Grande, NM, and La Primavera, Mexico, were 5.03 ± 0.26 and 1.52 ± 0.09, respectively.

Determination of Percent Total Organic Carbon

Percent total organic carbon (% TOC) was determined by loss-on-ignition using a procedure outlined by Davies (1974). About 10 g of un-sieved sediments were oven dried at 105 °C for 3 to 4 h and weighed, then placed in a muffle furnace and heated at 430 °C for 24 h. After cooling, sediments were re-weighed to determine the amount lost-on-ignition, representing total organic carbon. Contribution to the sediment weight loss by structural water expelled from clays is insignificant due to the fact that clays were present in non-detectable amounts. Also, carbonates do not to affect the loss-on-ignition value at temperatures of 430 °C (Davies, 1974).

X-Ray Diffraction

An attempt was made to separate clays for identification by X-ray diffraction (XRD). Removal of organic matter was done by addition of 5 to 6 g of >63 μ sediments to 10 ml of Chlorox (NaOCl) adjusted to pH 9 with HCl. This mixture is heated 15 min in a boiling water bath, then centrifuged for 5 min and decanted. This procedure is repeated several times until the decanted liquid is clear and shows no brown coloration indicating oxidized organic matter. Afterwards, the > 63 μ sample is placed in a beaker with distilled water and several drops of Calgon to keep the clays dispersed. This mixture is stirred, and after 10 min settling time 2 ml is pipetted on to a petrographic slide for X-ray diffraction analysis (XRD) on a Rigaku DMAX/2 X-ray diffractometer.

Dissolution of the organic matter with 0.02 M HNO_3 and 30 % H_2O_2 following the procedure of Tessier et al. (1979), described previously, was also tried. The same technique of clay dispersion and slide preparation was used on these samples as well.

X-Ray Fluorescence

Values of total As, Fe and Mn were determined by X-ray fluorescence (XRF) on a Phillips PW 2400 instrument at the New Mexico Bureau of Mines and Mineral Resources lab. Ground un-sieved sediments were used to make pressed powder pellets that were analyzed using standard procedures.

Modeling with Minteq

The aqueous geochemical modeling program MinteqA2, produced by the EPA, was used to model the water chemistry at La Primavera and to predict possible stable mineral phases present in the sediments. The new database for MinteqU, which includes corrected thermodynamic data and additional mineral species, was used in place of the older MinteqA2 database. Data for each sample location was input following standard procedures.

Quality Control

Before sample analysis, validation of the GFAAS for arsenic analysis was tested by running prepared solutions of known arsenic concentration for each type of matrix used. When matrix effects were encountered alternative analytical procedures were used. During each run on the GFAAS several prepared standards of 20 ppb As were included to determine the accuracy and precision of the instrument. A GFAAS detection limit of 3.7 ppb As was calculated as two times the standard deviation of the standards. Quality control was also maintained by running some of each of the extractions in duplicate and triplicate as a check on the reproducibility of the particular method on sediments. Reported reproducibility was calculated as the relative standard deviation of multiple measurements.

Statistical Analyses

Before statistical analyses were conducted, histograms were made for TOC and each of the elements to examine the type of distribution. Percent TOC was found to show a log-normal distribution, however no recognizable difference was found between use of normal or logorithmically reduced data in correlation matrices or regression analyses and may be due to the small number of samples used in this study. Further statistical analyses were conducted using un-modified data.

Correlation matrices (Appendix B), calculated in Microsoft Excel, were used first on the large data sets to uncover relationships between sediment components and waters. Although correlation matrices were useful in reducing the amount of data, they sometimes provided false correlations as a result of a wide spread of data points. This was handled by plotting data that seemed to show a relationship for visual inspection and subjecting it to regression analysis.

Sediment samples used in statistical analyses were those that were collected under redox conditions >0 mV, which included all samples sites except for 2, 3 (a.m.), 13, and

14. This was done to reduce some of the heterogeneity resulting from different mineral assemblages that are be stable under differing redox conditions. Evidence for this was seen particularly in Mn concentrations which were close to 0 in samples with Eh <0.

RESULTS

Sediment Petrology and Mineralogy

Sediment size fraction analysis conducted for each sample station showed the sediments to be dominated by material coarser than 0.5 mm (Fig. 5). On average less than 2% of the sediments fell into the <63µ size fraction (silt-clay). Although the size fraction analysis is somewhat biased in regards to the total range of sizes with the >2mm fraction excluded, it is intended to characterize the most active portion of sediments. The coarse nature of La Primavera sediments is also apparent in surface area measurements with an average value of only 1.5 m^2/gm (Appendix A).

Very little variation was seen in local geology and sediment mineralogy over the 10 km of stream reach. Study of the >2 mm fraction showed sediments to be composed of varying proportions of pumice, welded rhyolite tuff fragments and obsidian with Fe-oxides coating some grains (Appendix C). No quartz, feldspar or mafic grains were seen in the >2mm fraction. The study of 6 thin sections revealed a similar composition with approximately 80% volcanic glass, consisting of obsidian, welded rhyolite tuff and pumice fragments, 12% quartz, 7-8% sanidine and generally <1% magnetite and iron oxides. The thin sections showed more primary minerals as a result of being made up from the <2 mm size fraction. Many grains showed little evidence of transport with sharp edges still present on much of the glasses.

Iron oxides, present as mineral coatings, discrete grains, and as partially oxidized

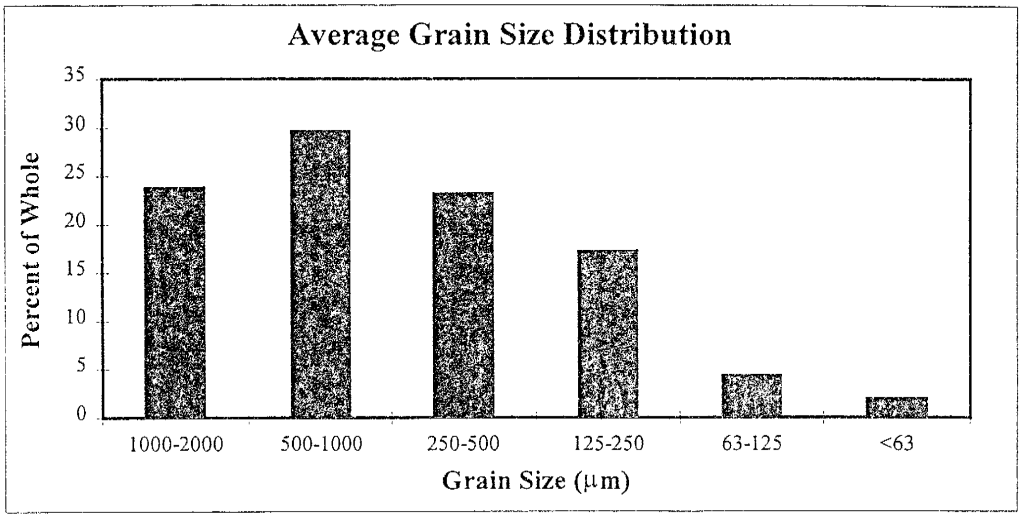

Figure 5. Average grain size distibution of La Primavera sediments. Sediments are dominantly coarse-grained and show little difference in grain-size distribution between sample sites.

mafic minerals were identified as hematite and goethite by VIS reflectance spectrophotometry. Figure 6 shows an example reflectance spectra with characteristic first derivative peaks for hematite at 555nm and goethite at 435nm. These spectra are qualitative in the sense that they only confirm the presence of hematite and goethite; quantification of the amount of oxides requires preparation of standard calibration curves for each oxide in a representative sediment matrix. The presence of manganese oxides was confirmed through several different selective dissolution procedures and occurred as thin dark coatings on some of the grains.

Spot-analysis using the electron microprobe showed Fe-oxide grains to contain As at levels 2-times above background glasses and minerals (Table 1). This method is not quantitative, but does confirm the enrichment of As in Fe-oxides over background. However, line scans traversing across Fe-oxide grains (Fig. 7) show no direct relationship between the amount of Fe and As (Fig. 8).

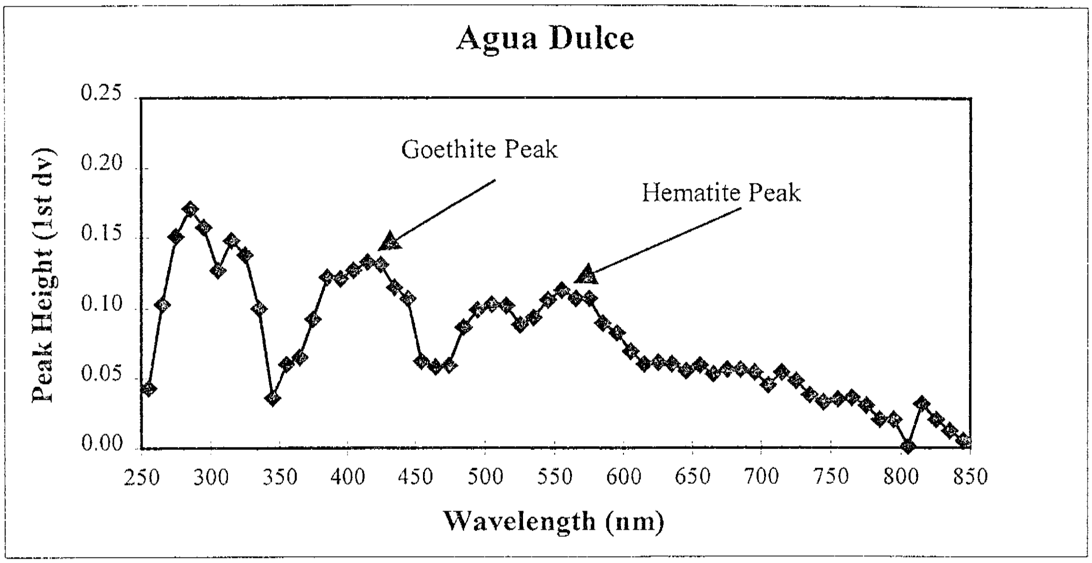

Figure 6. Reflectance spectra for a La Primavera sample collected at Agua Dulce. Peaks characteristic of hematite and goethite occurr at 555nm and 435nm, respectively.

Table 1. Counts of As measured for iron oxide and glasses by electron microprobe.

Sample ID	Mineral	Counts (As)	Sample ID	Mineral	Counts (As)
1	FeOx	2389	1	Glass	1536
1	FeOx	2375	1	Glass	1421
1	FeOx	2257	1	Glass	1558
1	FeOx	3273	1	Glass	1657
1	FeOx	2598	1	Glass	1572
1	FeOx	2667	1	Glass	1626
1	FeOx	2135	5	Glass	1510
1	FeOx	2927	5	Glass	1560
5	FeOx	4695	5	Glass	1576
5	FeOx	6688	5	Pyroxene	1966
5	FeOx	4398	8	Glass	1582
5	FeOx	3226	8	Glass	1628
5	FeOx	3059	9	Glass	1518
8	FeOx	2407			
8	FeOx	2162			
8	FeOx	3231			
9	FeOx	3005			
Average	FeOx	3140	Average	Glass	1593

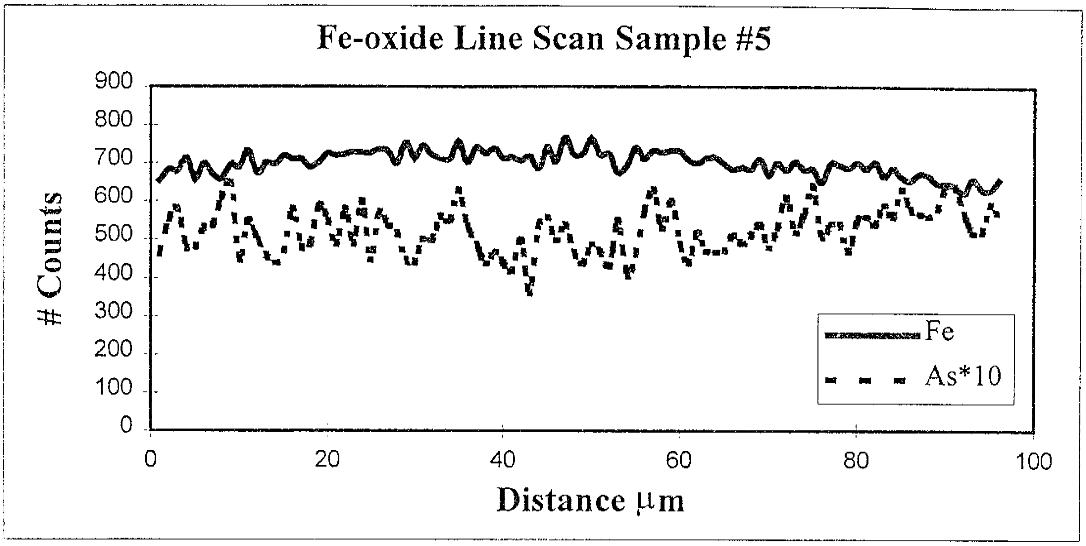

Figure 7. Electron microprobe line-scan across and Fe-oxide grain. No direct relationship exists between the amount of Fe and As in the grain.

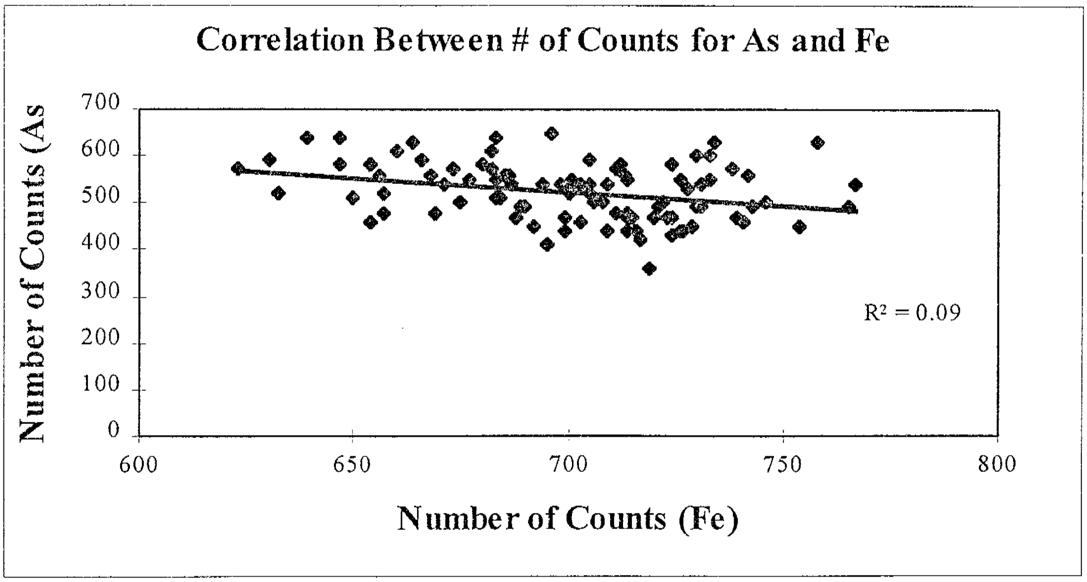

Figure 8. Correlation between the number of counts of As and Fe. There is no direct relationship between the amount of Fe and As in Fe-oxide grains determined by electron microprobe.

Carbonates were present as thickly laminated deposits of travertine at the spring sources and were also apparent in stream bank sediments as an effervescence due to acid reaction. Although carbonates were not visible in sediment thin sections their presence was confirmed by carbonate analysis using the system of vacuum lines and quadrupole mass spectrometer (Table 2). Percent carbonate ranged from non-detectable to 0.27% with a detection limit of 0.05% calculated as two times the relative standard deviation of a sample run in triplicate. Measured carbonate in sediments also showed some agreement with calculated saturation indices for calcite, dolomite and aragonite (Table 2). The presence of rhodochrosite ($MnCO_3$) in these waters is unlikely with negative saturation indices.

Comparison of initial modeling results, done with the older MinteqA2 database, to those of the MinteqU database revealed significant differences in predicted saturation indices for carbonate minerals. In the case of La Primavera, the calcium carbonate minerals calcite, dolomite and aragonite were under-predicted while rhodochrosite was over-predicted.

X-Ray diffraction analyses revealed the predominance of amorphous phases representing glasses and could only positively identify quartz. Attempts to isolate and concentrate clays were unsuccessful due to the very small amounts present relative to the large amounts of amorphous matter.

Total organic carbon in the sediments consisted of leaf, twig and algae fragments as well as thin algal coatings on some of the larger grains. Measured % TOC ranged from 1.2 to a relatively high value of 3.7 (Appendix A). The effect of interstitial water from

Table 2. Saturation indices predicted by MinteqU and measured by acid-evolved CO_2 and Quadrupole mass spectrometry. Negative saturation indices show undersaturated mineral phases while positive values indicate saturated phases.

	Saturation Indices Predicted by MinteqU			Measured Carb.
Sample ID	Calcite	Dolomite	Rhodochrosite	(wt%)
1	-0.16	-1.20	-0.83	0.07
4	0.38	0.17	-0.11	0.05
7	-0.41	-1.55	-0.62	ND
11	0.56	0.62	-0.09	0.09
13	-1.35	-2.60	-2.14	ND
17	0.67	1.01	-1.84	0.25
19	0.60	0.99	-1.44	0.08
Detection Limit (2*Relative Standard Deviation) = 0.05 wt%				

clays on measured % TOC is believed to be insignificant due to the vary small amount of clays present in sediments.

Rio Grande River samples were almost entirely composed of quartz-sand and silt with some small bits of organic material. Percent TOC is somewhat lower here than at La Primavera and averaged 0.9 % (Appendix D). Although a grain-size distribution analysis was not conducted on these sediments an average surface area measurement of 4.3 m^2/gm shows that these sediments are not significantly coarser than those from La Primavera (Appendix D).

Sediment Chemistry

Partial Extractions

Manganese determined by each of the extractions HNO_3, HNO_3+ HCl, H_3PO_4, and NH_2OH-HCl + HCl is proportional to total Mn measured by XRF (Fig. 9). However, only Fe determined by HCl+HNO_3 (Fig. 10) and As by HNO_3 (Fig. 11) show relationships to total Fe and As results from XRF. Percent recoveries of As, Mn and Fe relative to XRF totals are listed in Appendix A. Recoveries by the different extractions

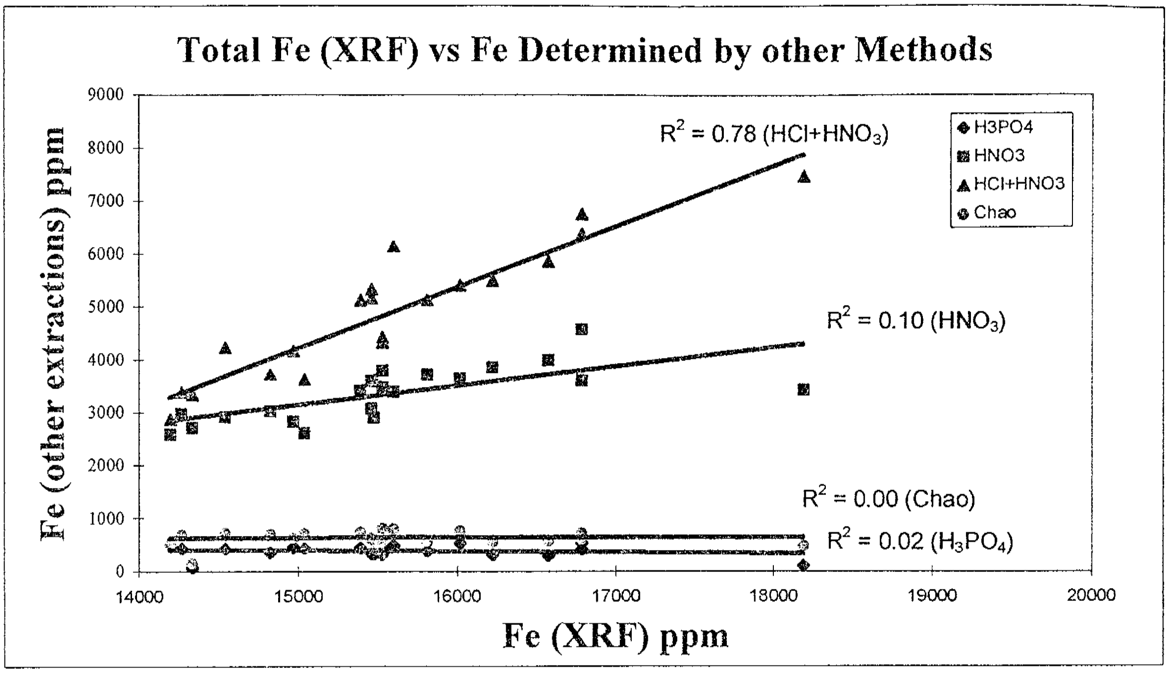

Figure 9. Correlation between total Mn determined by XRF and Mn determined by the other extraction methods. Manganese extracted by each method is proportional to XRF totals.

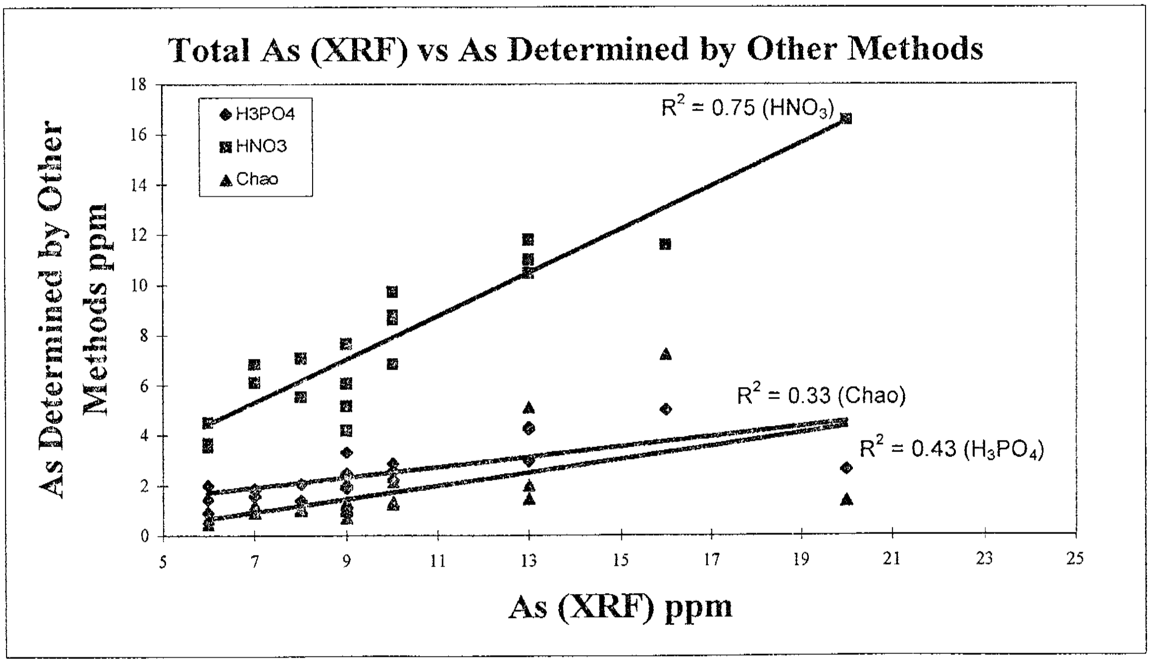

Figure 10. Correlation between total Fe determined by XRF and Fe determined by the other extraction methods. Only Fe extracted by HCl+HNO$_3$ is proportional to XRF totals.

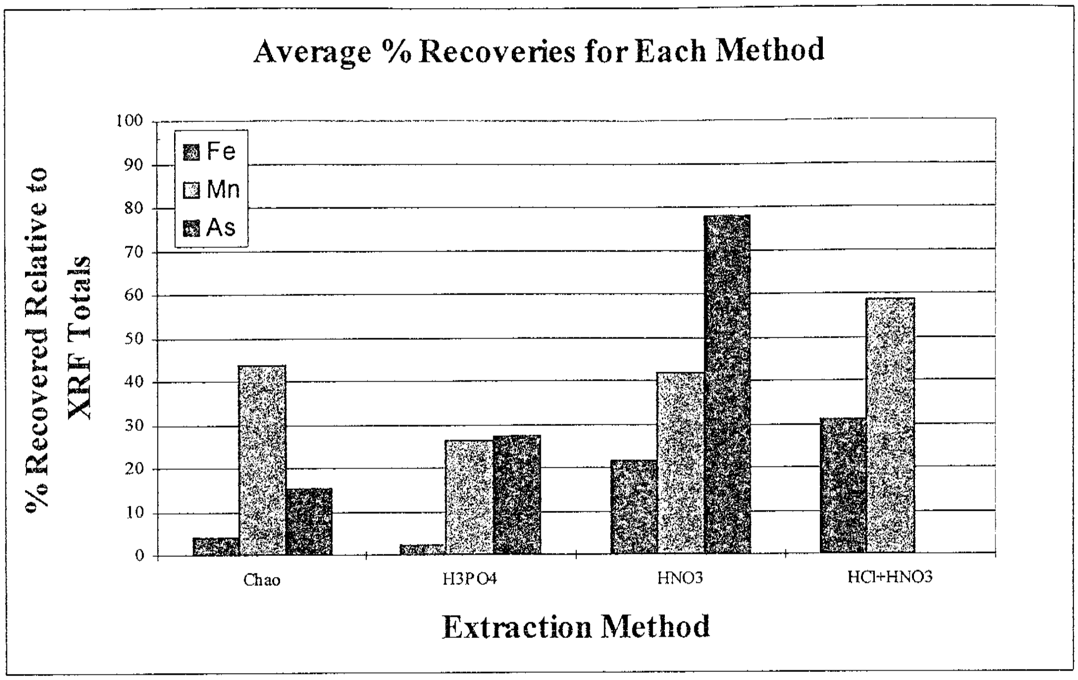

Figure 11. Correlation between total As determined by XRF and As determined by the other extraction methods. Only As extracted by HNO_3 is proportional to XRF totals.

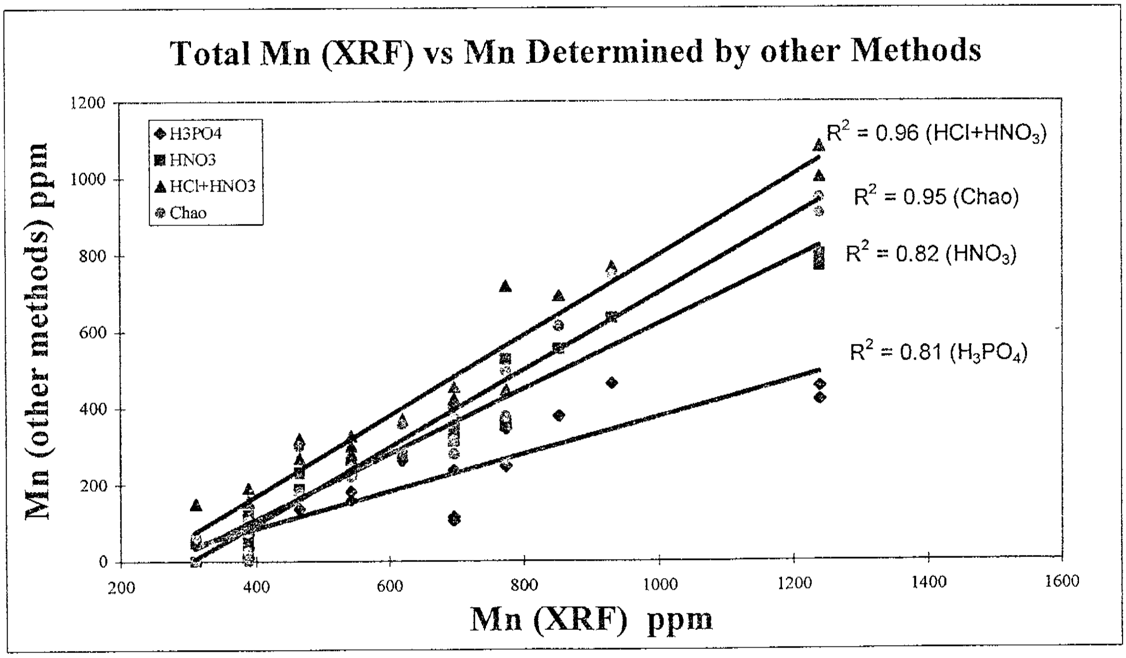

Figure 12. Average amount of Fe, Mn and As extracted from sediments by $HCl+HNO_3$, HNO_3, H_3PO_4 and $HCl+NH_2OH\text{-}HCl$ (Chao). Percent recoveries are reported relative to total Fe, Mn, and As determined by XRF. Arsenic was not determined in the $HCl+HNO_3$ extraction.

average 28 to 68% for Mn, 3 to 31% for Fe and 16 to 77% for As (Fig. 12). A large proportion of the total Mn, about 44%, was extracted by NH_2OH-HCl + HCl for dissolution of amorphous phases while only about 5% of the total Fe was solubilized. About 77% of the total As was extracted by HNO_3 which may result from the increased dissolution of Fe phases and organic matter by this extraction method. The contribution of As, Fe and Mn by dissolution of silicate minerals is believed to be insignificant as dissolved silica was very low, below 6 mg/l, in both NH_2OH-HCl+HCl and HNO_3 extracts (Appendix A). For comparison, silica found in the waters at La Primavera averaged about 250 mg/l.

Total As in sediments is not much higher than normal crustal abundances averaging about 8 ppm which is surprising given the high As concentrations of these waters (Appendix E). Analysis of the size fractions showed the $<63\mu$ fraction to contain the highest relative concentrations of As (Fig. 13); however, some samples showed a bimodal distribution with high concentrations in the coarser size fractions that may be related to Fe and Mn which also show similar distributions (Fig. 14). Although the silt-clay fraction has the highest relative concentrations it only amounts to a small percent of the whole sediment which results in most of the arsenic in a sample being contributed by the coarser size fractions (Fig. 15).

Results of the sequential extraction show As to be dominantly associated with organic matter and Fe/Mn-oxides with smaller amounts associated with the carbonate and exchangeable fractions (Fig. 16). About %80 of the Mn and 60 % of the Fe occurs in the Fe/Mn-oxide fraction indicating that most of the Mn and Fe is present as amorphous Arsenic(III) is also present in all samples and is proportional to As(V) with a positive

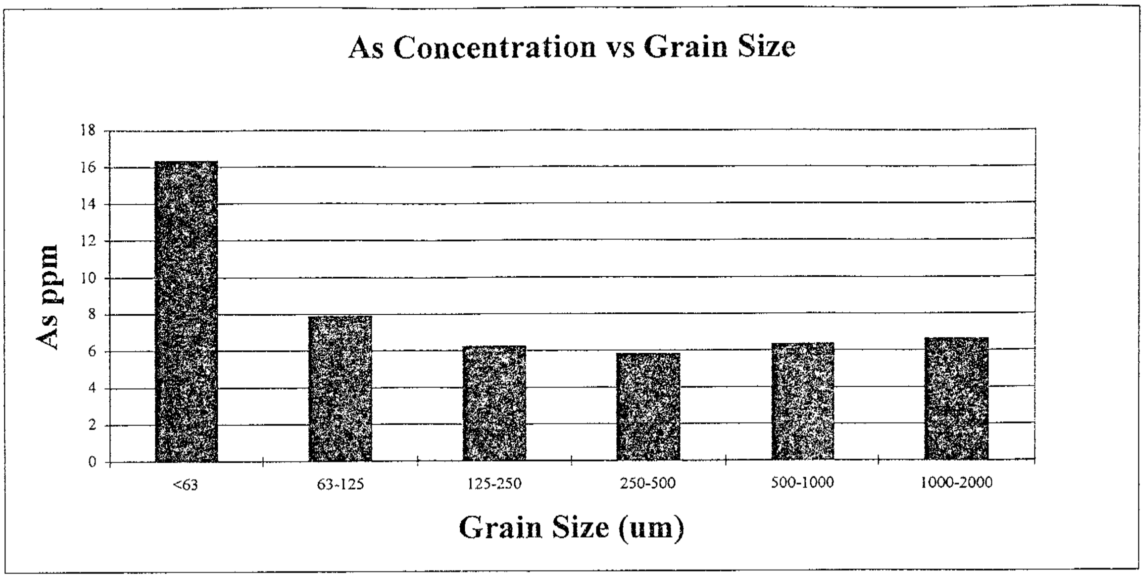

Figure 13. Average arsenic concentrations vs. grain size; results from HNO_3 digestions. Although the <63µm fraction contained the highest relative As concentrations some samples show a bimodal distribution with high concentrations in the 500-1000 and 1000 to 2000µm fractions.

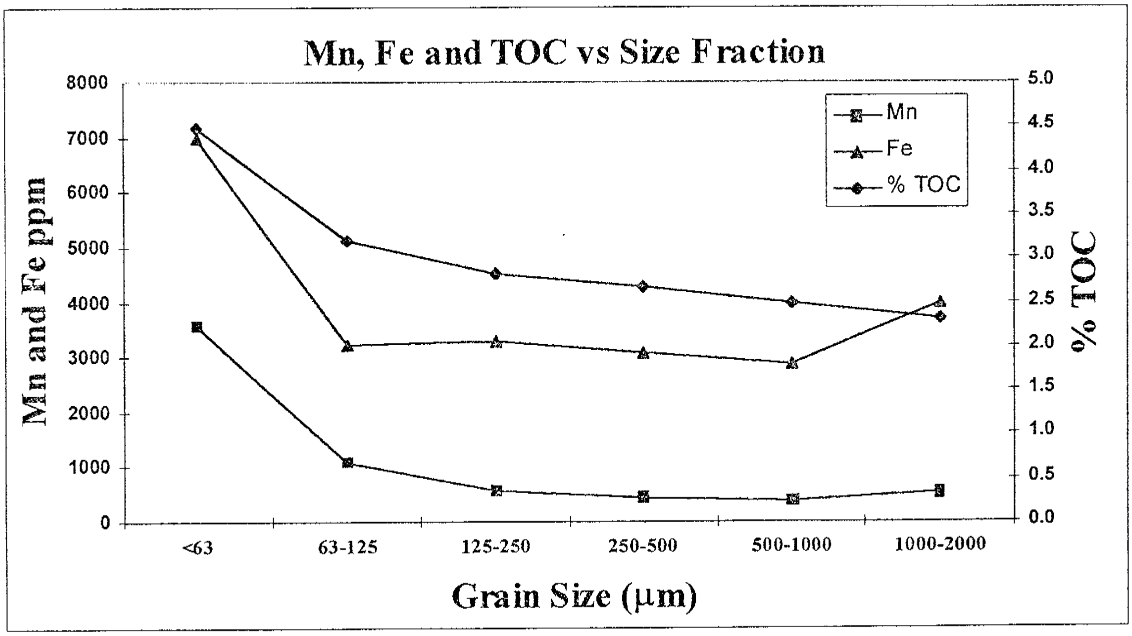

Figure 14. Relative amounts of Fe, Mn and %TOC as a function of grain size. Iron and Mn show a distribution similar to that for As with the highest amounts in the <63µm fraction and a slight increase in the 1000 to 2000µm fraction.

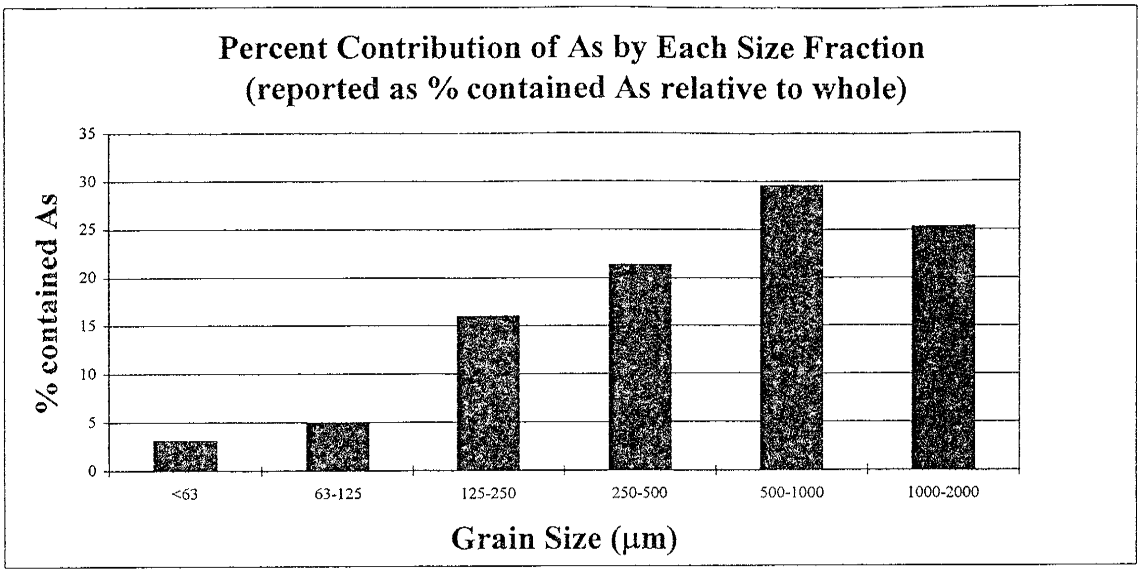

Figure 15. Plot showing the percent of As contributed by each size fraction towards the "whole" sample. Due to the fact that the <63µm sediment represents only a small fraction of the whole, most of the As in a sample is contained in the coarser material.

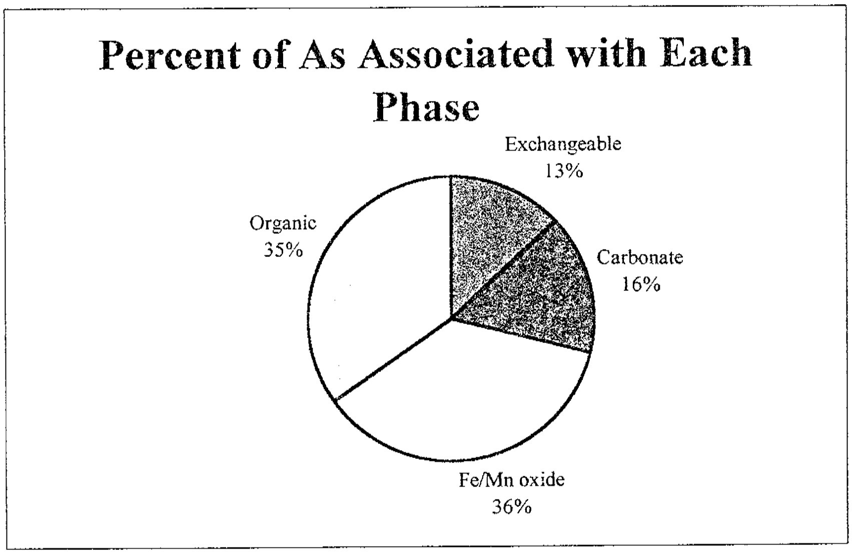

Figure 16. Relative proportions of As associated with the exchangeable, carbonate, Fe/Mn-oxide and organic phases. Arsenic primarily occurs with organic matter and Fe/Mn-oxide phases.

oxides (Fig. 17). These results also show some association of Mn with carbonate and a significant fraction of the Fe with organic matter.

Results of the sequential extraction procedure are intended to provide additional information that may be used to make inferences about mineral phases and possible associations with As. They are not to be regarded as absolute values as there is evidence that some re-adsorption and non-selective dissolution may occur (Kheboian and Bauer, 1987; Xiao-Quan and Bin, 1993). However, it is believed that the sequential extraction procedure can provide useful, valid information particularly when similar or supporting results can be obtained through alternate methods.

Arsenic Speciation of Sediments and Algae

Results of speciation of sediments for As(III), As(V), MMA and DMA show As(V) to be the dominant species present in La Primavera sediments (Fig. 18). correlation coefficient of 0.86 (Fig. 19). Qualitatively, MMA is also proportional to As(III) and As(V), but was below detection limits in many cases. DMA was found at only one sample site.

Algae contain between 18 and 68 ppm total arsenic on a dry weight basis (Appendix A) which is predominantly As(V), but also contain measurable As(III), MMA and DMA (Fig. 20).The two different morphological types of algae recognized at La Primavera also seemed to have differing capacities to uptake As. The type containing the highest concentrations of arsenic were those present as dense mats covering the rocks and stream bottom near the source where waters are the hottest. The filamentous algae that generally occurred in cooler waters contained lower total As.

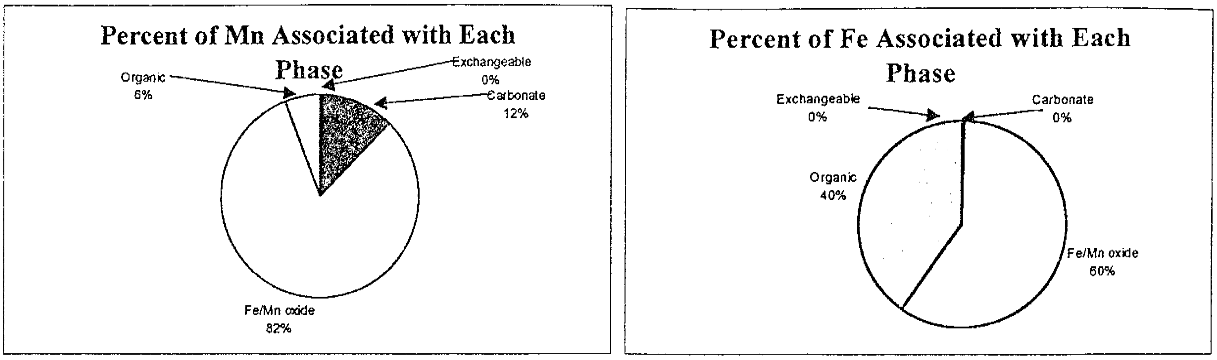

Figure 17. (a) Relative proportions of Mn associated with each phase; (b) relative proportions of Fe associated with each phase. Although a significant fraction of Fe is associated wih organic matter Fe and Mn appear to be present predomiantly as oxides.

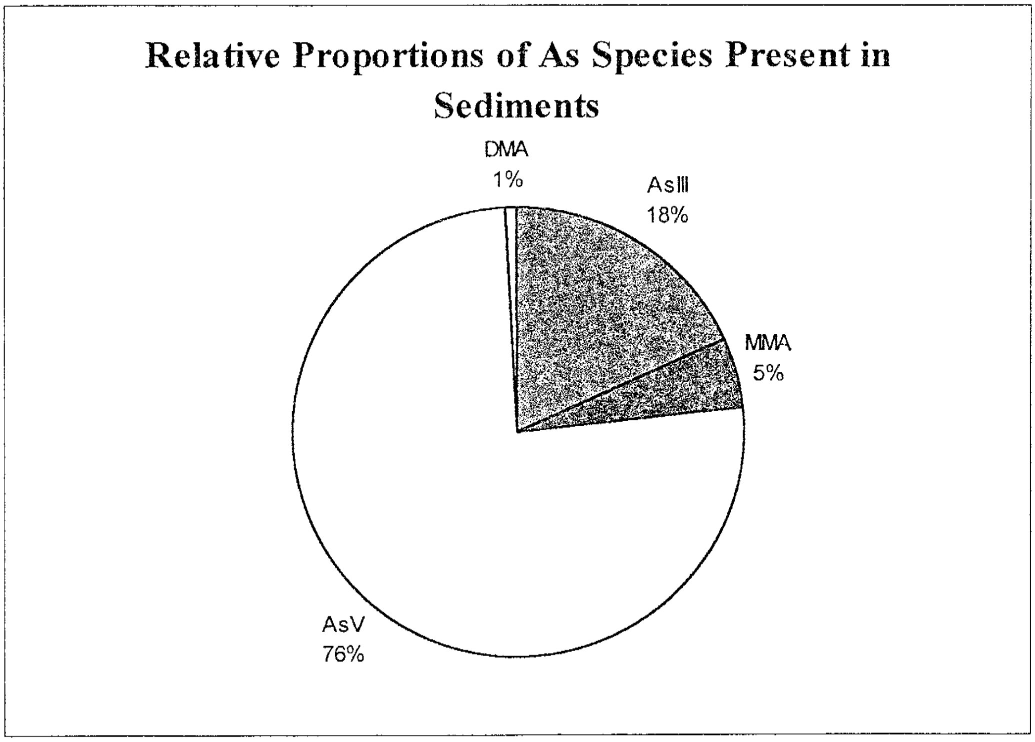

Figure 18. Plot showing the relative proportions of As(III), As(V), MMA and DMA present in sediments. At La Primavera As(V) is the dominant species present accounting for about 75% of the total As.

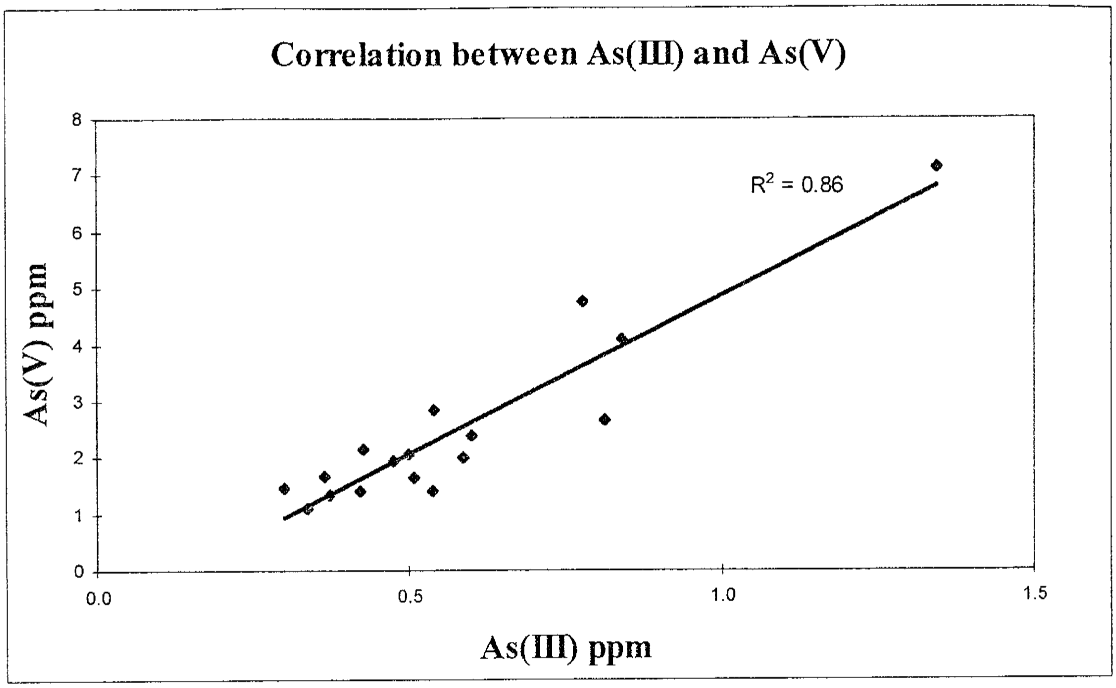

Figure 19. Plot showing the correlation between As(III) and As(V). Arsenic(III) is proportional to As(V) with a positive correlation coefficient of 0.86.

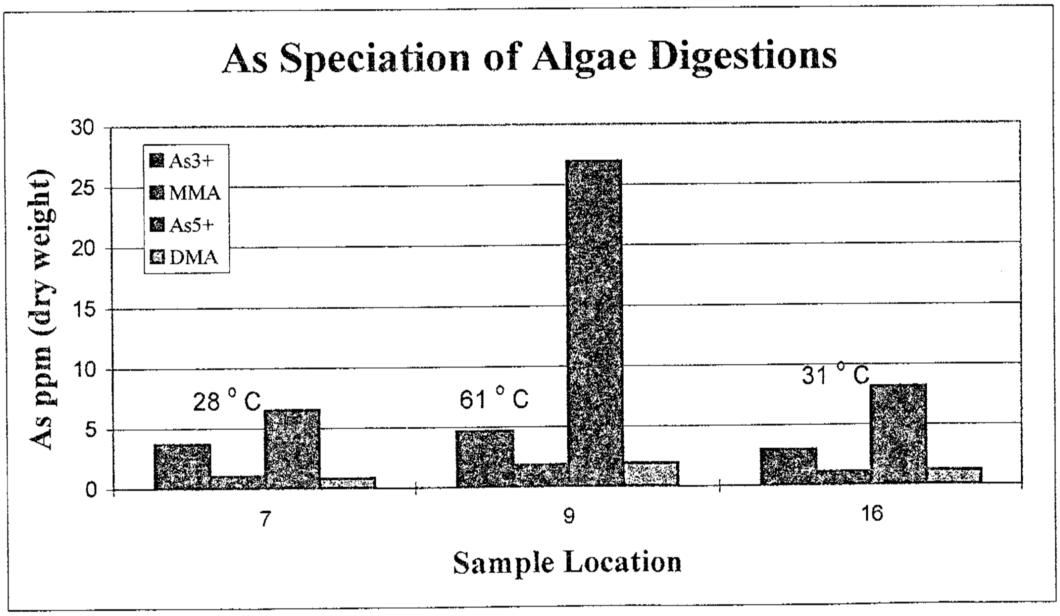

Figure 20. Plot showing the relative amounts of the As species present in algae extracts. Algae with the highest concentrations of As were those occurring in the hottest waters.

Comparisons Between Sediment and Water Chemistry

Total As concentrations in waters average about 1 ppm and are dominated by As(V); As(III) occurs at only a few localities where reducing waters are found (Appendix E). Comparison of total and speciated As concentrations of surface water and sediments (Fig 21) revealed no correlation between the two (Fig. 22). Also, no distinct trends were found between other elements in surface water and sediments. Although no correlation exists between surface water and sediments it is possible that correlations may exist between sediment pore-water and sediments, however these were not sampled for this study.

Sediment Comparison Between La Primavera and Rio Grande

Comparisons were made between La Primavera and Rio Grande sediments to explain the seemingly low As sediment concentrations found at La Primavera. Low As-Water/As-Sediment ratios of 0.125 for La Primavera compared to 0.0035 for the Rio Grande indicates that arsenic is more mobile in La Primavera waters with much less being retained in the sediments (Table 3). Average surface area is generally greater for Rio Grande sediments, but overlaps some with those from La Primavera. Rio Grande sediments also generally have lower % TOC and extractable Mn, but have higher Fe concentrations and Fe/Mn ratios. When ratioed to sediment surface area, As as well as Mn and % TOC ratios are about an order of magnitude higher for La Primavera sediments while Fe ratios are fairly similar.

Statistical Analysis and Inter-Element Relationships

Correlation matrices (Appendix B) and regression analyses indicated positive correlations between As and %TOC and Mn for each of the methods used (Figures 23-

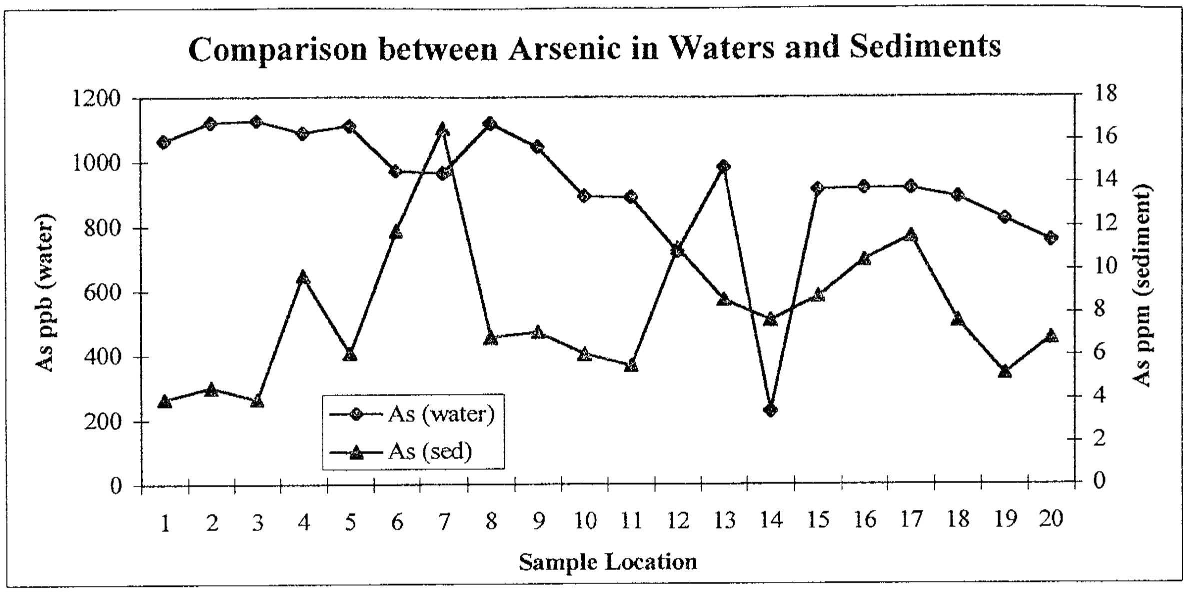

Figure 21. Figures showing the comparison between As in sediments and surface waters. No obvious trends are apparent in La Primavera samples.

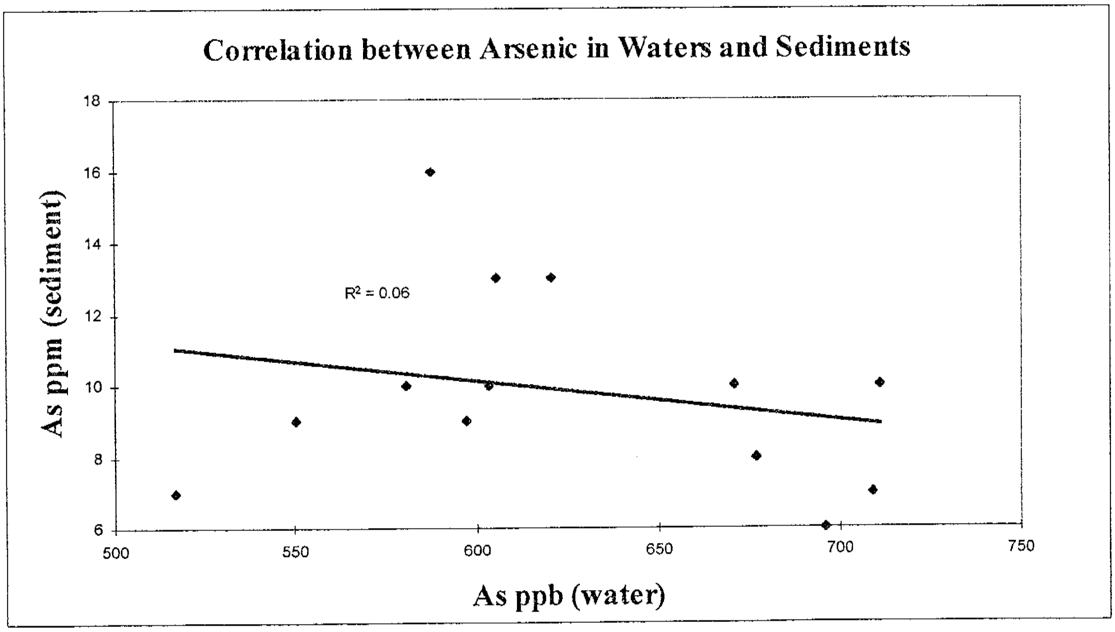

Figure 22. Figure showing the correlation between between As in sediments and surface waters. No obvious correlation exists between As in waters and sediments.

Table 3. Comparison of sediment components and surface area ratios for La Primavera and Rio Grande sediments.

	Average Actual Value		**Ratio to Sediment Surface Area**	
	Rio Grande	**La Primavera**	**Rio Grande**	**La Primavera**
Acid Sol. As (mg/kg)	1.4	8	0.28	5.3
% TOC	0.9	2.1	0.2	1.4
Acid Sol. Fe (mg/kg)	6700	3330	1340	2220
Acid Sol. Mn (mg/kg)	180	300	36	200
As-water (ppm)	0.005	1.0		
Surface Area (m^2/gm)	5	1.5		
As Ratio Water/Sediment	0.0035	0.125		
Fe/Mn Ratio	37	11		

29). Also, similar correlations occur with As(III), As(V) and Mn and TOC (Figures 30-31). Monomethylarsonate and DMA are not present in most of the samples and were not treated statistically. No correlations exist between As and Fe analyzed by any of the methods (Figure 32-34), or As and Al determined by HNO_3 or NH_2OH-HCl+HCl (Figure 35-36). Although the lack of correlation between Fe and As shows that they are not proportional to each other, results discussed previously in this study do indicate that Fe-oxides may be enriched in As.

Although no trends between surface water and sediments were observed for the stream reach, high values for filtered Fe at sample stations 16 and 17 seem to occur along with high values in sediments. These two locations are also places where sediments have higher concentrations of As, Mn and %TOC.

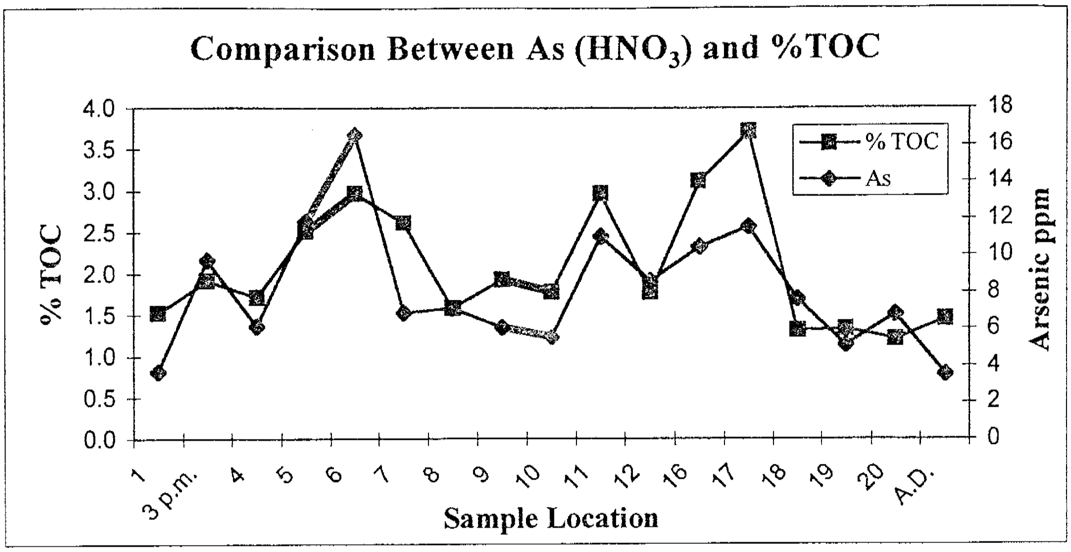

Figure 23. Plot showing the comparison between As, extracted by HNO_3, and % TOC. Arsenic showed a downstream trend similar to that of % TOC. The tributaries Agua Verde (samples 5 and 6) and Agua Brava (samples 9 and 10) are indicated by heavy lines on this plot.

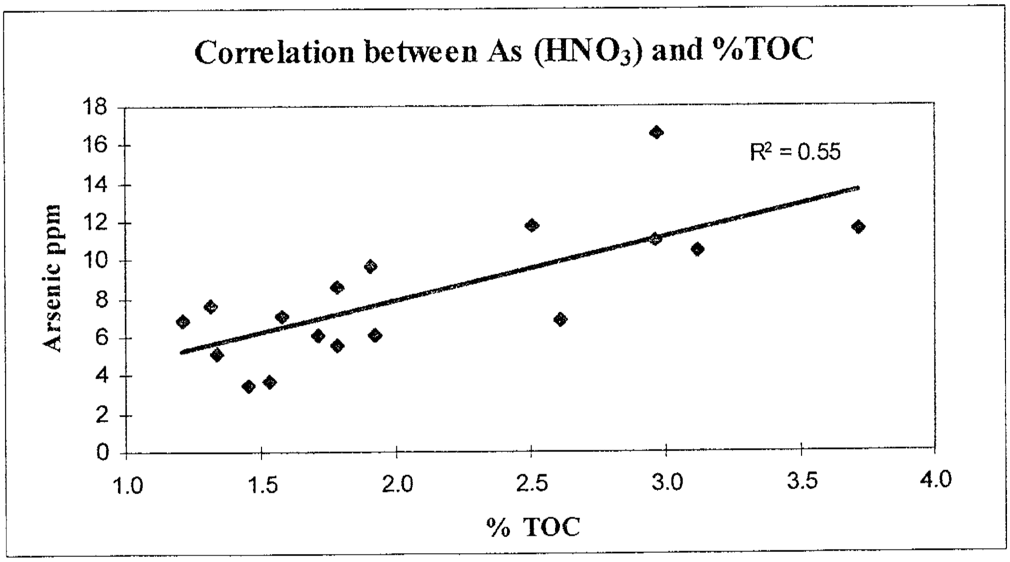

Figure 24. Correlation between As extracted by HNO_3, and % TOC. An r^2 of 0.55 indicates a positive correlation between As and % TOC in sediments.

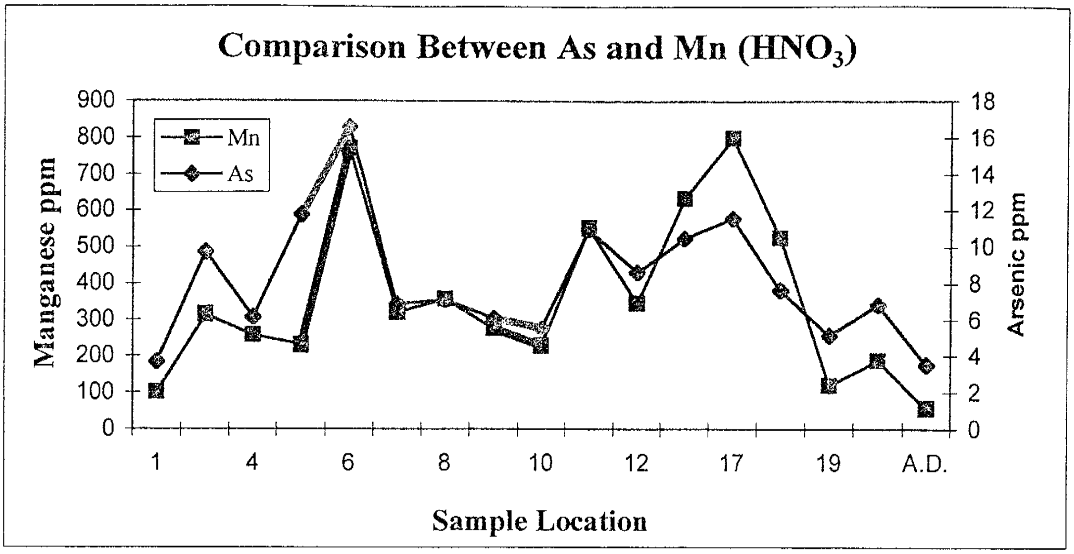

Figure 25. Comparison between As and Mn, both extracted by HNO_3. Arsenic also shows a downstream trend similar to that of Mn. The tributaries Agua Verde (samples 5 and 6) and Agua Brava (samples 9 and 10) are indicated by heavy lines on this plot.

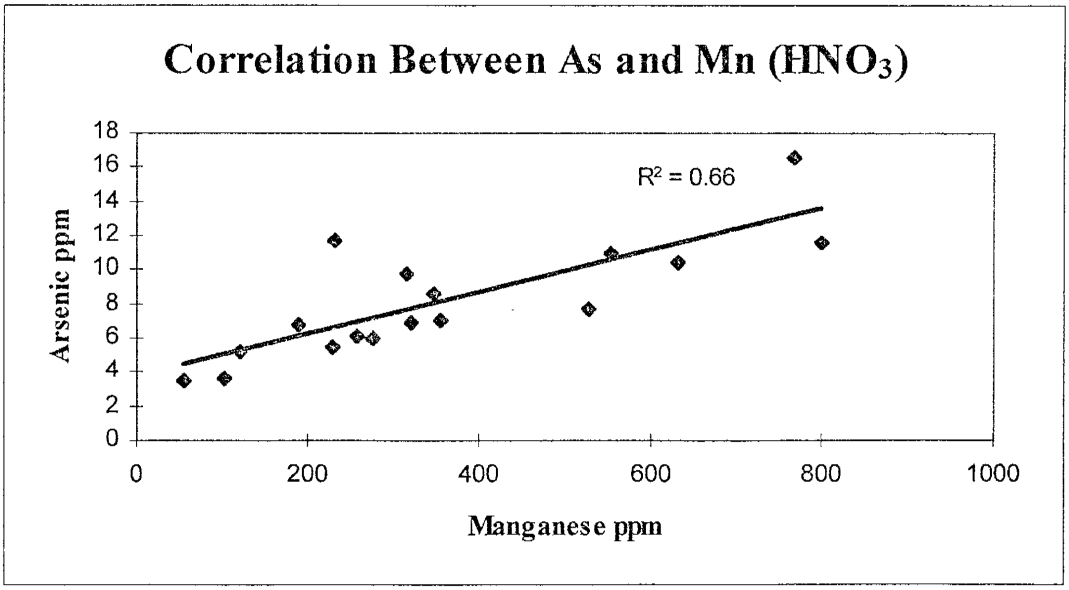

Figure 26. Correlation between As and Mn extracted by HNO_3. An r^2 of 0.66 indicates a positive correlation between As and Mn in sediments.

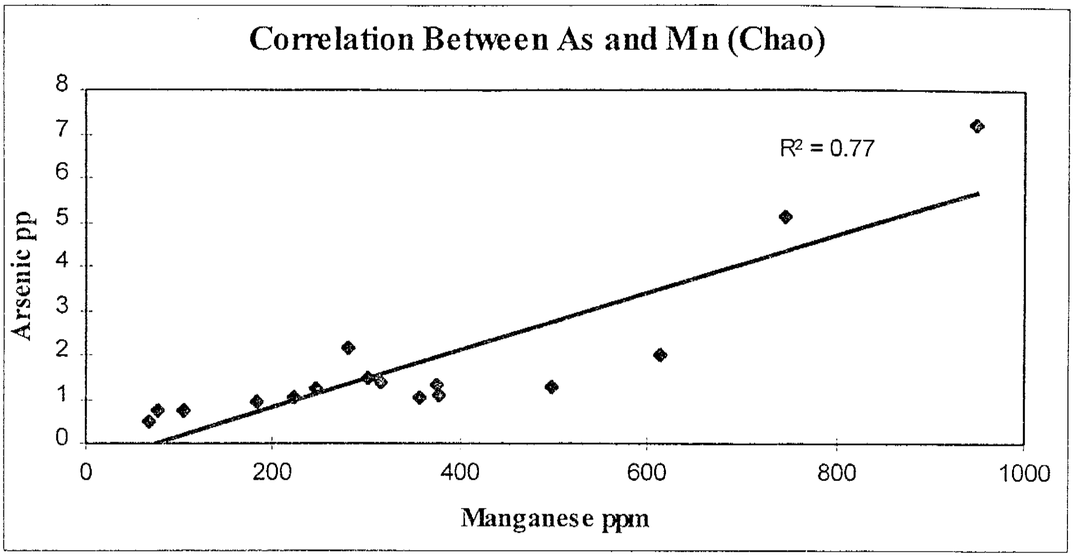

Figure 27. Correlation between As and Mn determined by HCl + NH_2OH-HCl (Chao). An r^2 of 0.77 indicates a positive correlation between As and Mn determined by this method.

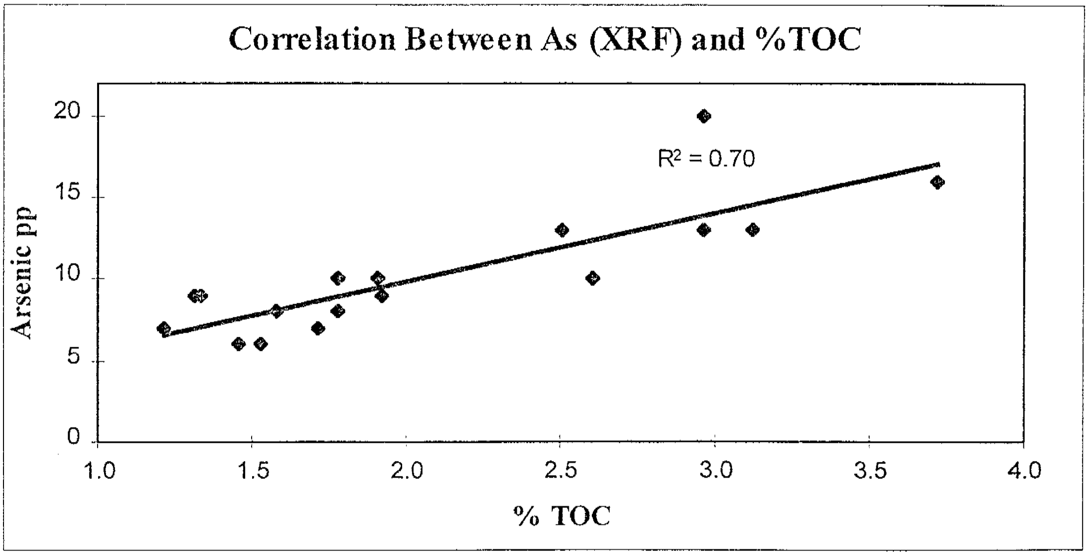

Figure 28. Correlation between total As, determined by XRF, and % TOC. An r^2 of 0.70 indicates a positive correlation between As and % TOC.

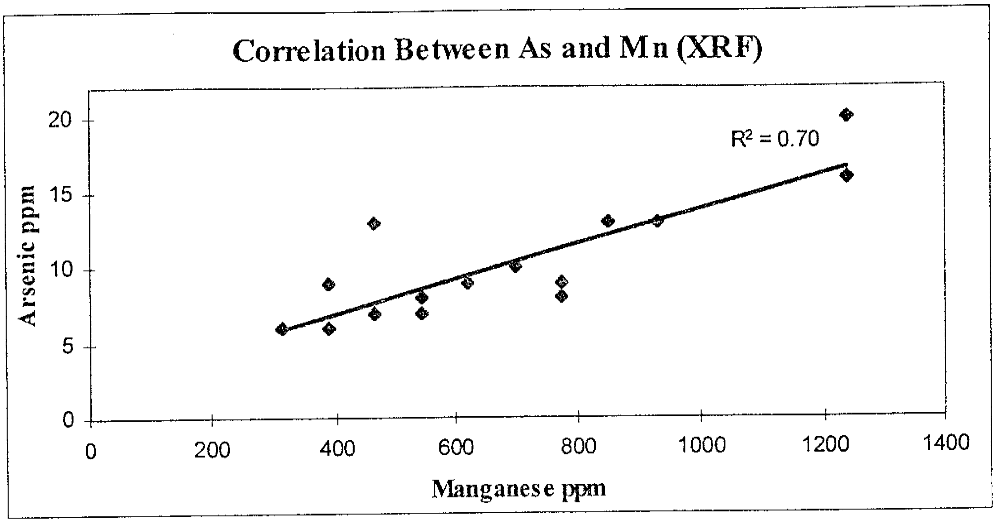

Figure 29. Correlation between total As and Mn determined by XRF. An r^2 of 0.70 indicates a positive correlation between As and Mn determined by this method.

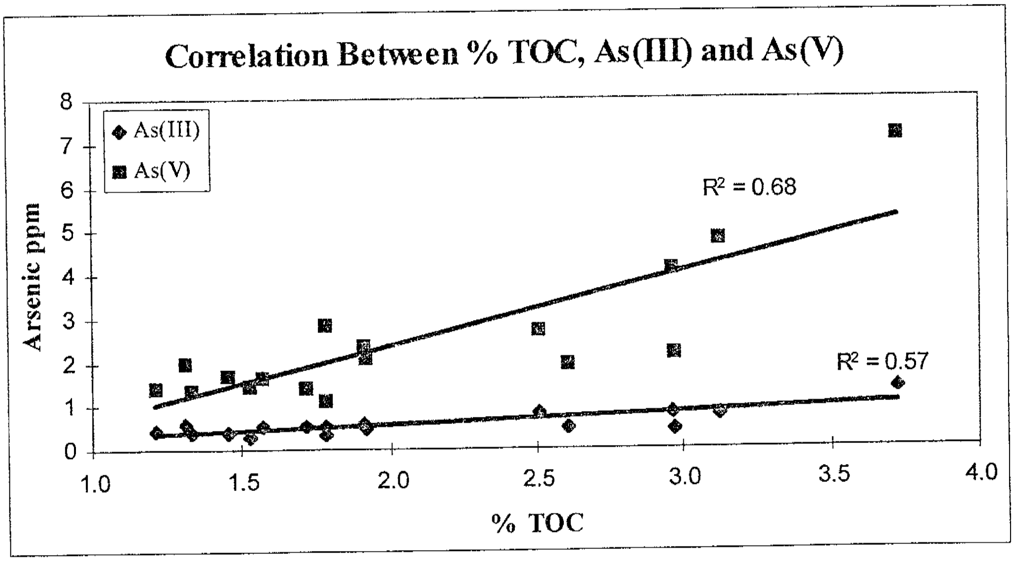

Figure 30. Correlation between %TOC and As(III) and As(V). Both As(III) and As(V) show positive correlations with %TOC.

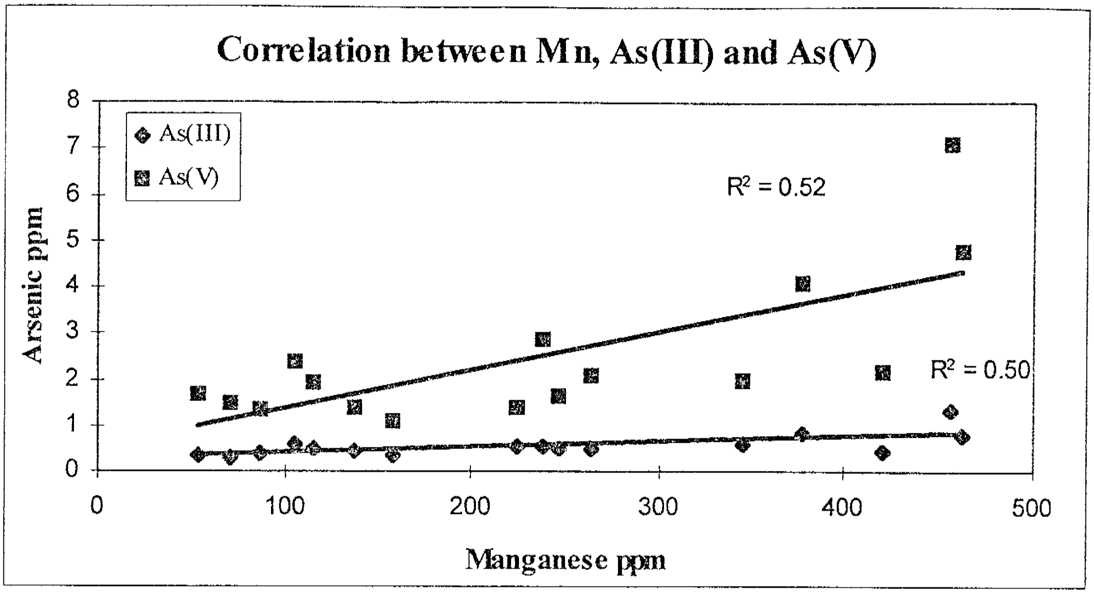

Figure 31. Correlation between Mn and As(III) and As(V). Both As(III) and As(V) also show positive correlations with Mn.

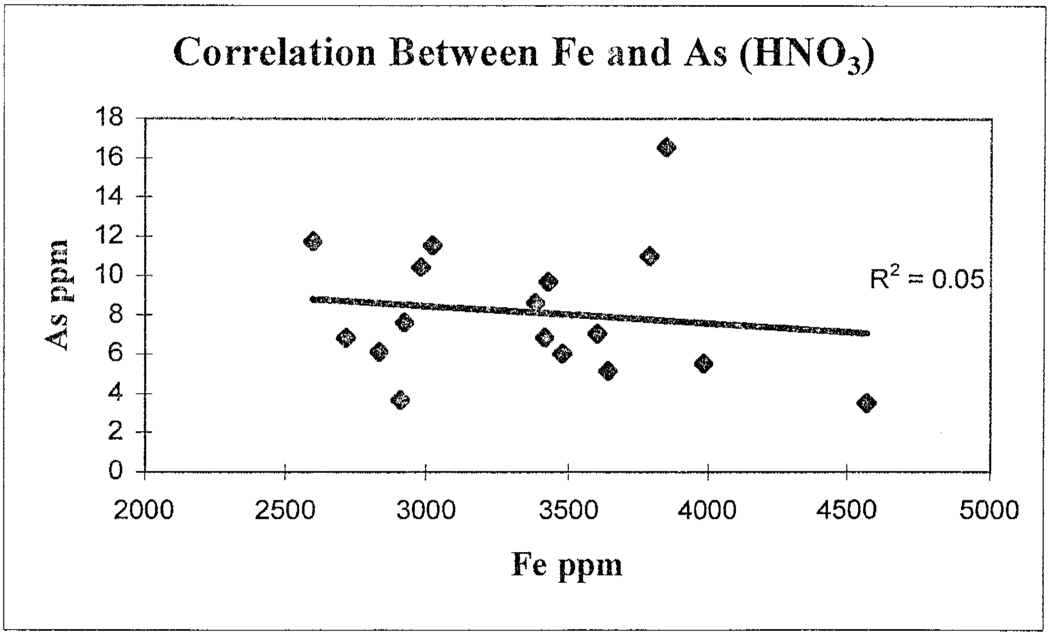

Figure 32. Correlation between Fe and As determined by HNO_3 digestion. No correlation was found between Fe and As in sediments determined by this method.

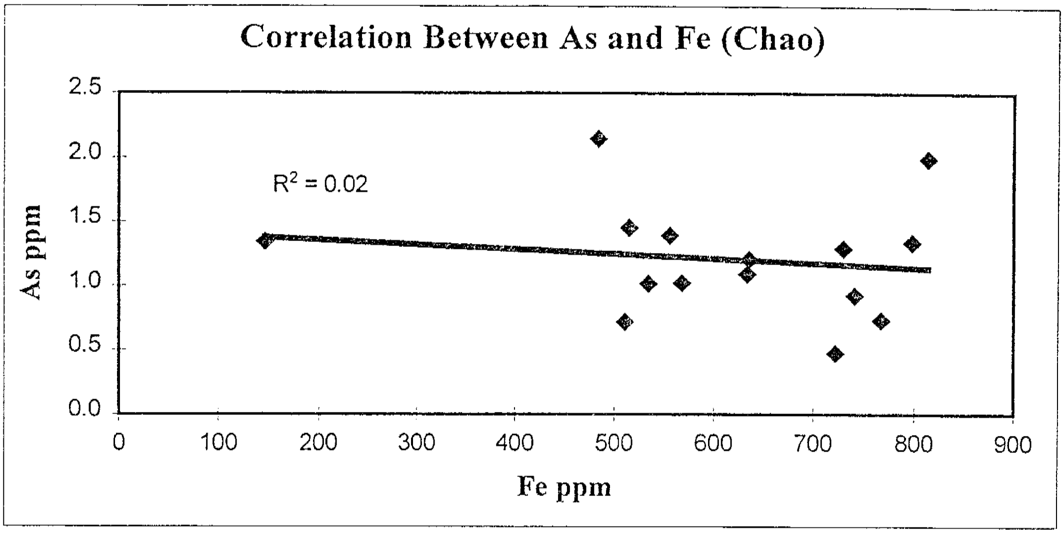

Figure 33. Correlation between Fe and As determined HCl+NH_2OH (Chao). No correlation was found between Fe and As in sediments determined by this method.

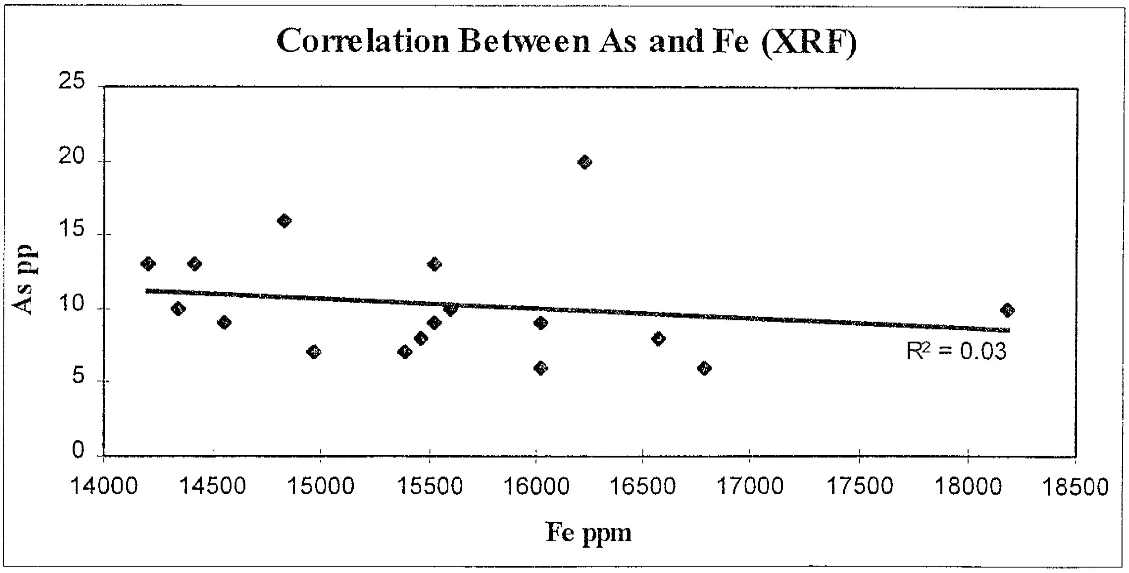

Figure 34. Correlation between Fe and As determined by XRF. No correlation was found between total Fe and As in sediments.

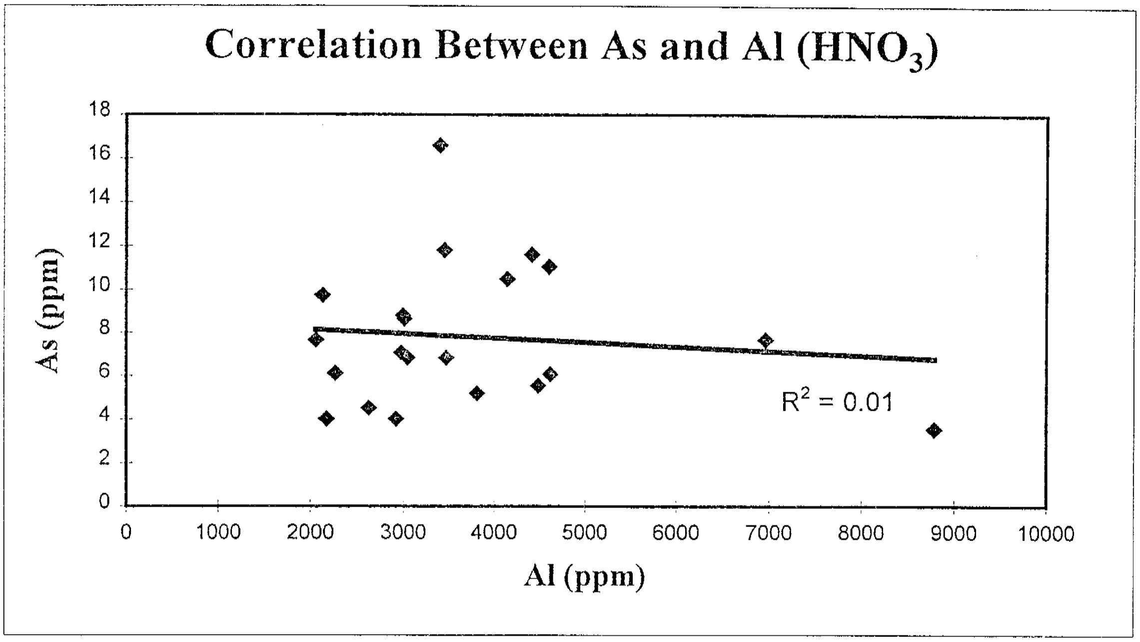

Figure 35. Correlation between As and Al determined by digestion with HNO_3. No correlation was found between As and Al determined by HNO3.

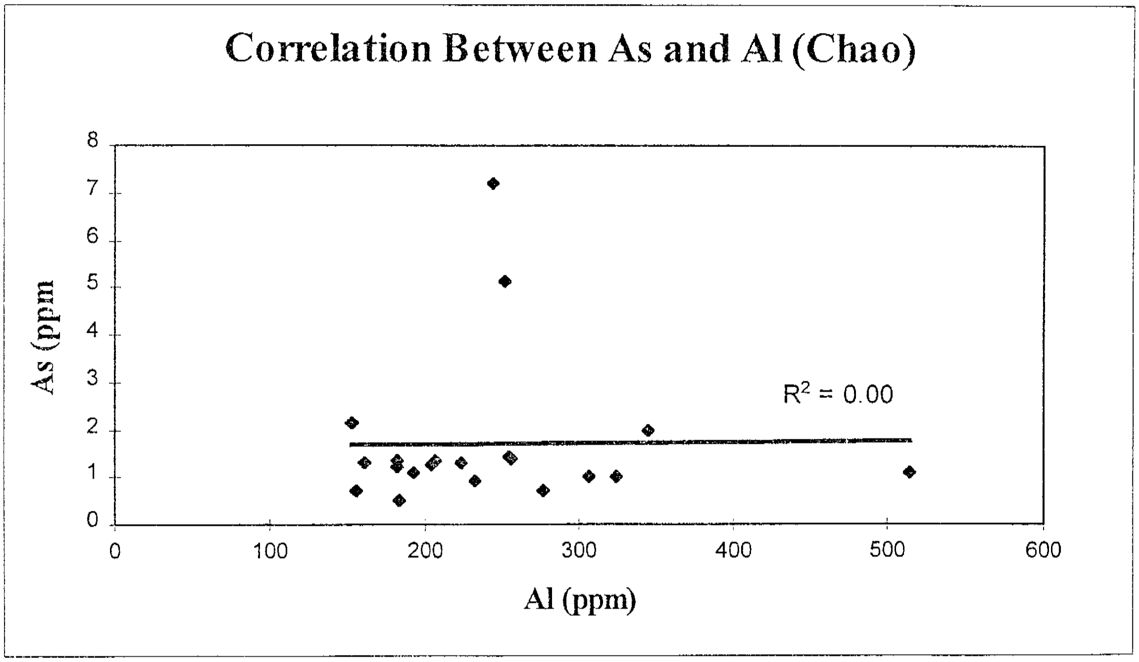

Figure 36. Correlation between As and Al determined by Chao extraction: No correlation was found between As and Al determined by this method. Removal of the two high As points does not improve the correlation.

DISCUSSION

Aspects of Sediment Mineralogy Inferred by Partial Extraction

The scavenging capacity of the amorphous phases of Fe and Mn-oxides is well known and is often the most important factor controlling trace element mobility (Chao and Theobald, 1976; Chao, 1984). They are highly reactive, particularly in water-logged environments, and retain an amorphous or weakly crystalline structure due to alternate dissolution and re-precipitation (Chao, 1984). Their scavenging capacity is attributed to their ability for non-stoichiometric coprecipitation with metals and an extremely large surface area that provides an abundance of sorption sites (Chao, 1984). In La Primavera sediments hematite and goethite were identified by electron microprobe, petrographic and spectral techniques. However, these methods do not necessarily confirm the presence of amorphous phases of Fe and Mn-oxides. Instead, they are inferred through partial extractions that are specifically designed for the selective dissolution of amorphous phases.

Evidence for the existence of amorphous Fe-oxides in La Primavera sediments is provided by results from the sequential extraction procedure. About 60% of the Fe extracted by this method was removed with the reagent designed for selective dissolution of amorphous Fe-oxides. Any re-adsorption of Fe on to organic matter that may have occurred would only lead to an underestimate of the proportion of Fe associated with amorphous phases. Also, Fe is virtually undetectable in the exchangeable and carbonate phases and should not contribute significantly, by re-adsorption, to the amount of Fe associated with Fe-oxides. However, it is not obvious why a significant portion of Fe would be found associated with organic matter and is here assumed that some of it was originally taken up by the plants and algae that make up much of the organic matter. This assumption was made in-part because Fe should behave similarly to Mn which showed very little evidence of re-adsorption on to the organic fraction, amounting to only about 5% of the total.

Other supporting evidence for the presence of amorphous Fe phases is found in comparison of Fe extracted by each of the methods to total Fe determined by XRF. Only Fe extracted by $HCl+HNO_3$ shows a correlation to total Fe measured by XRF. This particular method is relatively rigorous, extracting about 30% of the total Fe relative to XRF totals in comparison to the other methods that generally remove less than 15% of the total. Also, Fe extracted by the other methods does not show any correlation to Fe determined by $HCl+HNO_3$ or total Fe. These findings suggest that $HCl+HNO_3$ dissolves amorphous phases as well as some of the more residual forms of Fe-oxide while the other extractions, which are not as strong, remove mainly the more soluble amorphous phases.

Analysis of Mn in each fraction from the sequential extraction procedure indicated that about 80% of the Mn removed by this method resides as amorphous Mn-oxide. Given the predominance of Mn in this fraction, it is doubtful that re-adsorption or non-selectivity would significantly alter this finding. About 15% of the Mn is associated with the carbonate fraction. Although rhodochrosite ($MnCO_3$), is not predicted by MinteqU to be a stable phase in La Primavera waters other carbonate phases such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are stable and some substitution of Mn^{2+} for Ca^{2+} is possible. The presence of very small amounts of carbonate in these sediments is also confirmed by the method of acid-evolved CO_2 analysis on the quadrupole mass spectrometer used in this study. Black Mn-rich calcite found on some boulders in the stream at Agua Verde also gives some evidence to this possibility, but was not found in-place and its origin cannot be precisely determined.

Comparison of the amounts of Mn extracted by each method, relative to XRF totals, show Mn phases to be much more soluble than Fe phases. Also, Mn extracted by each method shows a good correlation with each other and total XRF Mn. These findings indicate that La Primavera sediments are probably dominated by amorphous or weakly crystalline Mn-oxides that account for about half of the total sedimentary Mn.

Associations of Arsenic With Sedimentary Phases

The finding that only As extracted by HNO_3 digestion is proportional to total As determined by XRF is most likely due to the fact that it removes, on average, about 77% of the total. The other extractions remove about one-fifth to one-third of the total As which is probably associated with amorphous phases. These results indicate that As is dominantly present in secondary mineral phases and organic matter, as little dissolution of silicate phases occurred. This also indicates that the varying proportions of pumice, welded tuff and obsidian, which are similar in composition, are non-reactive and have little effect on As mobility.

The sequential extraction showed relatively equal proportions of As to be associated with the exchangeable and carbonate fractions. Although it is possible that some of this may result from non-selectivity of the reagents and re-adsorption, these findings are not unreasonable. The relatively large amount of As, compared to Mn and Fe, extracted with the exchangeable fraction could be due to the fact that it is an oxyanion with different binding strengths than the cations. The association of As with carbonate is also reasonable given that small amounts of carbonate is present in La Primavera sediments. The sequential extraction also showed about 70% of the As to be equally associated with organic matter and Fe/Mn-oxides. This would seem to indicate that organic matter and Fe and Mn-oxides are a more important sink for As than are carbonates or ion-exchange processes at La Primavera.

The relationship between As, organic matter and secondary oxides found in the sequential extraction is also supported by positive correlations between %TOC and Mn for each of the other methods used. This relationship was found for As and Mn determined by XRF, HNO_3 and NH_2OH-HCl+HCl as well as both of the inorganic As species and Mn extracted with H_3PO_4. However, no correlation exists between As and Fe determined by any method. As with the partial extractions, results of the electron microprobe analysis also showed that As is not proportional to Fe in Fe-oxides. This does not mean that As is not associated with Fe-oxides, only that it is not proportional. Electron microprobe analysis of sediment samples did reveal an enrichment of As in Fe-oxide grains relative to nearby glasses and mafic minerals. It is also likely that much of the As removed in the amorphous Fe and Mn-oxide fraction of the sequential extraction can be attributed to amorphous Fe-oxides. The lack of correlation is probably due to the fact that the changes in As concentration between sample stations are several orders of magnitude smaller than are changes in Fe concentrations, and may not show up do to sample heterogeneity.

The positive correlation between As and Mn and lack of one with Fe is unexpected. Numerous studies have shown correlations between As and Fe and attribute this to a combination of adsorption and or coprecipitation (Manning and Goldberg, 1997; Sadiq, 1995; Bowell, 1994; Belzile and Tessier, 1990; Brannon and Patrick, 1987;

Elkhatib et al., 1984; Pierce and Moore, 1981; Pierce and Moore, 1980; Jacobs et al., 1970) while reported associations of As with Mn-oxides are not as common (Mok and Wai, 1990; Carpenter, 1986; Peterson, 1986; Takamatsu et al., 1985; Crecelius, 1975). A study by Takamatsu et al. (1985) has shown that adsorption of divalent cations Mn^{2+}, Sr^{2+}, Ba^{2+} and Ni^{2+} onto the surface of hydrous manganese oxides releases H^+ ions. This process results in the formation of a net positive surface charge with the capacity to adsorb anions. The process of anion sorption on to hydrous manganese oxides proposed by Takamatsu et al. (1985) is one mechanism that could help explain the findings at La Primavera. Other mechanisms that may contribute to the relationship between Mn-oxides and As are ligand exchange and coprecipitation.

The positive correlation between As and %TOC is also interesting because organic matter is generally believed to be an unimportant sink for As. Organic matter has an overall negatively charged surface and should only be important as a source of cation-exchange. In this case much of the As associated with organic matter may represent As originally taken up by the plants and algae that make up the organic matter. This does not seem unreasonable given that analysis of algae samples revealed total As concentrations ranging up to 68 ppm. Results of the sequential extraction also lends supporting evidence to the positive correlation between As and %TOC.

Some findings have shown that carbonates may act as a sink for As, particularly at higher pHs (Goldberg and Glaubig, 1988; Brannon and Patrick, 1987). The sequential extraction on La Primavera sediments does show some As being associated with the carbonate fraction and pHs are within the range in which carbonates retain a positive surface charge. However, the carbonate is present in amounts too small to quantify so that possible correlations between it and As can not be determined. Attempts to determine possible correlations between As and carbonate predicted in MinteqU were also inconclusive.

Arsenic has also been found to be associated with Al-oxides and hydroxides (Huang, 1975). However, no direct correlation was found between As and Al in La Primavera sediments. This may be due to the alkaline waters and the fact that Al-oxides and hydroxides have a net negative surface charge above pHs of 5 to 6. Aluminum phases would be expected to play a limited role in As sorption at La Primavera.

Arsenic Speciation of Sediments and Algae

Results of As-speciation of stream sediments and algae are suspect due to the fact that dried sediments were used instead of wet. Air-drying of the sediments and grinding to -80 mesh was chosen as a sample preparation technique to reduce heterogeneity resulting from the wide distribution of grain sizes. This technique provides better reproducibility, but may have caused some oxidation of As(III) to As(V) resulting in artificial proportions of inorganic As species. Atmospheric oxidation of As(III) to As(V) may also provide an explanation for the strong correlation between inorganic As species found among the samples. Given that each of the samples dried under the same conditions, oxidation of As(III) to As(V) should also occur at similar rates producing uniform As(III)/As(V) ratios. However, the proportions of inorganic As to organic As should not have been affected by sample preparation as methylation of inorganic As is unlikely to have occurred during the drying time.

Although inconclusive, speciation results show about 18% of the As, possibly more, to be present as As(III). Results also show that the inorganic As species dominate, accounting for over 90% of the total As in sediments and algae. Minor amounts of MMA and DMA found in La Primavera sediments are consistent with the findings of Maher (1984) who found organic species in pelagic and estuarine sediments and with Takamatsu et al. (1982) who found them in submerged soils. Marine algae have also been found to contain MMA and DMA (Maher, 1981) which suggests that the presence of organic arsenicals in La Primavera algae may also be reasonable.

The Relationship Between Sediments and Surface Water

No correlation exists between trace element concentrations of the surface water and sediments. This could result from several factors including the small sample size, heterogeneity of the samples, sediments in particular, and the wide range in sediment-water pH, Eh and temperature conditions found at La Primavera. In the case of As, the relatively small range in surface water concentrations may be swamped by the heterogeneity of sediment chemistry and not enough to produce noticeable and correlative changes in As sediment concentration. This also suggests that the amount of sedimentary As is primarily determined by the amount of TOC, Fe- and Mn-oxides in the sediments, not the amount of As in the water.

Though no trends between surface water and sediments were observed for the stream reach, high values for filtered Fe at sample stations 16 and 17 seem to occur with high values in sediments (Appendix D). These anomalous values for Fe in the water may be the result of thermal seeps as no springs were observed at this location. These two locations are also places where sediments have higher concentrations of As, Mn and %TOC.

Arsenic Mobility: Comparisons Between La Primavera and the Rio Grande

Comparison of As-water/As-sediment ratios indicated that As is more mobile in La Primavera waters than in the Rio Grande. This is most likely due to differences in sediment chemistry rather than water chemistry because both locations have similar Eh-pH conditions.

Iron is the only component analyzed, out of Fe, Mn, % TOC and surface area, that is significantly greater in Rio Grande sediments than those from La Primavera. Iron oxides are important sinks for As and it is possible that Rio Grande sediments retain more As relative to surface water concentrations because of a greater abundance of Fe-oxides. The prevalence of Fe in Rio Grande sediments is also seen in Fe/Mn ratios of 37 and 11 for Rio Grande and La Primavera sediments, respectively. The low Fe/Mn ratio for La Primavera indicates relatively large amounts of Mn relative to Fe and may also help explain the strong correlation between Mn and As seen La Primavera sediments.

Another explanation for the higher mobility of As in La Primavera waters is that the sediment's capacity to uptake As has been exceeded. If true, this may also account for the lack of correlation between sediments and surface waters found there. Though there must be a point at which the sediments become saturated with As, this idea has not been tested and proven for La Primavera or Rio Grande sediments.

Theoretical Calculations of Amorphous Iron Surfaces

Calculations were made to estimate the surface area of La Primavera amorphous Fe-oxide in order to determine whether it is large enough to adsorb the amount of As recovered in the amorphous extraction. The amorphous Fe phase was assumed to be of the form $Fe(OH)_2$ with each molecule covering approximately 4 $Å^2$, and is calculated from the amount of Fe recovered in the amorphous extraction. Arsenic was treated as $HAsO_4^{2-}$ with an approximated surface area of 3 $Å^2$ per molecule.

Calculations using the mass of Fe extracted (averaging about 0.6 mg) showed that a one-molecule thick layer of $Fe(OH)_2$ would cover about 1 m^2 of surface (about 75% of the average surface area of La Primavera sediments), while $HAsO_4^{2-}$ (averaging about 0.5 μg extracted) covers a surface about 3 orders of magnitude smaller with an average value of $1.2x10^{-3}$ m^2 (Appendix F). Though it is unlikely that $Fe(OH)_2$ exists as a mono-molecular layer in nature, the amorphous oxides are thought to have a sponge-like structure that is highly porous, with an extremely large surface area. It is still possible that the amorphous Fe-oxides in La Primavera sediments could retain most of the As by adsorption to its surface. If true, La Primavera amorphous Fe-oxides represent a highly reactive surface that could be affected by diurnal and seasonal changes in redox conditions resulting from changes in biological activity and high vs. low water levels. Changing redox conditions could cause alternate dissolution and precipitation of these amorphous oxides resulting in fluctuation of the daily and seasonal As concentrations in surface water.

Comparison of La Primavera As-Sediment Associations With Other Locations

Comparison of La Primavera As-sediment associations with other studies reveals some similarities and differences. The finding that Fe- and Mn-oxides are the predominant phases associated with As is also consistent with work by Tingzong et al. (1997), Azcue and Nriagu (1993), and Maher (1984) who found comparable results using similar sequential extractions on sediments. The insignificant amounts of As associated with the exchangeable and carbonate fractions at La Primavera is also consistent with their findings. The significant proportion of As found occurring with organic matter in La Primavera sediments is unique and has not been found in other studies. This could be due to the fact that this study was conducted in a natural setting that has not been subjected to contamination. Also, because the waters at La Primavera have probably had elevated As concentrations for thousands of years, the plants and algae that make up much of the organic matter may have differing affinities for As uptake than those occurring at other locations.

CONCLUSIONS

(1) The use of ion-exchange chromatography, modified after Grabinski (1981), results in good separation of As(III), As(V), MMA and DMA in plant and sediment extracts and is worthy of further development and application. It is also a promising method of sediment As speciation in that it can be performed in almost any laboratory setting and does not require expensive instruments or elaborate procedures.

(2) Arsenic is more mobile in La Primavera waters than Rio Grande waters and is most likely related to the amount of Fe occurring as Fe-oxide. The increased mobility of As at La Primavera could also occur as a result of the sediment's capacity to uptake As being exceeded.

(3) There is no correlation between As concentrations of the surface water and sediments. This indicates that the amount of As present in La Primavera sediments is determined by the amount of organic matter and, Fe- and Mn-oxides, not the concentration of As in surface waters.

(4) La Primavera sediments and algae primarily contain inorganic As which accounts for over 90% of the total.

(5) The primary sinks for As at La Primavera are organic matter and, Fe- and Mn-oxides. Although Fe-oxides are enriched in As, only TOC and Mn show direct correlations with As. The primary sediment components that include varying proportions of obsidian, welded tuff and pumice fragments have little affect on sediment As chemistry.

(6) The association between As and organic matter at La Primavera is unique among similar studies and suggests that plants and algae may represent a significant sink for As in some natural settings.

(7) Although La Primavera sediment As concentrations are not a great deal higher than normal crustal abundances, a significant portion of it is present in secondary mineral phases and is available for exchange with the waters.

FUTURE STUDIES

Future work could include further development of the ion-exchange chromatography method for speciation of arsenic in sediments. This should include testing other reagents to increase the amount of As extracted from the sediments as well as improving recovery of the species introduced on to the column. The effects of sediment drying on the proportion of As species should also be examined.

Another area of study could be to determine the As saturation point of various stream sediments to see if it can be quantified. This would be useful to know in the event of future contamination so that predictions on the upper limits of As sediment loadings as well as the mobility of As may be made.

Future studies at La Primavera could include extending the sampling of waters and sediments further downstream to Lake Chapala. This larger scale look at As mobility may provide additional information on its behavior in a natural setting. Sampling should also include sediment pore-waters that may show different relationships with sediments than surface waters.

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Appendix A

La Primavera Sediment Data

La Primavera Sediment Chemistry			Conc. Determined by H_3PO_4 Digestion		Element Conc. Determined by HNO_3 Digestion					Element Conc. Determined By HCl+HNO_3 Digestion				
Sample ID	Sed-Eh	% TOC	Fe mg/kg	Mn mg/kg	Fe mg/Kg	Mn mg/Kg	Al mg/kg	Amt. of sol Si by HNO_3 (mg/L)	Si mg/kg	Fe mg/kg	Mn mg/kg	Zn mg/kg	Ca mg/kg	Mg mg/kg
1	80	1.5	333	71	2908	103	2166	5	492	3629	156	15	85	131
2	<0	1.8	415	9	3602	18	2621	2	227	6383	98	43	288	484
3 a.m.	-120	2.0	383	35	3713	55	2916	3	379	5128	116	42	248	436
3 p.m.	125	1.9	106	106	3428	316	2127	3	343	7479	423	52	304	452
4	110	1.7	449	224	2830	258	2263	4	310	4171	327	19	162	214
5	>0	2.5			2595	232	3452	2	269	2882	320	23	87	76
6	67	3.0	307	420	3848	770	3402	2	297	5495	1003	50	399	434
7	20	2.6	70	115	2713	319	3470	4	405	3344	414	18	134	160
8	30	1.6	345	246	3601	356	2968	3	335	5334	447	56	238	379
9	12	1.9	324	263	3478	276	4610	2	215	4426	371	48	388	494
10	50	1.8	286	158	3984	228	4482	2	178	5855	281	59	689	624
11	10	3.0	456	377	3788	554	4597	1	138	4324	693	27	145	175
12	25	1.8	484	238	3383	347	3006	4	343	6145	455	48	365	462
13	0	3.1	434	-16	2611	0	6957	3	306	3635	51	23	383	222
14	-130	2.3	327	183	3078	230	2990	3	310	5169	302	52	313	378
16	80	3.1	434	462	2981	634	4139	3	352	3396	768	21	201	175
17	90	3.7	347	456	3024	800	4406	2	216	3733	1082	24	345	186
18	80	1.3	421	345	2923	526	2055	3	307	4243	718	42	286	369
19	150	1.3	524	87	3642	120	3808	1	128	5419	192	64	285	547
20	140	1.2	447	138	3415	189	3043	3	346	5126	268	56	241	483
A.Dulce		1.5	534	54	4569	56	8785	2	276	6763	151	91	257	701
Average		2.1	371	199	3339	304	3727	3	294	4861	411	42	278	361
STDEV		0.7	120	150	509	234	1627	1	88	1237	289	19	134	175
Reproducibility		0.1			73	15	163		80.5	213	9	1	29	10

*Reproducibility calculated as relative STDEV of multiple measurements of a sample

Appendix A (1). Tables of La Primavera chemical analyses performed on sediments.

Conc. Determined by 0.25M NH_2OH-HCl + 0.25M HCl for amorphous Fe							HNO						
Sample ID	Fe mg/Kg	Mn mg/Kg	As mg/kg	Al mg/kg	Amt. of sol. Si by HNO_3 (mg/L)	Si mg/kg	Un-sieved	<63 µ	63-125 µ	125-250 µ	250-500 µ	500-1000 µ	1000-2000 µ
1	511	76	0.7	155	5	259	4	18	7	3	3	8	4
2	602	0	0.5	183	6	273	5	6	5	3	4	4	4
3 a.m.	560	24	1.3	223	6	252	4	14	4	3	4	3	3
3 p.m.	484	280	2.1	153	7	344	10	44	11	11	7	8	12
4	635	244	1.2	182	6	272	6	12	7	5	5	2	4
5	515	302	1.5	254	5	272	12	30	10	8	9	11	10
6	556	907	1.4	256	7	357	17	21	13	10	12	17	20
7	146	316	1.3	181	4	240	7	12	8	6	5	6	6
8	633	377	1.1	192	5	301	7	17	8	7	6	6	5
9	534	357	1.0	325	7	365	6	15	6	7	5	5	5
10	568	221	1.0	307	6	346	6	7	6	4	4	4	6
11	814	613	2.0	345	7	349	11	22	10	7	4	3	7
12	798	375	1.3	206	7	334	9	12	8	8	7	5	7
13	719	0	1.1	514	7	411	8	16	7	6	4	4	4
14	623	225	1.2	204	6	304	9	20	12	5	5	4	8
16	690	746	5.1	252	7	360	10	19	10	8	8	8	9
17	706	948	7.2	243	8	411	12	13	10	10	13	15	7
18	730	498	1.3	160	5	242	8	13	7	5	6	5	5
19	767	104	0.7	277	7	328	5	11	6	5	6	7	5
20	741	182	0.9	232	7	359	7	13	5	4	4	3	6
A.Dulce	722	67	0.5	408	9	428	4	8	5	3	3	3	2
Average	622	327	1.6	250	6	324	8	16	8	6	6	6	7
STDEV	147	279	1.6	90	1	57	3	8	3	3	3	4	4
Reproducibility							0.32						

*Reproducibility calculated as relative STDEV of multiple measurements of a sample

Appendix A (2). Continued, tables of La Primavera chemical analyses performed on sediments.

H_3PO_4 Digestions for As speciation Reported values are for As ppm (mg/kg)					Surface Area	Measured Carbonate	Algae digestions	Saturation Indices Calculated with MinteqU			
Sample ID	AsIII	MMA	AsV	DMA	m^2/gm	wt%	As mg/kg	Aragonite	Calcite	Dolomite	Rhodochrosite
1	0.3	ND	1.5	ND	0.7	0.07		-0.26	-0.16	-1.20	-8.30
2	0.3	ND	0.6	ND	0.8			-0.19	-0.09	-1.02	-0.70
3 a.m.	0.7	0.3	2.6	ND							
3 p.m.	0.6	0.3	2.4	ND	1.2						
4	0.5	ND	1.4	ND	1.0	0.05		0.28	0.38	0.17	-0.90
5	0.8	0.4	2.7	ND	1.4						
6	0.4	ND	2.2	ND	2.0	ND		0.42	0.53	0.44	-0.52
7	0.5	0.2	2.0	ND	1.4	ND	26	-0.54	-0.41	-1.55	-1.37
8	0.5	ND	1.6	ND	1.0						
9	0.5	ND	2.1	ND	1.5		65				
10	0.3	ND	1.1	ND	1.4		31				
11	0.8	0.4	4.1	ND	2.1	0.09		0.45	0.56	0.62	-0.87
12	0.5	ND	2.9	ND	1.3						
13	0.8	0.3	2.4	ND	1.8	ND	18	-1.48	-1.35	-2.59	-2.90
14	0.7	ND	2.3	ND	1.5						
16	0.8	0.3	4.8	ND	2.7		20				
17	1.3	0.7	7.1	0.5	2.5	0.25		0.55	0.67	1.01	-0.95
18	0.6	0.3	2.0	ND	1.0						
19	0.4	ND	1.4	ND	1.4	0.08		0.46	0.60	0.99	-1.44
20	0.4	ND	1.4	ND	1.3			0.59	0.72	1.28	-1.43
A.Dulce	0.4	ND	1.7	ND	2.3		69 (A.E.)				
Average	0.6	0.2	2.4	0.0	1.5						
STDEV	0.2	0.1	1.4		0.5						
Reproducibility	0.2	ND	0.7	ND	0.01	0.025	4				

*Reproducibility calculated as relative STDEV of multiple measurements of a sample

Appendix A (3). Continued, tables of La Primavera chemical analyses performed on sediments.

Amounts of As, Mn and Fe Recovered by Each Method Relative to XRF totals
(values reported as percent)

	Arsenic Recovered			Manganese Recovered				Iron Recovered			
Sample ID	H_3PO_4	HNO_3	Chao	H_3PO_4	HNO_3	HCl+HNO_3	Chao	H_3PO_4	HNO_3	HCl+HNO_3	Chao
1	24	134	12	18	27	40	20	2	19	23	3
2	15	75	8	2	5	25	0	2	21	38	4
3 a.m.	26	131	15	9	14	30	6	2	23	32	4
3 p.m.	26	97	21	15	45	61	40	1	19	41	3
4	26	88	17	41	48	60	45	3	19	28	4
5	23	91	11	0	50	69	65	0	18	20	4
6	13	83	7	34	62	81	73	2	24	34	3
7	22	68	13	16	46	59	45	0	19	23	1
8	26	89	14	32	46	58	49	2	23	35	4
9	22	67	11	42	44	60	58	2	22	29	3
10	18	69	13	29	42	52	41	2	24	35	3
11	32	85	15	44	65	81	72	3	24	28	5
12	29	86	13	34	50	65	54	3	22	39	5
13	37	85	12	0	0	16	0	3	17	24	5
14	22	88	12	34	42	56	41	2	20	33	4
16	33	81	39	50	68	83	80	3	21	24	5
17	31	72	45	37	65	87	77	2	20	25	5
18	27	85	14	45	68	93	64	3	20	29	5
19	21	57	8	23	31	50	27	3	23	34	5
20	23	98	13	30	41	58	39	3	22	33	5
A.Dulce	33	59	8	17	18	49	22	3	27	40	4
Average	25	85	15	26	42	59	44	2	21	31	4
STDEV	6	19	10	15	20	20	24	1	2	6	1
Reproducibility											

*Reproducibility calculated as relative STDEV of multiple measurements of a sample

Appendix A (4). Continued, tables of La Primavera chemical analyses performed on sediments.

La Primavera Samples Grain Size Distribution (values reported as % of whole)							Proportion of Arsenic bound in each size fraction (reported as % of "whole" fraction)					
Sample ID	<63 µ	63-125 µ	125-250 µ	250-500 µ	500-1000 µ	1000-2000 µ	<63 µ	63-125 µ	125-250 µ	250-500 µ	500-1000 µ	1000-2000 µ
1	1	2	16	23	33	24	4	3	10	13	52	18
2	1	3	18	21	29	28	1	4	17	20	32	26
3 a.m.	0	2	18	19	29	36	1	2	16	20	28	33
3 p.m.												
4	0	3	17	23	31	25	1	5	22	27	19	26
5	2	9	25	26	21	17	6	10	20	25	22	17
6	2	6	17	27	30	16	3	5	12	22	35	23
7	2	7	22	27	30	13	3	7	19	17	25	30
8	0	2	16	26	27	29	0	3	20	24	27	25
9	2	2	6	17	37	36	6	2	8	16	33	35
10	2	2	6	17	36	37	3	3	5	14	32	43
11	2	5	18	30	28	15	8	11	24	21	17	20
12	2	6	16	19	30	27	4	6	19	19	22	30
13	2	5	14	26	33	20	6	7	17	23	30	17
14	3	6	18	29	30	13	7	11	34	19	17	12
16	15	14	53	15	2	1	27	14	44	13	2	1
17	1	5	27	41	19	6	1	4	24	43	23	4
18	0	2	13	23	35	27	0	2	13	26	33	26
19	1	3	11	17	33	34	1	3	10	17	41	27
20	0	0	2	12	47	39	0	0	1	11	36	51
A.Dulce	0	1	8	26	33	32	1	2	9	26	33	28
Average	2	4	17	23	30	24	3	5	16	21	29	26
STDEV	3	3	11	7	9	11	2	3	8	7	9	11
Reproducibility												

*Reproducibility calculated as relative STDEV of multiple measurements of a sample

Appendix A (5). Continued, tables of La Primavera chemical analyses performed on sediments.

Results of Sequential Extraction (Values reported in ppm) Relative Amount of As in Sediment Fractions					Relative Amount of Mn Sediment Fractions					Relative Amount of Fe Sediment Fractions				
Sample	Exch.	Cabonate	Fe/Mn-Ox	Organic	Sample	Exch.	Cabonate	Fe/Mn-Ox	Organic	Sample	Exch.	Cabonate	Fe/Mn-Ox	Organic
3 p.m. (a)	0.5	0.5	1.5	0.8	3 p.m. (a)	0	33	265	0	3 pm a	0	0	526	407
3 p.m. (b)	0.5	0.5	1.6	1.0	3 p.m. (b)	0	22	255	0	3 pm b	0	0	493	473
11	0.7	1.0	2.2	1.5	11	0	37	567	42	7	0	0	205	286
17	0.9	1.2	4.1	2.7	17	0	124	701	78	11	0	0	691	396
7	0.5	0.6	0.8	1.0	7	0	34	299	14	13	0	0	530	0
13	0.3	0.6	0.4	2.1	13	8	8	0	0	17	0	0	506	348
19 (a)	0.3	0.2	0.3	0.7	19 (a)	0	31	80	13	19 a	0	9	567	438
19 (b)	0.3	0.3	0.2	0.7	19 (b)	0	37	57	13	19 b	0	14	463	355
Average	0.5	0.6	1.4	1.3	Average	1	41	278	20	Average	0	3	497	338

Appendix A (6). Continued, tables of La Primavera chemical analyses performed on sediments.

La Primavera XRF Data (Values reported as mg/kg)

Sample	Sr	Rb	Th	Pb	Ga	Zn	Cu	Ni	%Fe2O3	%MnO	Fe	Mn	Cr	%TiO2	Ba	V	As	U	Y	Zr	Nb	Mo
1	14	134	16	14	22	89	28	40	2.29	0.05	16017	387	340	0.16	56	4	6	6	47	540	50	4
1 b	14	134	16	14	22	88	5	7	2.17	0.05	15178	387	60	0.16	57	4	6	5	48	539	49	3
1 c	14	134	16	15	21	97	12	14	2.21	0.05	15458	387	131	0.16	53	3	6	6	47	540	50	4
1 d	14	131	15	14	22	88	5	6	2.18	0.05	15248	387	62	0.16	58	ND	6	5	47	537	49	4
2	28	137	17	14	23	91	5	7	2.4	0.05	16787	387	58	0.29	98	11	6	5	46	515	50	3
3 a.m.	23	140	16	15	23	91	5	7	2.26	0.05	15807	387	75	0.19	83	9	9	6	48	526	51	3
3 p.m.	25	140	17	16	23	98	5	6	2.6	0.09	18186	697	65	0.25	90	10	10	6	49	532	52	4
4	26	140	17	15	23	89	5	6	2.14	0.07	14968	542	63	0.17	94	ND	7	7	47	512	49	3
5	6	166	20	22	24	113	7	6	2.03	0.06	14199	465	60	0.11	24	ND	13	8	63	442	63	4
6	21	159	18	20	23	110	5	6	2.32	0.16	16227	1239	47	0.14	58	5	20	7	56	442	58	5
7	16	144	17	17	23	93	5	4	2.05	0.09	14339	697	10	0.15	69	ND	10	6	50	499	52	3
8	26	136	16	15	22	96	5	5	2.21	0.1	15458	774	63	0.18	93	5	8	6	44	499	49	4
9	27	147	18	20	24	101	15	6	2.22	0.08	15528	620	49	0.19	88	7	9	6	51	499	56	4
10	41	143	17	17	23	100	6	7	2.37	0.07	16577	542	67	0.21	149	10	8	6	51	491	54	4
11	15	145	17	18	23	104	10	6	2.22	0.11	15528	852	55	0.15	70	4	13	7	53	491	54	4
12	24	139	15	15	23	95	6	6	2.23	0.09	15598	697	69	0.18	112	5	10	6	47	502	51	3
13	13	151	18	20	24	104	5	7	2.15	0.04	15038	310	88	0.15	52	ND	9	7	54	507	60	3
14	18	139	17	16	22	97	7	6	2.21	0.07	15458	542	52	0.17	73	7	10	6	47	416	51	3
16 a	18	139	17	17	22	96	9	12	2.06	0.12	14409	929	102	0.15	84	ND	13	5	48	477	51	3
16 b	18	137	17	16	23	95	7	9	2.02	0.12	14129	929	72	0.14	82	6	13	5	49	478	51	3
17	11	145	18	17	23	102	6	8	2.12	0.16	14828	1239	76	0.13	78	4	16	6	52	479	53	3
18	27	134	16	15	22	93	8	5	2.08	0.1	14548	774	55	0.17	117	4	9	5	45	499	47	3
19	27	168	19	17	24	102	6	7	2.29	0.05	16017	387	70	0.18	98	8	9	7	59	559	63	3
20	23	156	17	16	23	99	6	6	2.2	0.06	15388	465	58	0.17	95	5	7	7	53	557	57	4
A.D.	31	231	22	24	29	140	10	8	2.4	0.04	16787	310	55	0.17	80	7	6	8	77	688	95	2
Average	21	147	17	17	23	99	8	8	2	0	15508	613	76	0	80	6	10	6	51	511	55	3
STDEV	8	20	2	3	1	11	5	7	0	0	935	267	59	0	25	2	4	1	7	51	9	1

Appendix A (7). Continued, tables of La Primavera chemical analyses performed on sediments.

Appendix B

La Primavera Correlation Matrices

La Primavera Sediment Data
Correlation matrix for HNO_3 digestions on size fractions (size fractions are reported in µm)

	Sed-Eh	% TOC	Fe	Mn	Al	Si	As Un-sieved	As <63	As 63-125	As 125-250	As 250-500	As 500-1000	As 1000-2000	Sfc. Area
Sed-Eh	1.00													
% TOC	-0.15	1.00												
Fe	0.08	-0.22	1.00											
Mn	-0.32	0.78	-0.15	1.00										
Al	-0.09	0.37	-0.07	0.29	1.00									
Si	-0.39	-0.16	-0.44	-0.13	0.09	1.00								
As Un-sieved	-0.18	0.74	-0.14	0.81	0.14	-0.13	1.00							
As <63	0.15	0.22	-0.20	0.14	-0.01	0.16	0.48	1.00						
As 63-125	-0.27	0.75	-0.18	0.73	0.14	0.03	0.91	0.64	1.00					
As 125-250	-0.23	0.66	-0.21	0.71	0.14	-0.02	0.81	0.61	0.82	1.00				
As 250-500	-0.15	0.67	-0.26	0.75	0.16	-0.08	0.83	0.32	0.74	0.84	1.00			
As 500-1000	-0.06	0.63	-0.21	0.63	0.07	0.07	0.73	0.31	0.75	0.68	0.88	1.00		
As 1000-2000	0.08	0.52	-0.02	0.59	0.09	0.05	0.88	0.57	0.85	0.74	0.74	0.76	1.00	
Sfc. Area	0.00	0.71	0.31	0.55	0.60	-0.37	0.45	-0.07	0.35	0.33	0.42	0.34	0.26	1.00

Appendix B (1). Correlation matrix for elements determined by nitric digestions.

La Primavera Sediment Data
Correlation matrix for H_3PO_4 digestions

	Sed-Eh	% TOC	Fe	Mn	As(III)	MMA	As(V)	DMA	Sfc. Area
Sed-Eh	1.00								
% TOC	-0.15	1.00							
Fe	-0.03	-0.25	1.00						
Mn	-0.39	**0.73**	0.13	1.00					
As(III)	-0.12	**0.76**	0.00	**0.71**	1.00				
MMA	0.03	**0.74**	-0.22	**0.56**	**0.92**	1.00			
As(V)	-0.18	**0.83**	0.04	**0.72**	**0.93**	**0.86**	1.00		
DMA	-0.01	0.56	-0.04	0.42	0.78	0.69	0.77	1.00	
Sfc. Area	0.00	**0.71**	0.23	**0.56**	0.53	0.48	0.70	0.43	1.00

Appendix B (2). Correlation matrix for elements determined by phosphoric acid digestion.

La Primavera Sediment Data
Correlation matrix for Amorphous Phase digestions

	Sed-Eh	% TOC	Fe	Mn	As	Al	Si	Sfc. Area
Sed-Eh.	1.00							
% TOC	-0.15	1.00						
Fe	-0.08	-0.14	1.00					
Mn	-0.32	**0.83**	0.13	1.00				
As	-0.07	**0.77**	0.14	**0.88**	1.00			
Al	0.28	0.14	0.33	0.00	-0.05	1.00		
Si	0.18	0.26	0.45	0.27	0.37	**0.69**	1.00	
Sfc. Area	0.00	**0.71**	0.27	**0.62**	**0.64**	**0.63**	**0.73**	1.00

*note sample location #6 was excluded

Appendix B (3). Correlation matrix for elements determined by dissolution of amorphous metal oxides (Chao extraction).

La Primavera Sediment Data
Correlation matrix for amorphous sediment data vs. water data

	pH (water)	Eh (water)	Temp (water)	Cond (water)	Fe (sed)	Mn (sed)	As (sed)	Al (sed)	Si (sed)
pH (water)	1.00								
Eh (water)	0.09	1.00							
Temp (water)	-0.68	-0.14	1.00						
Cond (water)	-0.69	-0.12	0.62	1.00					
Fe (sed)	0.75	0.21	-0.16	-0.49	1.00				
Mn (sed)	0.36	-0.19	-0.03	-0.28	0.28	1.00			
As (sed)	0.30	-0.04	0.07	-0.11	0.18	0.88	1.00		
Al (sed)	0.30	-0.45	0.11	0.06	0.30	0.22	0.09	1.00	
Si (sed)	0.41	-0.05	0.08	-0.08	0.43	0.47	0.54	0.58	1.00

Appendix B (4). Correlation matrix for elements determined by dissolution of amorphous metal oxides (Chao extraction) and water data.

La Primavera Sediment Data
Correlation matrix for XRF Data

	% TOC	Fe	Mn	As	Sfc. Area
% TOC	1.00				
Fe	-0.32	1.00			
Mn	**0.77**	-0.19	1.00		
As	**0.84**	-0.18	**0.84**	1.00	
Sfc. Area	**0.71**	-0.10	0.50	0.58	1.00

Appendix B (5). Correlation matrix for elements determined by XRF.

La Primavera Sediment
Data
Correlation matrix for H_3PO_4 As-species sediment data vs.
water data

	Tot. As (water)	As(III) (water)	MMA (water)	As(V) (water)	DMA (water)	Tot. As (sed)	As(III) (sed)	MMA (sed)	As(V) (sed)	DMA (sed)
Tot. As (water)	1.00									
As(III) (water)	-0.09	1.00								
MMA (water)	0.07	0.02	1.00							
As(V) (water)	0.62	-0.03	0.02	1.00						
DMA (water)	0.58	-0.03	-0.33	0.55	1.00					
Tot. As (sed)	0.04	0.06	0.69	0.10	-0.25	1.00				
As(III) (sed)	-0.11	-0.06	-0.17	0.21	0.02	0.45	1.00			
MMA (sed)	-0.02	-0.22	-0.20	0.21	0.11	0.44	0.92	1.00		
As(V) (sed)	-0.16	0.05	-0.08	0.16	0.03	0.51	0.93	0.85	1.00	
DMA (sed)	-0.16	-0.07	-0.08	0.29	0.19	0.25	0.78	0.69	0.77	1.00

Appendix B (6). Correlation matrix for elements determined by phosphoric acid and water data.

La Primavera
Sediment Data
Correlation matrix for metals determined by $HCl+HNO_3$
vs. water data

		Mg (water)	Fe (water)	Si (water)	Mn (water)	Ba (water)	Sr (water)	B (water)	CO_3^{2-} (water)	HCO_3^- (water)	Fe (sed)	Mn (sed)	Zn (sed)	Ca (sed)	Mg (sed)
Ca (water)	1.00														
Mg (water)	0.11	1.00													
Fe (water)	0.05	0.34	1.00												
Si (water)	-0.45	-0.77	-0.17	1.00											
Mn (water)	-0.03	-0.50	-0.26	0.24	1.00										
Ba (water)	0.01	0.76	0.75	-0.52	-0.46	1.00									
Sr (water)	0.50	0.45	0.12	-0.51	0.05	0.29	1.00								
B (water)	0.07	-0.67	-0.42	0.46	0.13	-0.65	-0.36	1.00							
CO_3^{2-} (water)	-0.08	0.62	0.44	-0.29	-0.72	0.63	0.05	-0.38	1.00						
HCO_3^- (water)	-0.25	0.09	0.33	0.02	-0.39	0.16	-0.14	-0.34	0.23	1.00					
Fe (sed)	-0.11	0.08	-0.30	-0.01	0.00	-0.25	-0.06	-0.11	-0.02	0.33	1.00				
Mn (sed)	-0.32	0.00	0.54	0.28	-0.15	0.41	-0.14	-0.08	0.44	0.12	-0.12	1.00			
Zn (sed)	0.08	0.38	-0.37	-0.38	-0.13	-0.03	0.16	-0.05	0.12	-0.01	0.79	-0.18	1.00		
Ca (sed)	0.22	0.10	-0.08	-0.19	-0.16	-0.01	-0.16	0.28	0.17	-0.07	0.57	0.14	0.66	1.00	
Mg (sed)	0.12	0.33	-0.35	-0.38	-0.23	-0.05	0.01	0.06	0.10	0.03	0.79	-0.21	0.94	0.79	1.00

Appendix B (7). Correlation matrix for elements determined by $HCl+HNO_3$ digestion and water data.

Appendix C

La Primavera Sediment Descriptions

La Primavera Sediments

Sample	Description of Sediments >2mm
1	75% pumice, 20% welded tuff fragments, 5% obsidian, <1% grains coated with FeOx's, minor twig frag's + some algae coatings on larger grains
2	58% welded tuff fragments, 30% pumice, 10% obsidian, 2% grains coated w/FeOx's, trace organic matter
3 a.m.	70% pumice, 20% welded tuff fragments, 8% obsidian, 2% grains coated w/FeOx's, <1% organic matter as twig and leaf fragments and algae coatings
3 p.m.	70% pumice, 20% welded tuff fragments, 8% obsidian, 2% grains coated w/FeOx's, <1% organic matter as twig and leaf fragments and algae coatings
4	50% welded tuff fragments, 33% pumice, 15% obsidian, 2% grains coated w/FeOx's, <1% organic matter as leaf and twig fragments
5	65% pumice, 20% welded tuff fragments, 12% obsidian, 3% grains coated w/FeOx's, <1% organic matter as leaf and twig fragments
6	80% pumice, 15% welded tuff fragments, 2% obsidian, 2% grains coated w/FeOx's, 1% organics-twigs, some algae coatings (sample has relatively less >2mm sed)
7	80% pumice, 13% welded tuff fragments, 6% obsidian, 1% grains coated w/FeOx's, <1% organic matter as leaf and twig fragments
8	80% welded tuff fragments, 10% pumice, 8% obsidian, 2% grains coated w/FeOx's, <1% organic matter as twig and leaf fragments
9	60% welded tuff fragments, 15% obsidian, 12% pumice, 2% grains coated w/FeOx's, <1% organic matter as leaf and twig fragments
10	60% welded tuff fragments, 25% pumice, 12% obsidian, 3% grains coated w/FeOx's, trace organic matter present
11	45% welded tuff fragments, 45% pumice, 10% obsidian, 2% grains coated w/FeOx's, <1% organic matter as leaf and twig frags and algae coatings on larger grains
12	15% obsidian, 50% welded tuff fragments, 32% pumice, 3% grains coated with FeOx's, <1% as leaf and twig fragments
13	70% obsidian, 20% pumice, 6% welded fragments, 2% grains coated w/ FeOx's, 2% organic matter as leaves and twigs
14	50% welded tuff fragments, 40% pumice, 8% obsidian, 2% grains coated w/FeOx's, <1% organic matter as leaf and twig fragments
16	69% pumice, 25% welded tuff fragments, 5% obsidian, 1% grains coated w/FeOx's, Trace organics (almost no sediment >2mm represented ~ 1-2% of total at that site)
17	80% pumice, 12% welded tuff fragments, 4% organic matter as leaf and twigs, 3% obsidian, 1% grains coated w/FeOx's
18	45% pumice, 33% welded tuff fragments, 20% obsidian, 2% grains coated w/FeOx's, <1% organic matter as leaf and twig fragments
19	75% welded tuff fragments, 17% pumice, 6% obsidian, 2% grains coated w/FeOx's, <1% organic matter as twig and leaf fragments
20	43% pumice fragments, 30% obsidian, 25% welded tuff fragments, 2% grains coated w/FeOx's, <1% organic matter as twig and leaf fragments and algae coatings
A.Dulce	50% welded tuff fragments, 45% pumice, 4% grains coated w/FeOx's, 1% obsidian, trace organic matter

Appendix C. Description of La Primavera sediments (>2mm).

Appendix D

Rio Grande Data

Rio Grande Sediment-Water Data

Sample ID	Eh-Sed.	pH-Sed	TOC	Fe mg/kg	Mn mg/kg	As mg/kg	sfc area	pH water	Eh water	Location description
RG-1	105	7.4	0.7	6073	163	1.3	5.0	8.5	54	San Antonio bridge
RG-2	57	8.5	0.9	6953	168	1.4	4.9	8.5	54	San Antonio bridge
RG-3	43	8.0	1.0	7993	200	1.5	6.9	8.2	39	Escondida bridge
RG-4	40	7.9	0.6	6414	147	1.3	3.6	8.2	39	Escondida bridge
RG-5	52	8.1	1.3	6639	192	1.7	4.8	8.2	39	Escondida lake
RG-6	44	8.3	0.9	6312	189	1.3	23.0	8.3	44	Socorro-Rio Grande Park
RG-7	44	8.2	0.8	6524	188	1.3	2.8	8.3	44	Socorro-Rio Grande Park
ave		8.1	0.9	6701	178	1.4	7.3	8.3	44.7	

Appendix D. Location and sediment chemistry data for Rio Grande River samples.

Appendix E

La Primavera Water Chemistry Data

La Primavera Water Chemistry						Arsenic in waters (reported values in ppb)					
Sample ID	date	pH	Eh (mV)	Temp (°C)	Conductivity (S/cm)	As(III)	MMA	As(V)	DMA	Sum of species	Direct
1	1/10/98	6.53	90	61	1406	0	18	1130	146	1293	1065
2	1/5/98	7.75	-142	46	1395	69	23	1085	94	1269	1121
3 a.m.	1/8/98	7.81	127		1220	5	11	1178	91	1284	1126
3 p.m.	1/10/98	7.82	80	48	1291	8	34	998	154	1193	1088
4	1/10/98	8.4	87	42.5	1277	4	18	1188	72	1281	1109
5	1/6/98	6.49	38	54	1353	0	9	1044	24	1077	970
6	1/5/98	8.48	82		1287	3	148	962	18	1130	964
7	1/6/98	8.4	24	28	1289	1	20	918	121	1060	1119
8	1/9/98	7.89	108		1269	16	50	896	94	1055	1046
9	1/6/98	7.64	26	61.5	1289	0	23	827	83	932	893
10	1/7/98	8.45	26.67	42	1249	0	16	750	74	840	888
11	1/7/98	8.67	40		1232	5	23	951	80	1058	722
12	1/7/98	8.44	22		1207	133	27	815	70	1044	983
13	1/12/98	7.36	8	29	316	8	7	218	22	254	227
14	1/7/98	8.45	64		1130	28	23	756	66	872	911
16	1/8/98	8.51	69		1130	15	45	1006	36	1102	918
17	1/8/98	8.76	57		1233	6	9	957	51	1023	918
18	1/8/98	8.76	66	34	936	0	18	956	33	1006	890
19	1/11/98	8.73	75	28.5	1245	0	7	1083	9	1098	821
20	1/11/98	8.91	95	27.7	1005	0	11	981	25	1017	756
A.Dulce	1/11/98	7.96	67	29	443						

Appendix E (1). La Primavera water chemistry data. This data set was provided by Greg Miller of New Mexico Institute of Mining and Technology; see Miller (1999) for additional information.

La PrimaveraWater Chemistry
(Filtered Waters)

Sample ID	Ca ppm	Na ppm	Mg ppm	Fe ppb	Li ppm	Si ppm	K ppm	Mn ppb	Ba ppb	Sr ppb
1	3.8	292	0.2	11	1	227	13	64	0	8
2	3.8	306	0.2	14	1	239	13	66	0	8
3 a.m.	3.1	307	0.3	26	1	236	13	90	0	7
3 p.m.	3.5	297	0.3	41	1	231	13	105	0	7
4	3.0	295	0.3	22	1	240	13	26	0	3
5	3.7	290	0.3	6	1	222	14	165	0	8
6	2.8	267	0.2	4	1	242	14	61	0	6
7	3.8	294	0.3	37	1	237	14	19	0	8
8	3.8	285	0.3	19	1	234	14	38	0	7
9	4.2	268	0.3	8	1	209	14	53	0	7
10	4.2	269	0.3	2	1	217	14	38	0	6
11	3.8	289	0.3	11	1	228	14	27	0	7
12	3.8	271	0.6	21	1	223	14	50	0	7
13	2.6	68	1.4	1	0	118	4	2	0	5
14	3.7	254	0.7	29	1	216	13	31	4.5	7
16	3.8	265	0.6	178	1	214	13	24	5.9	8
17	3.7	260	0.6	148	1	220	13	22	5.4	7
18	3.6	262	0.6	26	1	222	13	22	4.6	7
19	3.7	242	0.9	16	1	206	13	7	3.7	9
20	3.5	226	0.9	32	1	193	12	7	3.5	8

A.Dulce

Appendix E (2). La Primavera filtered water chemistry data. This data set was provided by Greg Miller of New Mexico Institute of Mining and Technology; see Miller (1999) for additional information.

La Primavera Water Chemistry (Unfiltered Waters)

Sample ID	Ca ppm	Na ppm	Mg ppm	Fe ppb	Li ppm	Si ppm	K ppm	Mn ppb	Ba ppb	Sr ppb	Cl ppm	SO4 ppm	F ppm	B ppm	CO_3^{2-} ppm	HCO_3^- ppm
1	3.2	296	0.2	88	1.0	248	14	57	0	8	93	27	15	7	0	416
2	3.8	312	0.2	14	1.0	249	14	79	0	8	93	28	15	9	0	392
3 a.m.	3.4	280	0.3	28	1.0	236	14	78	2	7	93	28	16	7	0	408
3 p.m.	3.6	280	0.3	27	1.0	242	13	117	2	7	92	28	16	4	0	424
4	3.4	306	0.3	50	1.0	244	14	29	0	7	90	29	16	7	40	408
5	3.7	276	0.3	2	1.0	232	14	149	0	7	74	20	14	7	0	328
6	2.7	270	0.2	1	1.0	240	14	10	0	6	79	20	15	9	44	388
7	3.8	300	0.3	42	1.0	240	14	29	2	7	92	28	16	9	28	376
8	3.7	298	0.3	23	1.0	236	14	40	2	7	87	26	15	8	38	410
9	4.2	275	0.3	5	0.9	211	14	90	0	6	74	19	13	9	0	368
10	4.1	275	0.3	4	0.9	212	14	43	0	6	75	19	14	9	52	374
11	3.7	287	0.3	14	0.9	225	14	33	0	7	83	23	15	6	80	396
12	3.8	280	0.6	32	0.9	228	14	64	6	7	77	22	15	7	44	396
13	2.5	64	1.4	4	0.2	119	4	1	0	5	17	6	6	4	0	88
14	3.7	270	0.6	30	0.9	224	13	40	6	7	74	22	15	6	20	376
16	3.7	266	0.6	23	0.9	228	14	29	5	7	76	22	15	5	76	408
17	3.7	265	0.6	20	0.9	219	14	35	5	7	76	22	15	5	76	408
18	3.5	266	0.7	18	0.9	215	13	20	5	7	74	21	15	5	48	376
19	3.7	255	0.9	27	0.8	207	13	13	5	8	71	20	14	5	72	364
20	3.4	244	0.9	52	0.8	197	12	11	4	8	64	18	12	4	68	432
A.Dulce																

Appendix E (3). La Primavera unfiltered water chemistry data. This data set was provided by Greg Miller of New Mexico Institute of Mining and Technology; see Miller (1999) for additional information.

Appendix F

Theoretical Calculations of Amorphous Fe-oxide Surfaces

La Primavera Sediments (Amorphous Fe-oxide Calculations)

Sample	Fe mg/Kg	Mass Fe (mg) Extracted	atoms Fe Extracted	Amorph. $Fe(OH)_2$ m^2	As mg/kg	Mass As (mg) Extracted	atoms As Extracted	$HAsO_4^{2-}$ m^2	Ratio As/Fe surface	Sfc Area m^2/gm	% of LP Sed covered by Fe(OH)2	% of LP Sed covered by $HAsO_4^{2-}$
1	511	0.49	5.32.E+18	8.52.E-01	0.7	0.0007	5.56.E+15	5.00.E-04	5.87.E-04	0.7	116.01	6.81.E-03
2	602	0.63	6.74.E+18	1.08.E+00	0.5	0.0005	4.12.E+15	3.70.E-04	3.44.E-04	0.8	132.50	4.55.E-03
3 a.m.	560	0.63	6.78.E+18	1.09.E+00	1.3	0.0015	1.20.E+16	1.08.E-03	9.91.E-04			
3 p.m.	484	0.49	5.28.E+18	8.45.E-01	2.1	0.0022	1.75.E+16	1.57.E-03	1.86.E-03	1.2	72.32	1.35.E-02
4	635	0.70	7.53.E+18	1.21.E+00	1.2	0.0013	1.07.E+16	9.61.E-04	7.98.E-04	1.0	121.68	9.70.E-03
5	515	0.51	5.46.E+18	8.73.E-01	1.5	0.0014	1.15.E+16	1.03.E-03	1.18.E-03	1.4	61.16	7.23.E-03
6	556	0.54	5.86.E+18	9.37.E-01	1.4	0.0014	1.09.E+16	9.83.E-04	1.05.E-03	2.0	46.00	4.83.E-03
7	146	0.13	1.44.E+18	2.30.E-01	1.3	0.0012	9.83.E+15	8.84.E-04	3.85.E-03	1.4	16.88	6.49.E-03
8	633	0.53	5.68.E+18	9.09.E-01	1.1	0.0009	7.31.E+15	6.58.E-04	7.24.E-04	1.0	88.17	6.39.E-03
9	534	0.51	5.50.E+18	8.80.E-01	1.0	0.0010	7.80.E+15	7.02.E-04	7.98.E-04	1.5	56.80	4.53.E-03
10	568	0.52	5.59.E+18	8.94.E-01	1.0	0.0009	7.49.E+15	6.74.E-04	7.54.E-04	1.4	65.90	4.97.E-03
11	814	0.81	8.77.E+18	1.40.E+00	2.0	0.0020	1.60.E+16	1.44.E-03	1.02.E-03	2.1	67.23	6.88.E-03
12	798	0.83	8.99.E+18	1.44.E+00	1.3	0.0014	1.12.E+16	1.01.E-03	7.02.E-04	1.3	108.14	7.59.E-03
13	719	0.61	6.56.E+18	1.05.E+00	1.1	0.0009	7.44.E+15	6.70.E-04	6.38.E-04	1.8	57.11	3.64.E-03
14	623	0.58	6.25.E+18	1.00.E+00	1.2	0.0012	9.31.E+15	8.38.E-04	8.37.E-04	1.5	66.04	5.53.E-03
16	690	0.70	7.53.E+18	1.21.E+00	5.1	0.0052	4.17.E+16	3.75.E-03	3.11.E-03	2.7	45.49	1.42.E-02
17	706	0.71	7.67.E+18	1.23.E+00	7.2	0.0073	5.83.E+16	5.25.E-03	4.28.E-03	2.5	49.41	2.11.E-02
18	730	0.71	7.62.E+18	1.22.E+00	1.3	0.0013	1.00.E+16	9.04.E-04	7.41.E-04	1.0	120.32	8.92.E-03
19	767	0.78	8.37.E+18	1.34.E+00	0.7	0.0007	5.93.E+15	5.34.E-04	3.98.E-04	1.4	96.76	3.85.E-03
20	741	0.69	7.40.E+18	1.18.E+00	0.9	0.0009	6.85.E+15	6.17.E-04	5.21.E-04	1.3	93.94	4.89.E-03
A.Dulce	722	0.75	8.11.E+18	1.30.E+00	0.5	0.0005	3.98.E+15	3.58.E-04	2.76.E-04	2.3	55.34	1.53.E-03
Average	622	0.61	6.59.E+18	1.06.E+00	1.6	0.0016	1.31.E+16	1.18.E-03	1.21.E-03	1.5	7.69.E+01	7.35.E-03

Appendix F. La Primavera Amorphous Fe-oxide surface calculations. Values for Fe-oxide and arsenic surfaces were calculated using Fe and As data collected from the Chao extraction for selective dissolution of amorphous Fe-oxides.