ASSESSMENT OF ARSENIC AND OTHER GROUNDWATER IMPAIRMENTS IN THE GALLINAS WATERSHED, LAS VEGAS, NEW MEXICO

Justin Johns-Kaysing
New Mexico Highlands University

Advisors: Jennifer Lindline, Associate Professor of Geology and
Michael L. Meyer, Associate Professor of Geology

ABSTRACT

The Gallinas River is the primary source of water for Las Vegas, NM (population 18,000), providing 95% of its domestic water supply. Water quality studies show that the river contains elevated concentrations of arsenic (0.039 mg/L) during periods of elevated flow ($1.98 m^3/s$). Total recoverable arsenic in surface water samples is strongly correlated with total suspended solids ($R^2 = 0.98$) and was determined to originate from Permian and Cretaceous shales that underlie a large area (>60%) of the Gallinas Watershed. This study hypothesized that a correlation exists between arsenic in ground water and bedrock geology. To test this hypothesis, we sampled ground water from eleven sites throughout the watershed to measure arsenic levels. We also addressed other potential impairments to domestic, agriculture, and stock water supplies in the Gallinas Watershed including heavy metals, hardness, pH, and dissolved oxygen. Arsenic concentrations throughout the study area were consistently low (< 2.5 ug/L) and below the human health criteria and that which is considered safe for livestock and irrigation watering. Heavy metals were also found in low concentrations. Uranium values were also consistently low throughout the watershed (0.16 to 7.9 ug/L), but showed concentration (7.88 ug/L) in the east-southeast portion of the study area. Hardness, alkalinity, conductivity, pH, dissolved oxygen and nitrate nitrogen values were observed to be within standard state levels.

INTRODUCTION

The Gallinas River is the primary source of water for Las Vegas, NM (population 18,000), providing 95% of its domestic water supply. Water quality studies show that the river contains elevated concentrations of arsenic (0.039 mg/L) during periods of elevated flow ($1.98 m^3/s$). These results exceed the US EPA drinking water standard of 0.010 mg/L. Total recoverable arsenic in water samples is strongly correlated with total suspended solids ($R^2 = 0.98$) and was determined to originate from Permian and Cretaceous shales that underlie a large area (>50%) of the Gallinas Watershed. There exist approximately forty domestic well users in the upper watershed and hundreds more in the eastern plains. No ground water quality data exists for these wells. We sampled ground water from eleven sites throughout the watershed to address impairments to domestic, agriculture, and stock water supplies caused by arsenic and other heavy metals, uranium, hardness, pH, and dissolved oxygen (DO).

The Gallinas River originates on the eastern flank of the southern Sangre de Cristo Mountains in Precambrian crystalline rock and flows southeast over a range-bounding fault and through Paleozoic and Mesozoic strata of the Las Vegas sub-basin. The Gallinas River is a tributary to the Pecos River and typically yields 3,100 acre feet of water annually (Montoya 2000). In recent years, flow has been below average. The yield of the river is allocated among many users and thus requires careful management and protection of water quality.

Significant baseline water quality data have been presented in previous studies, including: Garn and Jacobi (1996); Evans and Lindline (2004); and Johns-Kaysing and Lindline (2005). These studies focused on spatial differences in surface water chemistry from the Gallinas headwaters to approximately 40km downstream. Most studies found water degradation attributed to chemical loading from limestone and shale formations which underlie a large part of the Gallinas

Watershed. This study explored ground water chemistry to determine if arsenic and other water parameters are influenced by bedrock geology and if they present health concerns to the water users. Water samples were collected from eleven ground water sites from the upper watershed to the eastern plains. Surface water samples were collected from Storrie Lake, a reservoir for Las Vegas, in the form of a depth profile at 10m, 5m, 1m, and surface (samples 8-11 respectively). All samples were tested for hardness, alkalinity, nitrate, pH, DO, arsenic and other heavy metals.

GOALS

The goals of this study were to:

- Collect baseline ground water quality data from wells throughout the Gallinas Watershed;
- Examine spatial differences in ground water quality;
- Evaluate variations in water quality as a function of bedrock geology and other natural influences; and
- Determine whether arsenic and other heavy metal loading poses a health risk to domestic well users.

STUDY AREA

Gallinas Watershed

The Gallinas Watershed is approximately 52,000 acres in area. It originates on the eastern flank of Elk Mountain and is bounded to the west by the Rio Grande Watershed and to the east by the Canadian River Watershed. The Gallinas River flows to the southeast to merge with the Pecos River approximately 80 km downstream. Land ownership is composed of 62% federal, 21% private, and 17% state/county entities (Montoya, 2000). The river’s designated uses are: domestic water supply, high quality coldwater fishery, irrigation, livestock watering, wildlife habitat, municipal and industrial water supply, and secondary contact (New Mexico Water Quality Control Commission, 1991).

Geology

The Las Vegas area straddles the boundary between the High Plains and the Southern Rocky Mountain physiographic provinces. Tectonic uplifting of Precambrian basement rock to the west occurred along the Montezuma fault, which was active during the mid-Proterozoic (1000 million years ago) related to Grenville contraction (Erslev et al., 2004); late Proterozoic (750 million years ago) related to rifting of the Rodinia supercontinent (Erslev et al., 2004); and late Mesozoic in association with the Laramide orogeny (Lessard, 1976). Fault movement has led to steep dipping of the stratagraphic beds of the Las Vegas sub-basin. These beds eventually overturn and create a strike ridge trending north through the study area (Fig. 1). The overturned Cretaceous Dakota Sandstone, which is relatively resistant to weathering, forms the Creston Ridge. The rock layers fold to the east in an asymmetrical syncline and eventually lie horizontally, becoming the Raton Basin. The bedrock consists of Mesozoic and Upper Paleozoic sedimentary rocks and Precambrian crystalline rock. The sedimentary strata include limestones, shales, quartz sandstones, gypsum- and salt-bearing siltstones, and conglomerates (Figs. 1-3). The shales of the Madera and Niobrara/Carlile formations are of interest as they are exposed in the majority (>60%) of the study area and were observed to bear elevated concentrations (>12 parts per million) of arsenic in the form of microcrystalline pyrite, FeS_2 (Duran et al., 2005).

RESEARCH METHODS

Multiple samples from each site were collected in acidified and washed Nalgene bottles during the Summer 2006. For ground water collection, water was pumped from wells for approximately three minutes before samples were taken. All bottles were filled to the rim and refrigerated. Samples were sent to Activation Laboratories, Ontario, Canada for ICP-MS elemental analysis. Hardness, alkalinity, DO, pH, conductivity, and nitrate + nitrate-N tests were conducted at New Mexico Highland University (NMHU). Spearman's rank correlation coefficients, non-parametric measures of correlation between variables in a dataset, were calculated to test whether a relationship exists between any of the measured parameters. The closer the Spearman's correlation coefficient is to +1 or -1, the stronger the correlation is between two variables. Another value, the p-value, is a calculation of the regression of ranks. A $p\text{-value} < 0.01$ is significant; a $p\text{-value} < 0.05$ is strongly significant.

Hardness and Alkalinity

Hardness and alkalinity tests were conducted at NMHU by Simone Yelah Tar. The formulas and procedures used were taken from *Standard Methods for Examination of Water and Wastewater*, 20th edition (1998). Titration was done using 50mL milliliter samples for hardness and 20mL for alkalinity. Formulas used are as follows:

Hardness (mg $CaCO_3$/l) = A x B x 1,000/ mL sample
Where: A= mL titration for sample and B= mg $CaCO_3$ equivalent to 1.00 EDTA titrant.

Alkalinity (mg $CaCO_3$/ls) = A x N x 50,000/ mL sample
Where: A = mL standard acid used and N = Normality of standard acid (.0212)

RESULTS

Table 1 and Figures 4-10 contain all water chemistry results. The following is a summary of those data.

Hardness

Ground water values for hardness as $CaCO_3$ increase from high to low elevations in the watershed. The waters from shallow wells have concentrations beginning at 32.5 mg/L near the headwaters to some 1883.2 mg/L on the eastern edge of the city proper. Waters from the local hot springs (Sample 1) and university golf course well (Sample 14) (>600 feet deep) returned very low hardness concentrations (approximately 20 mg/L). Storrie Lake registered values from 126-148 mg/L (samples 8-11 respectively).

Alkalinity

Alkalinity values range from 118 to 435 mg/L ($CaCO_3$). Concentrations increase with progressive drops in elevation. Storrie Lake has values from 120-165 mg/L (8-11 respectively)

Conductivity

Conductivity values ranged from 165 microSiemens/cm (uS/cm) in the high elevation wells to 1700 uS/cm) in lower elevation wells. Wells located along the eastern edge of the study area (Sites 13, 14 and 15) had conductivity values greater than 1500 uS/cm.

pH

All ground water and Storrie Lake samples are slightly alkaline, having pH values between 7.1 and 9.7.

Dissolved Oxygen

Dissolved Oxygen values ranged from 1.3 - 8.07 mg/L which represent a wide range of oxidizing and reducing conditions. The interpretation of this data, however, is done with reservation because our sampling procedure—physical mixing from pumping at well sites—may have returned erroneous values.

Nitrate

Nitrate nitrogen (as N) is consistently low throughout the watershed. The majority of values are below 1.00 mg/L which falls below the 10 mg/L quality standard (New Mexico Water Quality Control Commission, 1991). The highest nitrate value (5.13 mg/L) was measured in the southeastern most corner of the study area (Site 15) in a location which has a history of agricultural use.

Heavy Metals

Heavy metals typically show low levels of concentrations in the watershed; however, both the Montezuma Hot Springs (Site 1) and sites on the eastern edge of the study area (Sites 13, 14, and 15) show elevated values of arsenic, bromine, rubidium, and uranium. Arsenic concentrations throughout the study area are consistently low (< 2.5 ug/L) and fall within the US EPA drinking water standard of 0.10 ug/L. An analysis of variance showed that mean arsenic concentrations are statistically significantly higher (Spearman's correlation coefficient = -0.8839; rank $p<0.05$) at lower elevations (1,900 to 2,100 m) compared to higher elevations (2,100 to 2,600 m) with 0.05 and 0.60 ug/L, respectively. Storrie Lake lies above the Niobrara/Carlile shales and shows higher arsenic values (0.72-0.83 ug/L v. 0.06 ug/L baseline). Samples 7, 13, 14, and 15 show between 11 to 24 times background concentrations for the halide bromine. Uranium values are below EPA standards yet show high concentration in the lowermost portion of the study area and within the bottom sample of the Storrie Lake profile.

DISCUSSION

The general trend of chemical and mineral loading occurring across the study area represents a dynamic interaction between surface water, ground water, and lithography. The levels of measured water parameters in the upper Gallinas Watershed are relatively low and steady, as the Gallinas River flows through Precambrian silicate minerals which are slow to release ions. Water quality shifts markedly as waters cross the Montezuma fault into sedimentary rock. These materials contribute large amounts of the major cations (Ca, Mg, Na) and anions (Cl and SO_4) to the system (Evans and Lindline, 2004). These sedimentary rocks also contain arsenic and other heavy metals (Johns-Kaysing and Lindline, 2005). The dynamics that control mineral loading and arsenic mobility in ground water are still under investigation. Arsenic adsorption to and desorption from clay particles plays a key role in arsenic mobility. The severe drought conditions during May 2006 (observed to significantly lower the water table in many places) may have affected the arsenic levels in ground water. Arsenic which binds to metal oxides, especially iron, may concentrate at the oxidation/reduction boundary in the subsurface and later be reintroduced to the system when the water table once again rises and chemistry reverts to reducing conditions. The observed arsenic levels are also correlated with pH values ($p<0.01$). Desorption of arsenic from iron-oxide surfaces becomes favored as pH values turn alkaline (Fuller and Davis, 1989; Dzombak and Morel, 1990), where the negative net surface charge of iron-oxide can repel negatively charged ions such as arsenate. Because of the pH dependence of arsenic adsorption, geochemical evolution towards alkaline pH from water-rock diagenesis can induce desorption of arsenic (Stumm and Morgan, 1996). Dissolved oxygen in water samples is a proxy for oxidation/reduction conditions in the sampling environment. Accurate DO values are required for this study in order to assess whether the range of conditions suggested by the measured DO values is correct. The marked anthropogenic impairments, such as uranium concentrations down-slope of an impromptu dump, contrast natural occurrences of bromine in the study area which are found originating at the local hot springs and again diffusing in the lower elevation portion of the study area.

CONCLUSION

As hypothesized, a correlation exists between arsenic in ground water and bedrock geology. Arsenic values are lower in wells in the upper watershed where Precambrian crystalline rocks dominate and higher in wells in the lower watershed where the Madera and Niobrara/Carlile shale formations dominate. Arsenic concentrations throughout the watershed are below US EPA water quality criteria (< 2.5 ug/L). All other water quality characteristics examined also fall within state water quality levels; water quality does however degrade as waters cross the range-bounding fault into Mesozoic sediments. Despite the low concentrations of dissolved arsenic and uranium in the study area, it is important to understand the mechanisms related to their mobilization and transport. This repository of baseline ground water quality data can now be contrasted to future studies to investigate temporal changes in water chemistry. A similar terrain with slightly different conditions (pH, redox chemistry, source material) could result in very different behavior of natural contaminants. Further research is needed to determine the effects of changes in pH on the sorption or desorption of arsenic, uranium and other elements.

FUTURE WORK

- Collect well log data to understand the dynamics of individual hydrostratigraphic layers to chemical/elemental loading.
- Evaluate data from a second sampling series collected during the Fall 2006.
- Compare Fall 2006 data to Summer 2006 data to see if there are seasonal variations in water quality.

ACKNOWLEDGEMENTS

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FIGURES

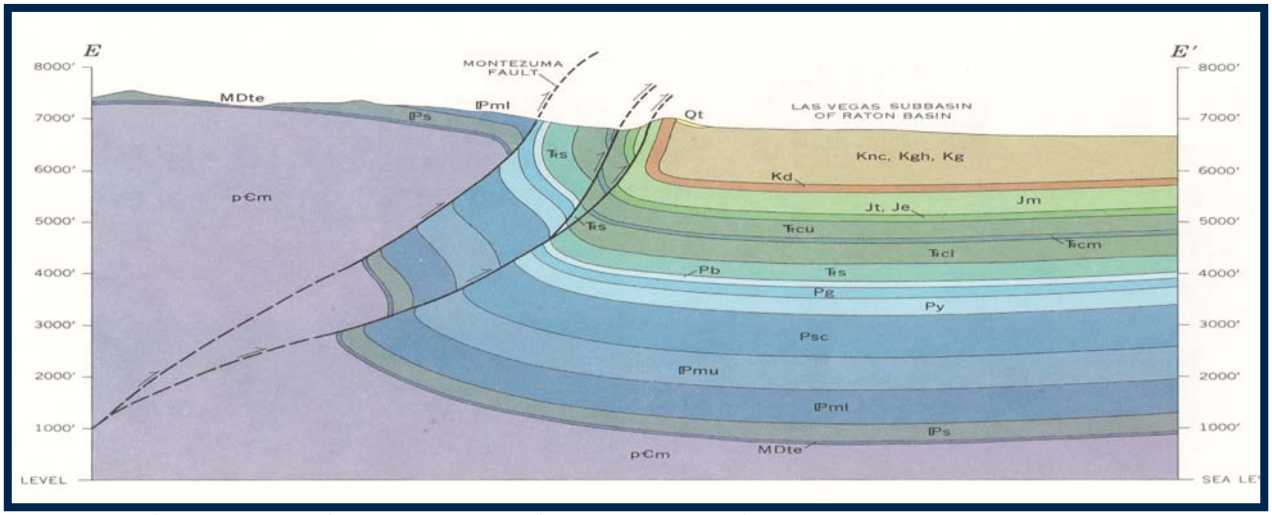

Figure 1. Cross section of regional geology (Baltz, E. H., 1972).

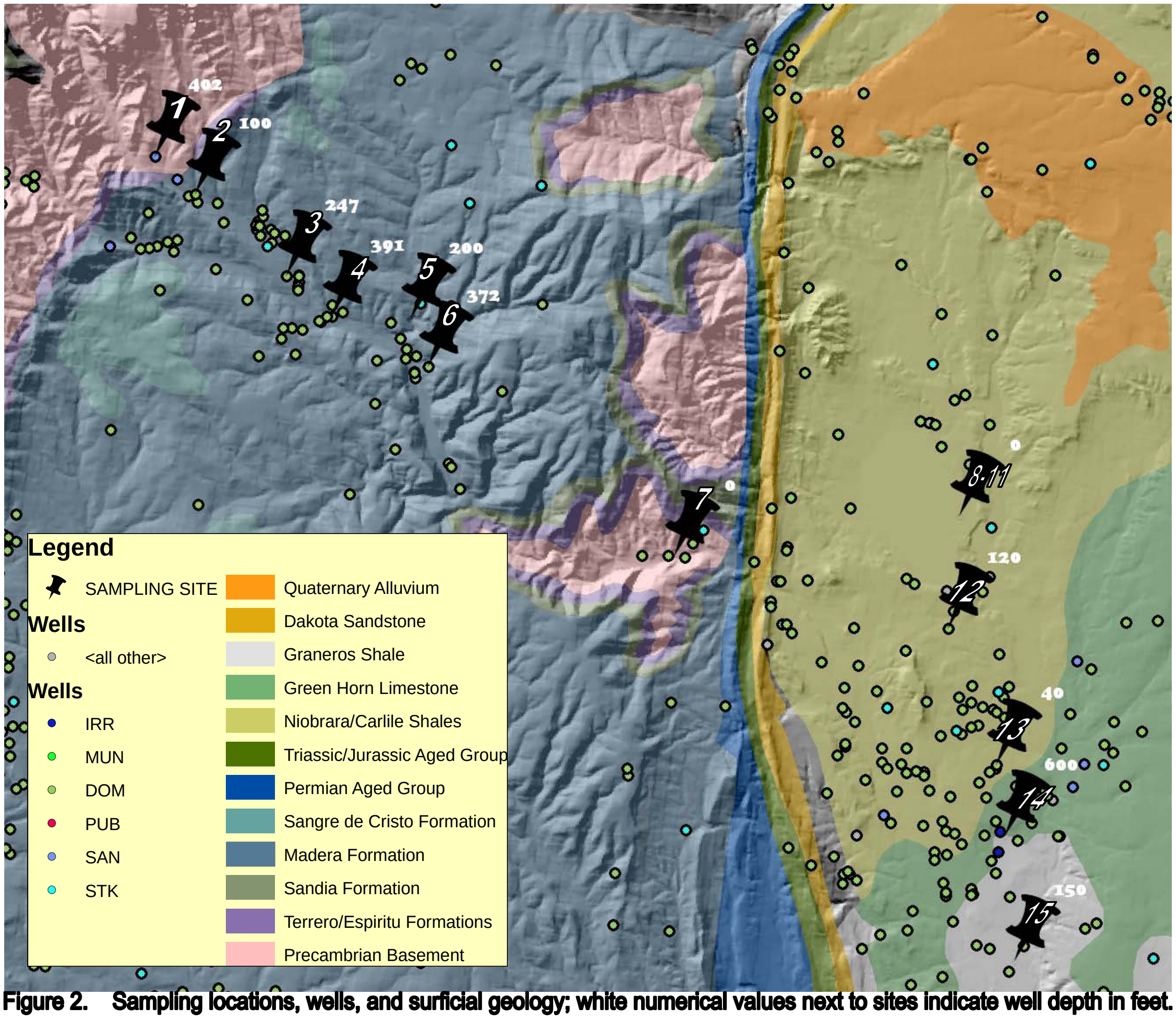

Figure 2. Sampling locations, wells, and surficial geology; white numerical values next to sites indicate well depth in feet.

AGE	LITHOLOGIC UNITS	THICKNESS
CRETACEOUS	NIOBRARA FM. –	
	SMOKY HILL MARL MBR.	900'
	FT. HAYS LS. MBR.	0-55'
	BENTON FM.	
	CARLILE SH.	165-225'
	GREENHORN LS.	20-70'
	GRANEROS SH.	175-400'
	DAKOTA SS.	140-200'
	PURGATOIRE FM. – SS. & SH.	100-150'
JURASSIC	MORRISON FM.	150-400'
	WANAKAH FM.	30-100'
	ENTRADA SS.	40-100'
TRIASSIC	DOCKUM GROUP – SH'S & SS'S	0-1200'
PERMIAN	BERNAL FM.	0-125'
	SAN ANDRES LS.	10-20'
	GLORIETA SS.	50-200'
	YESO FM.	200-400'
?	SANGRE DE CRISTO FM.	700-5300'
PENNSYLVANIAN	MAGDALENA GRP. – LS'S., SH. & SS.	4000-5000'
MISSISSIPPIAN	TERERRO FM. – LS'S.	40-50'
DEVONIAN ?	ESPIRITU SANTO FM. – DOL. LS.	25'
PRE-CAMBRIAN	MAFIC GNEISS GRP.	7000' ?
	METAQUARTZITE GRP.	5000' ?
	GRANITE & GRANITE GNEISS	4000'?

Figure 3. Abbreviated stratigraphic column of Raton basin (Ewing and Kues, 1976).

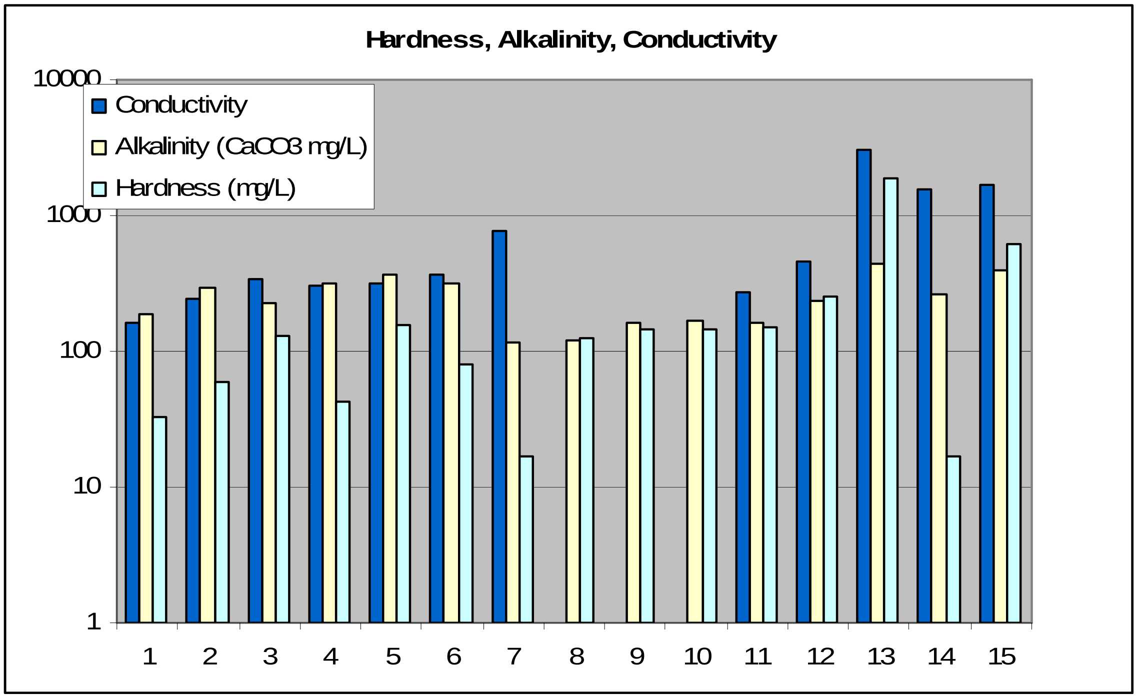

Figure 4. Hardness, Alkalinity, and Conductivity values in the Gallinas Watershed. Numbers on horizontal axis correspond to sample sites on Figure 2. Note the chemical loading down gradient.

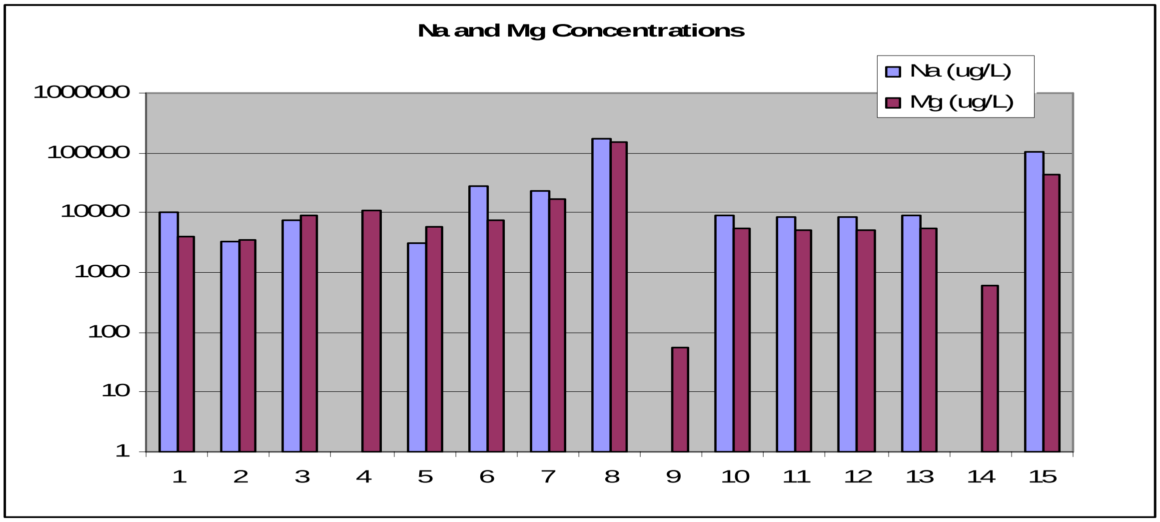

Figure 5. Sodium and Magnesium concentrations in the Gallinas Watershed. Numbers on horizontal axis correspond to sample sites on Figure 2.

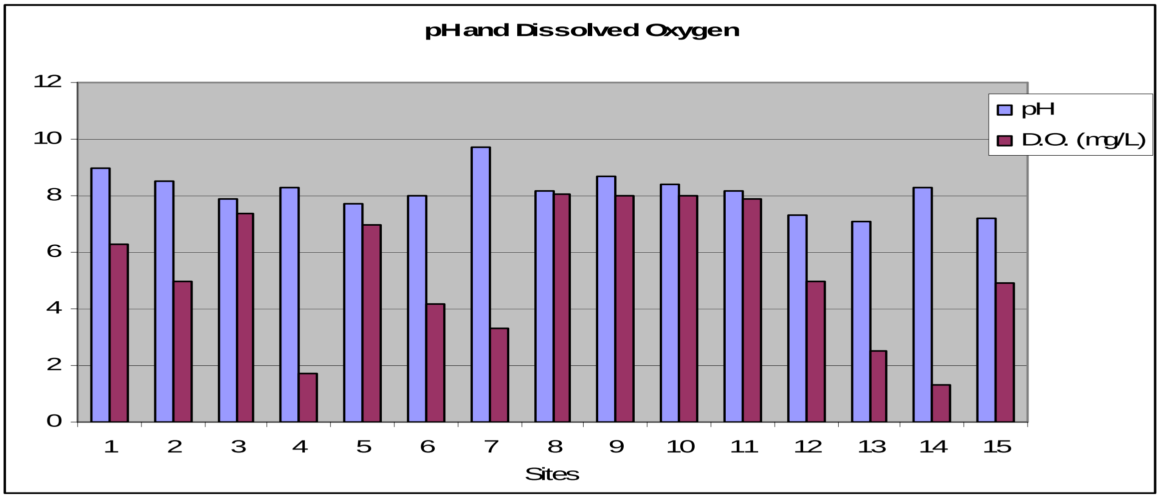

Figure 6. pH and Dissovlved Oxygen levels in the Gallinas Watershed. Numbers on horizontal axis correspond to sample sites on Figure 2.

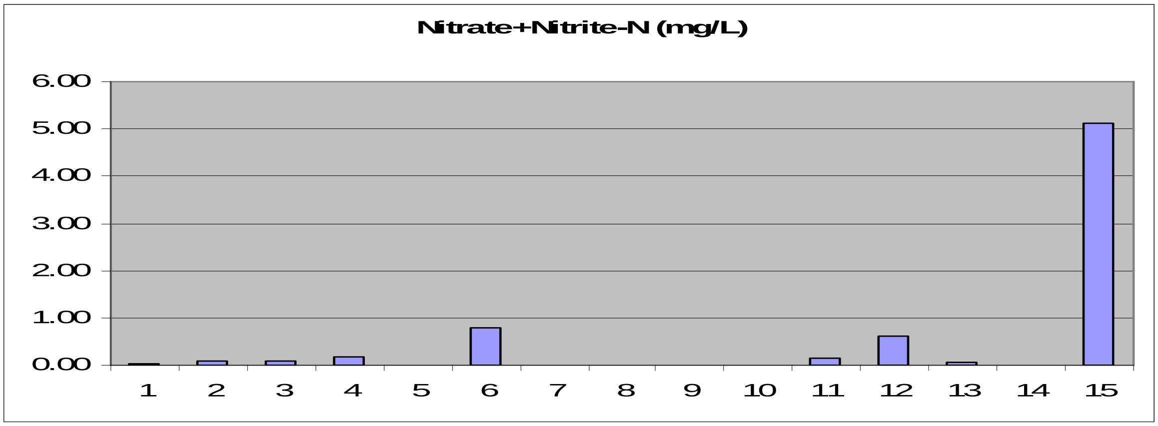

Figure 7. Nitrate and Nitrite-N concentrations in the Gallinas Watershed. Numbers on horizontal axis correspond to sample sites on Figure 2.

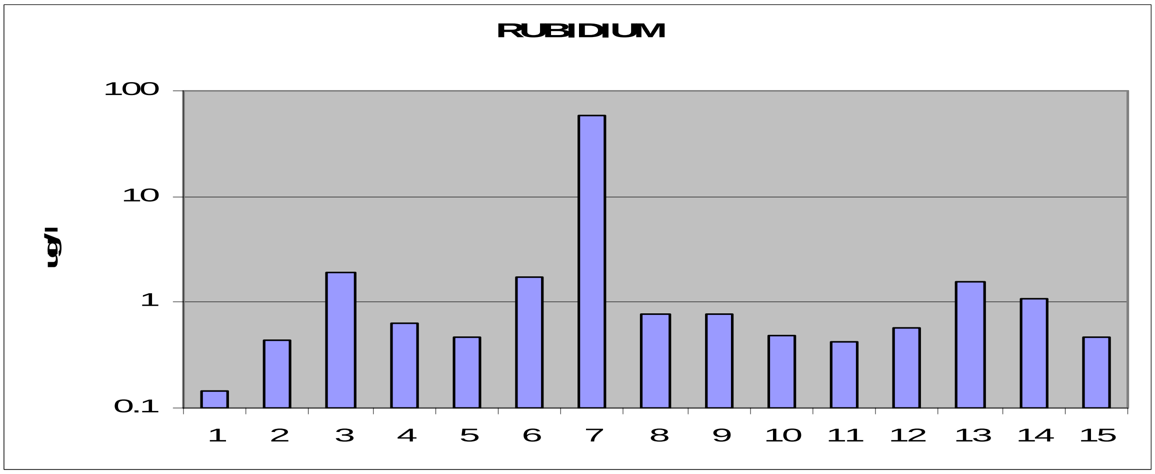

Figure 8. Rubidium concentrations in the Gallinas Watershed. Numbers on horizontal axis correspond to sample sites on Figure 2.

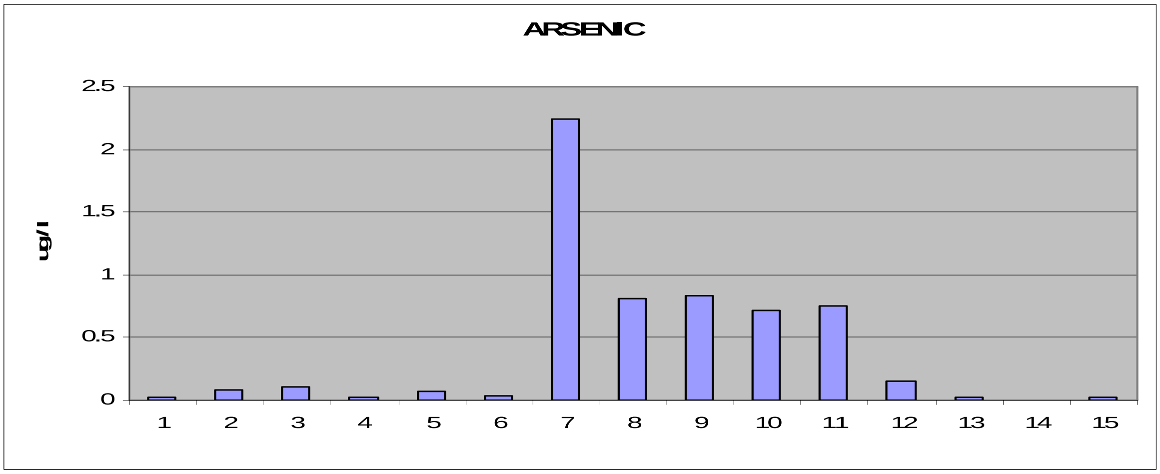

Figure 9. Arsenic occurances in the Gallinas Watershed. Numbers on horizontal axis correspond to sample sites on Figure 2.

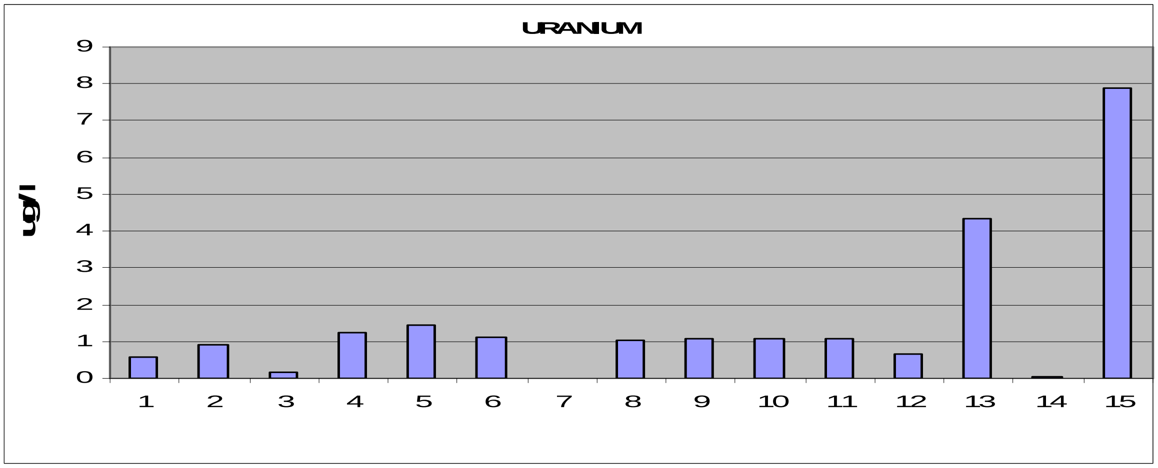

Figure 10. Uranium concentrations in the Gallinas Watershed. Numbers on horizontal axis correspond to sample sites on Figure 2.

Sample Name	pH	DO (mg/L)	Alkalinity (CaCO3 mg/L)	Cond (mS/cm)	Hardness (mg/L)	Nitrate+Nitrite-N (mg/L)	Arsenic (ug/L)	Uranium (ug/L)	Na (ug/L)	Mg (ug/L)	Rb (ug/l)	Cs (ug/l)	Br (ug/l)
1	9	6.3	190.8	165	32.5	0.03	0.029	0.574	10300	4080	0.143	0.005	24
2	8.5	5	296.8	240	60	0.10	0.08	0.89	3270	3410	0.441	0.003	14
3	7.9	7.4	227	335	128	0.09	0.029	0.158	7540	10600	0.636	0.003	24
4	8.3	1.7	318	310	42.5	0.18	0.1	1.22	> 35000	9230	1.92	0.019	19
5	7.7	7	364	320	154	<0.01	0.07	1.46	3050	5880	0.464	0.015	39
6	8	4.2	318	365	80	0.80	0.03	1.11	28300	7640	1.72	0.067	44
7	9.7	3.3	118	770	17.12	0.01	2.24	0.006	> 35000	57	58.4	50.2	867
8	8.2	8.07	120	---	126	---	0.81	1.05	8880	5380	0.781	0.048	40
9	8.7	8	163	---	144	---	0.83	1.055	8465	5240	0.766	0.041	43
10	8.4	8	166	---	144	---	0.72	1.06	8400	5090	0.486	0.019	39
11	8.2	7.9	165	270	148	0.16	0.75	1.07	8900	5540	0.429	0.011	49
12	7.3	5	235	460	256.8	0.61	0.15	0.644	23300	16700	0.574	0.003	67
13	7.1	2.5	435	3050	1883.2	0.07	0.029	4.33	176000	154000	1.55	< 0.01	550
14	8.3	1.3	265	1550	17.12	<0.01	-----	0.05	-----	620	1.065	0.025	505
15	7.2	4.9	400	1700	616.32	5.13	0.029	7.88	107000	44000	0.46	< 0.01	410

Elemental anaylsis was conducted using the ICP-MS method, Activation Labratories, Ontario.

Table 1. Water chemistry in the Gallinas Watershed. Sample numbers refer to site locations in Figure 2.