Water Resources Center
Annual Technical Report
FY 2008

Introduction

The Rhode Island Water Resources Center has supported one information transfer project, "Clean Drinking Water in Rhode Island," and two research projects, "Long-term, State-wide Analysis of the Relationship Between Water Quality and Demographic Changes in the State of Rhode Island," and "Utilization of Silver Nanoparticles as Chlorine-free Biocide for Water Treatment". The information transfer project had as its goal the training of high school, undergraduate and graduate students and water professionals. This was accomplished using a summer camp and the Second Annual Clean Water Conference. The two research projects had as their goals the enhancement of water supplies through either a better understanding of the impacts of population on water quality to enhance planning or a novel treatment of contaminated water. During this year the New England Water Resources Center Directors met to discuss methods of enhancing their programs through joint efforts.

Research Program Introduction

The goals of the two research projects were to investigate methods to improve water supplies. Craver's research project investigated a novel treatment method to reclaim contaminated water. Meyerson's project investigated the links between demographics and water quality. Meyerson's research could lead to better protection of watersheds.

Long-term, state-wide analysis of the relationship between water quality and demographic changes in the state of Rhode Island

Basic Information

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Publication

1. Meyerson, Laura and Fred Meyerson, Long-term Analysis of the Relationship Between Water Quality and Demographic Changes in Rhode Island, National Academy of Sciences, in preparation.

Long-term, state-wide analysis of the relationship between water quality and demographic changes in the state of Rhode Island

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ABSTRACT

Water quality data was obtained from 262 freshwater sites in Rhode Island that represent a wide range of land use settings within the state, from protected watersheds to sites highly impacted by human activities. This data, collected over a twenty-year period, included samples taken over a regular basis (ranging from weekly to twice yearly, depending on indicator) for water clarity, algal density, dissolved oxygen, water temperature, alkalinity and pH, nutrients, and bacteria. This data was analyzed to determine if any temporal or spatial trends were evident. Several indicators of water quality showed a substantial variation among sites and a trend of degradation over the period of observation for many sites. Most significantly, mean chloride levels increased from 16 to 36 mg/l over the period 1988-2008. Other indicators, such as phosphorus, ammonia, and water clarity, showed similar trends. An initial assessment of chloride concentrations at individual sites indicated a relationship between proximity to roads and development and the level of chloride in the water.

KEYWORDS: water quality, environmental monitoring, water pollution

INTRODUCTION

The ability to assess water quality is of great importance, both because of our need for drinking water and as an indicator of environmental health. Water quality is impacted by many human activities, including development, industrialization, and agriculture. By assessing water quality trends and determining their relationship with human factors, tools could be developed for managers and planners to assist in making prudent decisions that affect our watersheds.

Water quality data was obtained, with 23 indicators sampled, from 262 freshwater sites in Rhode Island, spanning the period 1988-2008. This data was analyzed in order to

determine temporal and spatial trends, with the intent of gaining insight into how water quality has been affected by human activity.

METHODOLOGY

Water quality data was obtained through the University of Rhode Island (URI) Watershed Watch monitoring program. The URI Watershed Watch program works with local communities to assess water quality and to provide information for more effective management of critical water resources. The URI Watershed Watch helps local governments and other organizations to recruit and train volunteers to become citizen scientists gathering detailed, quality assured monitoring data. The protocols for collecting and analyzing samples and procedures for training volunteer monitors are established in detail[1]. URI Watershed Watch data are intended to be used by the local programs that help support it, including the Rhode Island Department of Environmental Management (RIDEM), Rhode Island Department of Health, the US Environmental Protection Agency (USEPA), as well as researchers at URI and elsewhere. Thus, rigorous quality control procedures are implemented to ensure that the quality of the data meets the standards of these agencies[2].

The URI Watershed Watch program incorporates procedures and protocols recommended and approved by national organizations to ensure that monitoring results accurately reflect the conditions of the sampled water bodies. Results from laboratory staff and volunteers are regularly checked against known standards and quality control samples. State-of-the-art research grade instruments are generally used, permitting high resolution and excellent detection limits.

The water quality analysis performed by the URI Watershed Watch is primarily focused on providing information on nutrient enrichment (eutrophication), lake acidification, and bacterial contamination. They do not routinely screen for industrial pollutants or pesticides. When abnormal water quality conditions are observed, they may conduct additional tests beyond the routine sampling.

The water quality indicators that are measured the URI Watershed Watch include water clarity, algal density, dissolved oxygen, water temperature, alkalinity and pH, nutrients, and bacteria. Depending on the particular indicator, these are sampled weekly, biweekly, monthly, tri-seasonally, or biannually. Not all indicators have been monitored over the entire twenty-year period. For instance, monitoring of sodium levels was discontinued in 1992 as the equipment required to measure sodium is expensive, and as sodium levels were observed to follow levels of chloride, it was determined that the sodium observed in water samples originating primarily in road salt and thus chloride

would be a reliable proxy for sodium. Water quality indicators are measured according to the following schedule:

Weekly:
- Water clarity
- Temperature

Biweekly:
- Algal density
- Dissolved oxygen
- Salinity

Tri-seasonally or monthly:
- pH and alkalinity
- Nutrients
- Bacteria

Biannually (formerly tri-seasonally):
- Chloride

The URI Watershed Watch has collected data from over 200 sites at lakes, ponds, rivers, and streams in Rhode Island (sampling sites in salt ponds and estuaries were not considered in this study). This data has been collected from 1987 through the present, although most sites have not been continuously monitored over that period. Initially, the sampling areas were contained within the Wood-Pawcatuck watershed (the Wood-Pawcatuck Watershed Association initiated a water monitoring program in 1987 which became the URI Watershed Watch). Subsequently, other sites were added throughout the state.

The URI Watershed Watch dataset consisted of 58,457 individual data samples. The data was obtained from 262 sampling sites. As some streams, rivers, and larger lakes are sampled at multiple locations, this does not represent unique bodies of water. Most of the sites were only sampled for part of the total duration; only fourteen sites were sampled continuously from 1989 to 2005.

A total of 23 water quality indicators were sampled. This includes seven nutrients (nitrogen is measured five ways and phosphorus two), three bacteria (enterococci, E. coli, and fecal coliform) and other indicators such as water clarity (Secchi depth), temperature, pH, and salinity. Again, most of the indicators were not sampled for the entire duration of the study, and thus it is only feasible to assess temporal trends for some of them. The list of indicators and the period of years for which data was available for each of them is shown in Table 1.

The dataset contained sampling data through 2005. Data has been gathered continuously through 2008 (and sampling has been initiated for 2009), but at the time of this study only chloride data was available for the period 2006-2008.

RESULTS

Temporal water quality trends

An initial assessment of the data was made to assess trends for the different indicators over the course of the observations. This was done by taking the aggregate data for all sites for each of the indicators, plotting the level of concentration vs. time, and performing linear regression. The results of this preliminary analysis are discussed in the following sections and are presented in Appendix A. In general, a trend of degradation was observed in most water quality indicators where data was available for all or most of the period of study. This was most pronounced in chloride levels, which essentially doubled over the period.

However, as the initial sites that were monitored were contained within the Wood-Pawcatuck watershed, an area of relatively low population density, and sites in more urbanized areas were added later, the trends observed in this analysis could be skewed by the greater number of samples from urbanized areas in the later period of the study. As only a few sites were sampled for all or most of the twenty-year period, considering only those sites would greatly minimize the amount of data and the results would be skewed toward less urbanized areas which were sampled for the longest periods. For the purposes of calculating means, any site that was sampled for less than five years was eliminated. Mean levels of concentration for each of the indicators were determined for these sites, and the analyses are discussed in the following sections

<u>Chloride</u>

Chloride contamination is of great concern, as chloride levels greater than 230 mg/L are considered toxic to fish and other aquatic organisms. Plant toxicity is also a concern, particularly with grasses and other native plants near roadways that are subject to salting.

Chloride enters ground and surface water from a number of sources. Some chloride is natural, due to leaching from rocks. Chloride found in discharge from septic systems. In bodies of freshwater that are near the coast, saltwater intrusion may lead to increased chloride levels if pumping of freshwater exceeds the rate of recharge. In much of the U.S., particularly the northeast, the primary factor in chloride contamination is the use of salt on roadways. Rising levels of chloride have been observed in many watersheds in

the northeast. A study by Kaushal *et al*.[3] examined seven stream and rivers in the Northeast US over periods of 20 to 40 years and found steady increases in chloride levels; most dramatically in New Hampshire, where chloride levels have risen an order of magnitude since the 1960s, in some cases over 100 mg/l. The same study focused on streams in a rapidly urbanized area around Baltimore, and found a logarithmic relationship between the degree of impervious cover in a watershed and the mean chloride concentration in streams.

Samples from the freshwater sites were filtered and then analyzed on an autoanalyzer using a colorimetric technique to determine chloride concentration[4]. The most significant trend among all of the constituents measured was in chloride concentration. Mean chloride levels increased from 15 to 35 mg/L in the period 1988-2008 (Figure 1). Sodium contamination is also of concern in watersheds, and observation of similar trends in sodium levels would substantiate that road salt usage was a contributing factor. Unfortunately, measurement of sodium levels was discontinued in 1992 and there is insufficient data to determine any meaningful trends in sodium levels.

It is hoped that we will be able to determine if the rise in chloride levels was correlated with road salt usage in the watersheds in the study. This data was not available at the time of this study, but the increase in road salt sales in the U.S. is shown in Figure 2, which would seem to relate to rising chloride concentrations.

Sodium

Sodium was only measured by the Watershed Watch over the period 1988-1992. The regression shows a slight increase in average sodium concentration observed during this period, from 10.8 mg/l in 1988 to 11.6 mg/l in 1992 (Figure 3); however, the mean values for 1988 and 1992 are nearly the same at 12.2 mg/l. The short period of observation is not sufficient to establish a significant trend. Monitoring of sodium was discontinued in 1992 due to the cost of the equipment required, along with the view that sodium contamination would be primarily due to road salt and thus chloride serves as a proxy for sodium. However, the availability of long-term sodium data would serve to confirm this assumption. It would also provide insight on how these elements are getting into the watersheds. If road salt takes a direct path to streams from surface runoff, the amounts of sodium and chloride reaching the streams would be about the same. However, if the primary means of transport is groundwater, the ratio of sodium to chloride would be lower due to the greater mobility of chloride ions vice sodium ions[5].

Magnesium and Calcium

Magnesium and calcium are essential elements for human health and occur naturally in most water sources. Magnesium and calcium salts are dissolved in water that comes in contact with soil and rock formations. Water softening treatment removes these salts.

Magnesium and calcium are particularly important in regulating the cardiovascular systems, and medical studies have found that there is an inverse relationship between drinking water hardness and incidence of cardiovascular disease[6].

Magnesium and calcium were both only measured for the period 1988 through1992. Magnesium (Figure 4) shows a slight decrease, but the trend is not very well defined (R^2 = 0.1116). Calcium (Figure 5), on the other hand, shows a very definite (R^2 = 0.9825) trend upward, from 4.1 mg/l in 1988 to about 4.7 mg/l in 1992.

Nutrients

Nutrients (total and dissolved phosphorus, ammonia, total and nitrate-nitrogen) are analyzed from water samples collected tri-seasonally. These parameters are used to assess the degree of eutrophication, or nutrient enrichment, along with measurements of chlorophyll content and water clarity[7].

Phosphorus is a nutrient required by all organisms, and occurs naturally in rocks, soils, and organic material. Dissolved phosphorus is readily available for plants, and consists of inorganic orthophosphate and organic phosphorus-containing compounds. Particulate phosphorus comes from the remains of plants and animals. As phosphorus clings to soil and is taken up by plants, phosphorus levels should be low in healthy aquatic ecosystems. Phosphorus is used in fertilizers and other chemicals, so high phosphorus concentrations are indicative of human activity. Phosphorus pollution is of particular concern in freshwater systems, as high levels of phosphorus leads to eutrophication, which results in harmful algal blooms, loss of habitat, and possibly fish die-offs.

Nitrogen fixation by bacteria in lakes and streams converts atmospheric nitrogen into ammonia, and further into organic compounds. Ammonia also occurs in the discharge from wastewater treatment plants. Ammonia is highly toxic to fish. Nitrifying bacteria oxidize ammonia and form nitrites, which are converted into nitrates by other bacteria.

The nitrogen cycle is influenced in a variety of means by human activity. Nitrogen and hydrogen are used to make fertilizers through the Haber-Bosch process. Pollution from automobiles and industrial activity has doubled the amount of nitrogen that is transformed into biologically-available forms[8]. Nitrates are highly soluble and easily enter groundwater. High levels of nitrate in drinking water can adversely affect blood-oxygen levels in infants. Excess nitrogen loading into freshwater systems leads to eutrophication and its associated effects.

Phosphorus levels rose significantly during this period. Total phosphorus (Figure 6) doubled from 1989 to 2005, increasing from 22 to 44 µg/l. Dissolved phosphorus (Figure 7) was sampled beginning in 1993, and it rose rapidly from 2.8 to 22.6 µg/l from 1993 to

2005; thus dissolved phosphorus was the main component of the increase in total phosphorus.

Total nitrogen concentrations rose from 484 to 680 µg/l over the period 1993-2005 (only a limited number of sites were sampled in 1992). Total ammonia data was only available for two years (1988 and 2002), but dissolved ammonia (Figure 8) doubled from 1999 to 2005 (only a couple of sites were sampled in 1997-1998). However, the lowest levels of dissolved ammonia were recorded in 2002 and 2003, and given the short period that dissolved ammonia is measured and the weak linear trend ($R^2 = 0.2$) this may or may not be indicative of the long term trend. Total nitrate doubled from 1993 to 2002 (limited data was available for the years prior to 1993), increasing from 60 to 120 µg/l (Figure 9).

Water clarity

Water clarity is measured through the use of a Secchi disk[9]. The disk is lowered until the observer begins to lose sight of it, and the depth is recorded off of a calibrated line. The Secchi depth is an indication of the amount of suspended particulates in the water, including sediments and algae.

Water clarity data was available for the period 1993-2004. Mean Secchi depth (Figure 10) decreased from 3.0 to 2.2 m during that time; indicating greater turbidity. Secchi depth is often used as a measure of algal density and a means of monitoring eutrophication, but in order to do this it is necessary to calibrate readings with measure of chlorophyll concentration.

Chlorophyll

Chlorophyll is a more reliable indicator of algal density than Secchi depth (which also is a measure of sediments and other particulates), but is not a simple to measure. However, if the greatest contributor to water turbidity is algal density, then one would expect to find an inverse relationship between water clarity and chlorophyll.

The concentration of chlorophyll-a is generally used to estimate phytoplankton biomass[10]. Samples are collected and either filtered in the field or upon arrival at the laboratory. The filtered samples are then kept frozen until they are extracted and analyzed using a fluorometer. The value returned by the fluorometer is the raw chlorophyll-a concentration. The final chlorophyll-a concentration is determined through calculation[11].

Chlorophyll data was obtained for the period 1993-2005. The mean concentration of chlorophyll (Figure 11) rose significantly during this period, from 4 to 9 µg/l.

Temperature

Water temperature is an indicator of interest, because of the concern about environmental effects of global warming. Water temperature data was only available for the period 2000-2005. If there is a warming trend due to climate change, this short period of observation would not be likely to capture it. The mean water temperature is plotted (by month, to show seasonality) in Figure 12, and shows virtually no change from 2000 to 2005. While the seasonal variation does seem to be increasing, this is mainly due to a low temperature of 10º C in November 2004 and there is not sufficient data to see if this is a persistent trend. This indicator should be reassessed in future studies to determine if there is an effect on local freshwater water temperature as a consequence of global warming.

Bacteria

The Watershed Watch monitors three types of bacteria- E.coli, enterococci, and fecal coliform. Enterococci counts have only been measured since 2001. The Rhode Island Department of Environmental Management (RIDEM) now uses enterococci rather than fecal coliform as the indicator used for assessing water quality at beaches in the state, as it is considered a better indicator of human pathogens. Bacteria counts were determined as per the protocols endorsed by the American Public Health Association[12].

Unlike other water quality indicators, bacteria counts tend to be sporadic in nature due to rapid growth and declines of populations of bacteria. Thus a much more meaningful statistic than mean bacteria levels is the number of events that exceed a predetermined bacteria count threshold. So that these statistics would be more indicative of adverse water quality conditions, the standards set by regulatory authorities were used to construct threshold values. RIDEM considers a fecal coliform bacterial count of 200 most probable number (MPN) per 100 ml to be an acceptable level for recreational use (not drinking water). For enterococci, RIDEM considers 61 colonies per 100 ml to be the single sample maximum, and is the standard used for beach advisories. RIDEM does not publish an acceptable level of concentration for E. coli, so the US Environmental Protection Agency (USEPA) standard for a single sample of 235 MPN/100 ml was used.

Fecal coliform, E. coli, and enterococci counts are shown in Figures 13, 14, and 15 respectively. In each case, the number of samples for each year that exceeded the thresholds described above were counted, and then divided by the total samples taken that year to obtain a fraction of samples that exceed the threshold. Both fecal coliform and E. coli exhibit an annual increase in the fraction of samples that were above the threshold. The fraction of samples over the threshold for enterococci declined overall, but data for enterococci was only available from 2001 through 2005, and 2005 showed an increase over the two preceding years.

Spatial differences in chloride concentration

Most of the individual sampling sites showed similar trends in the increase of chloride concentration that was exhibited in the mean level for all of the sampled sites. However, some differences were observed among particular sites that are indicative of differences in land use and degree of industrialization.

Figure 16 shows four sites that depict varying degrees of influence from development and proximity to populated areas. Alton Pond is representative of a typical site among all of those sampled. Chloride concentration in Alton Pond doubled over the period 1989-2008, from 15 to 30 mg/L; a similar trend to that found in the mean of all sites sampled.

Boone Lake exhibited an increase in chloride concentration from 45 to 70 mg/L. While the rate of increase is not as high as that of the mean of all sites, the level of chloride contamination is the highest among all of the sites. This is likely due to Boone Lake's proximity (about one-half mile) to Interstate 95, the major thoroughfare in Rhode Island. Runoff from this highway would drain toward Boone Lake. Additionally, Boone Lake is entirely surrounded by residences.

White Pond is an example of a site that is fairly isolated from human activity. There are only a few home sites near the pond and few roads in the immediate vicinity, and it is not near any industrial activity. Chloride levels in White Pond were very low, about 5 mg/L, and showed no indication of increase.

Only one site, Yawgoo Pond, exhibited a noticeable decrease in chloride concentration, from 15 to 10 mg/L. A possible explanation is the closure of a shellfish processing plant near Yawgoo Pond in 1990. Massive algal blooms were observed in Yawgoo Pond in 1989 and 1990. It is apparent from the plot that chloride levels actually were increasing during those years. An investigation by the Rhode Island Department of Environmental Management (RIDEM) led to the plant closure, and this coincides with the decreasing trend in chloride levels commencing in 1991, although there was resurgence to about 20 mg/L in the period 1999-2002.

CONCLUSIONS

The URI Watershed Watch program has, for the last two decades, played an instrumental role in monitoring the health of watersheds in Rhode Island. Through the use of volunteer monitors and quality assurance protocols, they allow citizen involvement while ensuring the accuracy of the water quality data. The dataset is an excellent resource and has been useful in assessing spatial and temporal trends in

water quality. It is also understood that the purpose of this program is to monitor water quality, not to provide data for long-term analysis as in this study. However, inclusion of more data would make this an even more useful resource for this type of analysis. One of the difficulties in getting a good picture of how water quality trends have developed is that not all sites are monitored continuously over a long period of time; in fact most sites have dropped in or out of the program over the two decades of observation. If a set of sites was designated for long term continuous observation, with attention given specifically to including sites in various locations through the state in each of the watersheds and in both urbanized and undisturbed areas, a more rigorous assessment of water quality trends could be made.

Inclusion of additional water quality indicators would be useful as well. The data collected by the Watershed Watch serves the purpose of identifying degraded water quality. Some indicators are not monitored because other indicators serve as proxies for this purpose. However, continuous monitoring of additional indicators would facilitate analysis of the sources of contaminates, and would provide ecological information. For instance, sampling for sodium was discontinued by the Watershed Watch in 1992 due to the expense involved, and the consensus that chloride serves as a proxy for sodium. However, sodium toxicity to plants is a concern, and analysis of chloride and sodium over time would better permit an assessment of how much of it is due to road salt, as sodium does not occur naturally. Likewise, monitoring of calcium and magnesium was discontinued in 1992. Magnesium and calcium contribute to water hardness, and their presence in watersheds may be due to discharge from water treatment systems. Additionally, magnesium and calcium levels can effect the distribution of fish, crustaceans, and other organisms[13,14].

The assessment of water quality indicators that were monitored continuously shows a general trend of decreasing water quality. Over the period 1988-2008, average concentrations of chloride more that doubled. There was an increasing incidence of bacterial counts that exceeded thresholds for human health established by regulatory agencies. Nutrient indicators (phosphorus and nitrogen) rose significantly along with chlorophyll, while water clarity diminished. This is indicative of eutrophic conditions and could represent a threat to constituent species in the lakes, ponds and streams. This is indicative of a trend of increasing contamination of watersheds due to the influence of anthropogenic factors such as development, roads, and industrialization. This is further supported by the initial look at spatial trends that was done in this study. Sites that were closer to major roadways showed significantly higher levels of chloride contamination.

FUTURE WORK

The temporal and spatial trends that were observed in water quality indicators are likely related to changes in land use and population distribution. The population in Rhode Island has remained relatively constant (Figure 17) over the last few decades[15]. While the population in Rhode Island is concentrated in the cities of Providence, Warwick, Cranston, and Pawtucket (Figure 18a), there has been a shift in population (Figure 18b) from these urban areas to the areas in the western and southern parts of the state in recent years[16]. Development in the state has grown much faster than population. While the population of Rhode Island only increased five percent from 1970 to 1988, the amount of developed land increased 40 percent during the same period[17]. This is evidenced by the greatly increased amount of developed land per person (Figure 19).

Land use data will be obtained from the Rhode Island Geographic Information Systems (RIGIS) database as well as other sources, such as historical air photos. Characterizing each of the watersheds according to land use will enable spatiotemporal water quality trends to be correlated with trends in development and industrialization. Additionally, census data will be examined for shifts in population density in the region, and this will be statistically correlated with water quality trends as well. Other data regarding contaminates will be incorporated; for example, road salt usage by the towns and cities in each of the watersheds, or the number of households that use septic systems. It would also be informative to introduce more rigorous statistical analysis to further refine the trend analysis and to assess the correlation between these trends and anthropogenic factors. For instance, nonparametric statistical methods such as neural networks are very robust to missing or noisy data and are useful in determining trends and relationships that are not necessarily linear.

Climatic data will be considered as well. Precipitation is a factor in water quality, but how it effects it may vary. For instance, an influx of fresh water into a lake from precipitation may drive down concentrations of contaminants; on the other hand, increased runoff from precipitation may increase contaminant levels. Snowfall for each of the years will be factored in to provide more insight into the effects of road salt. Finally, although a twenty-year period is relatively short in the overall climatic record, the effects of increasing temperatures and heightened climatic variability will be examined for any evidence of climate change on water quality.

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Table 1. List of indicators sampled and years obtained

INDICATOR	UNITS	PERIOD
Alkalinity	ppm*	1991-2002
Calcium	mg/l	1988-1992
Chloride	mg/l	1988-2008*
Chlorophyll a	ug/l	1993-2005
Dissolved Oxygen	mg/l	2000-2005
E.coli	#/100mL	1991-2004
Enterococci	#/100mL	2001-2005
Fecal Coliform	#/100mL	1993-2005
Magnesium	mg/l	1988-1992
Nitrogen, Ammonia Dissolved as N	ug/l	1997-2005
Nitrogen, Ammonia Total as N	ug/l	1988, 2002
Nitrogen, Nitrate Dissolved	ug/l	2000-2005
Nitrogen, Nitrate Total	ug/l	1988-2002
Nitrogen, Total	ug/l	1992-2005
pH	S.U.	1988-2005
Phosphorus, Dissolved	ug/l	1993-2005
Phosphorus, Total	ug/l	1989-2005
Salinity, (ppt)	ppt	2001-2005
Secchi Depth	m	1993-2004
Sodium, Total	mg/l	1988-1992
Sulfate as SO4	mg/l	1988-1988
Temperature	°C	2000-2005
TSS	mg/l	2001-2003

*at the time of this study, only chloride data was available for 2006-2008, although the other indicators were sampled.

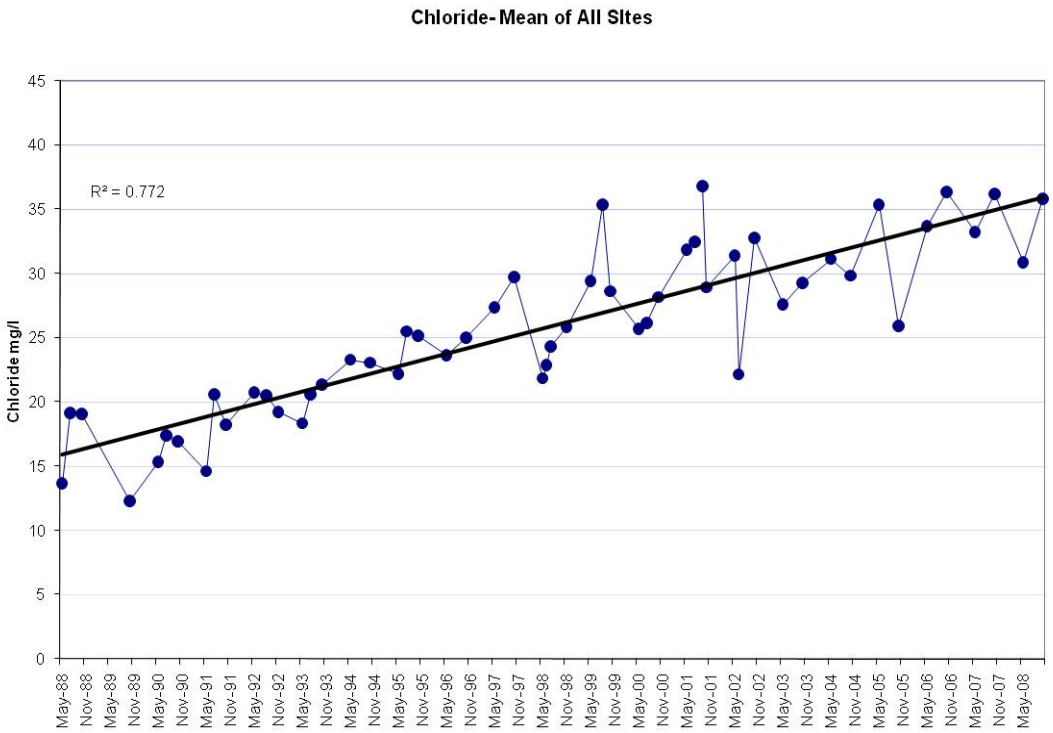


Figure 1. Mean chloride concentrations 1988-2008

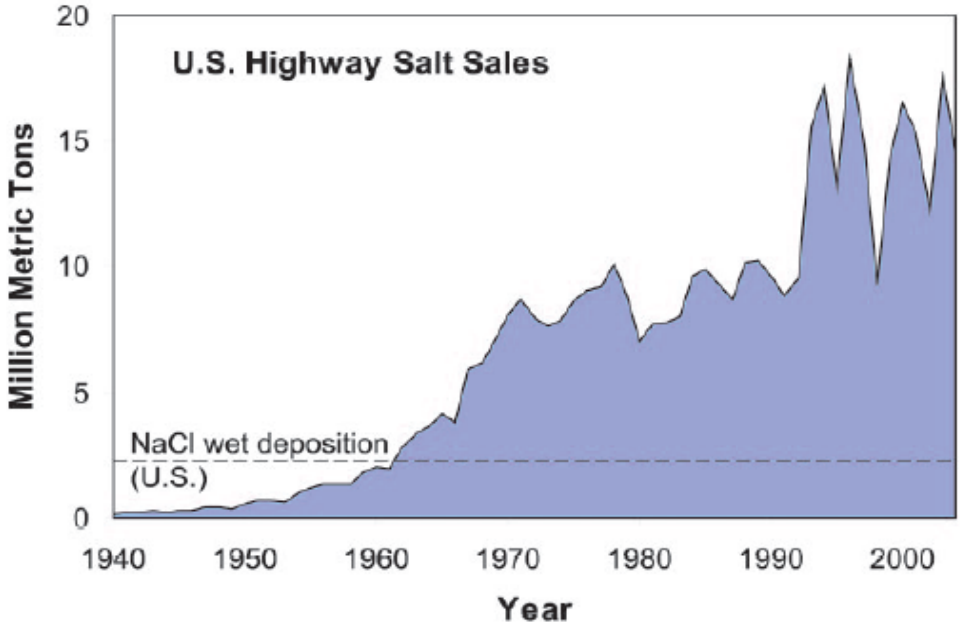


Figure 2. U.S. highway road salt sales 1940-2004 (from Jackson and Jobbagy, 2005)

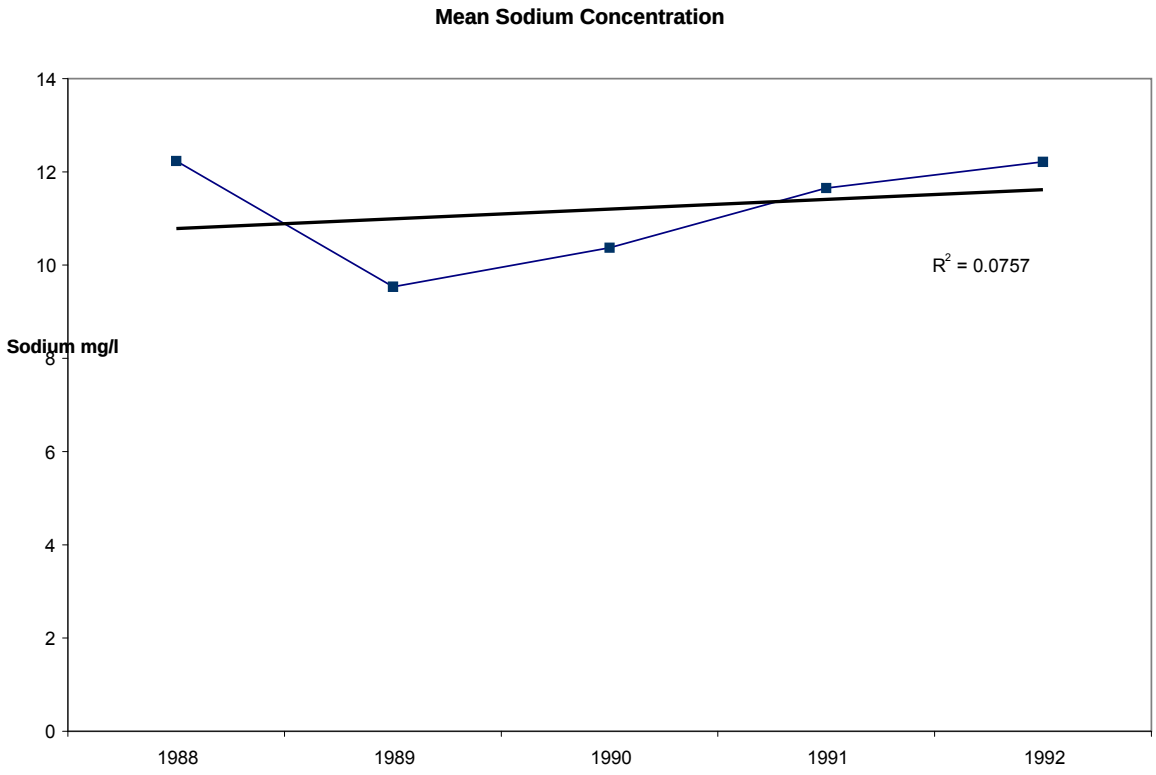


Figure 3. Mean sodium concentration 1988-1992.

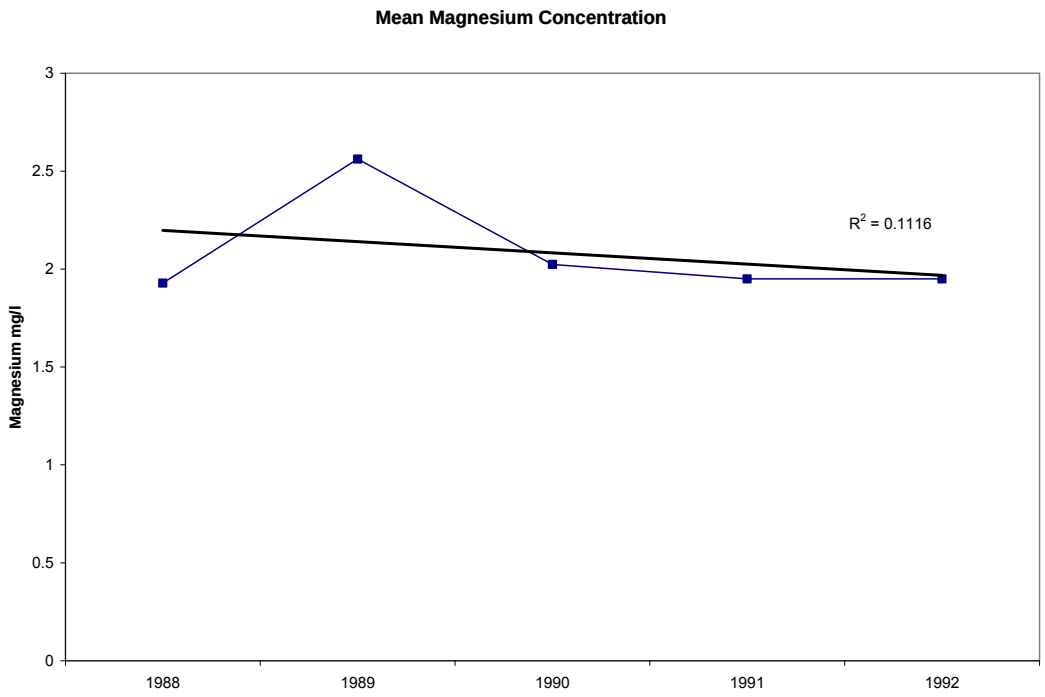


Figure 4. Mean magnesium concentration 1988-1992.

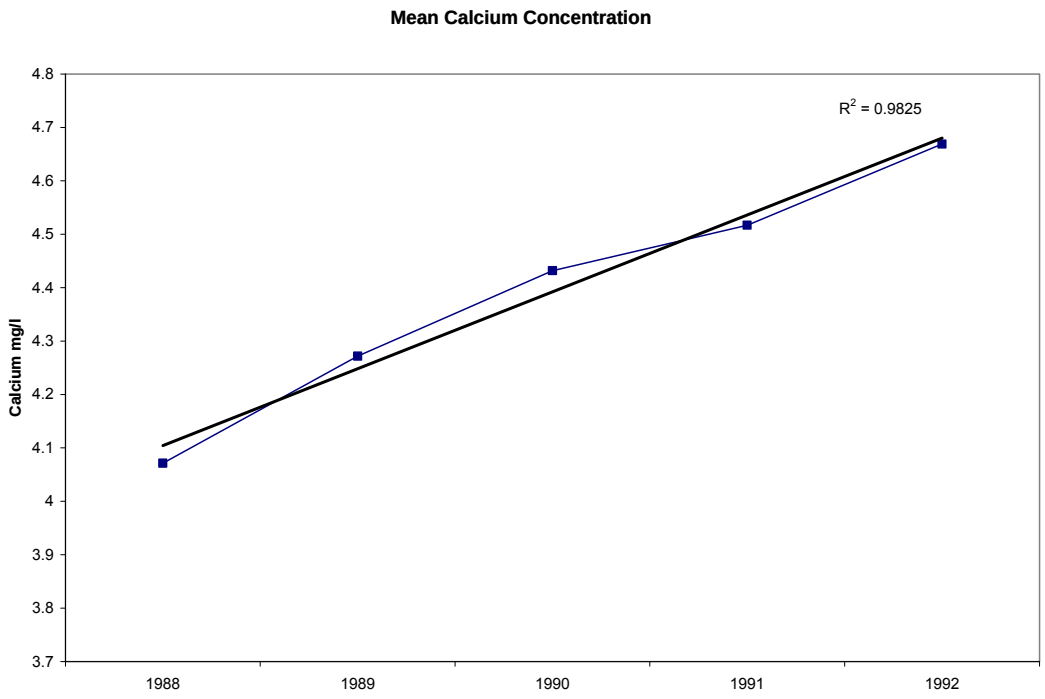


Figure 5. Mean calcium concentration 1988-1992.

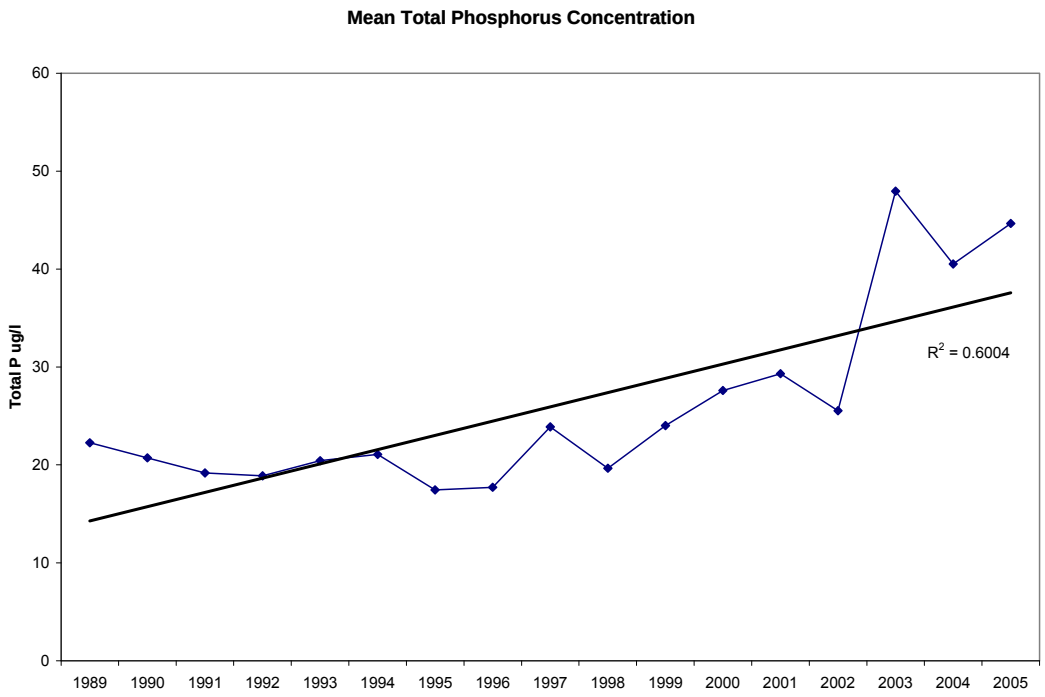


Figure 6. Mean total phosphorus concentration 1989-2005.

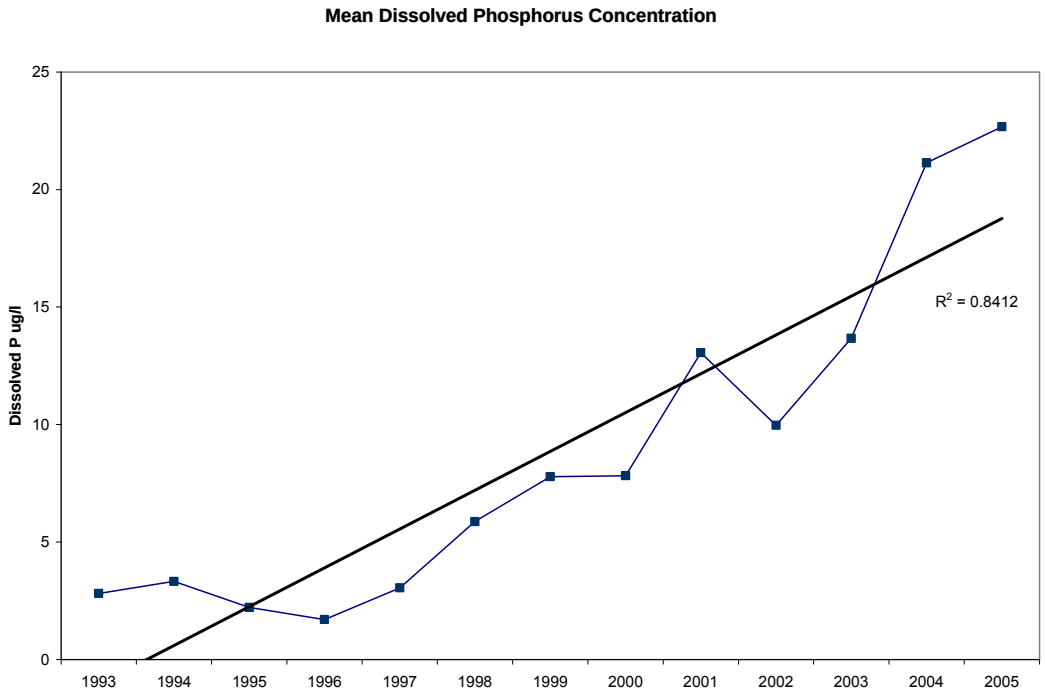


Figure 7. Mean dissolved phosphorus concentration 1993-2005.

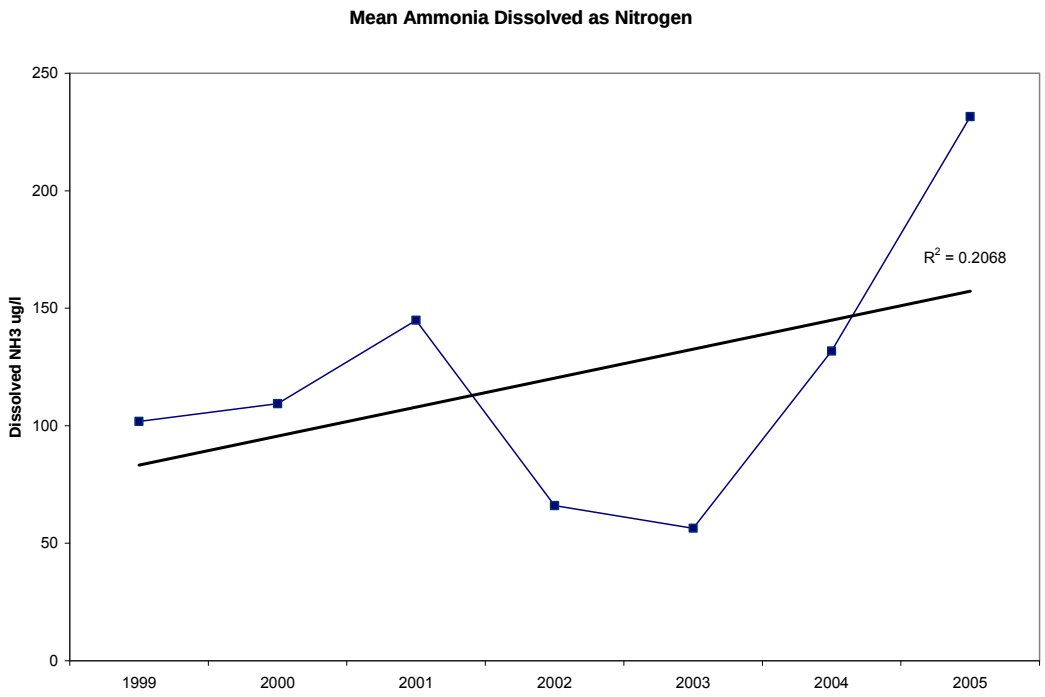


Figure 8. Mean dissolved ammonia concentration 1999-2005.

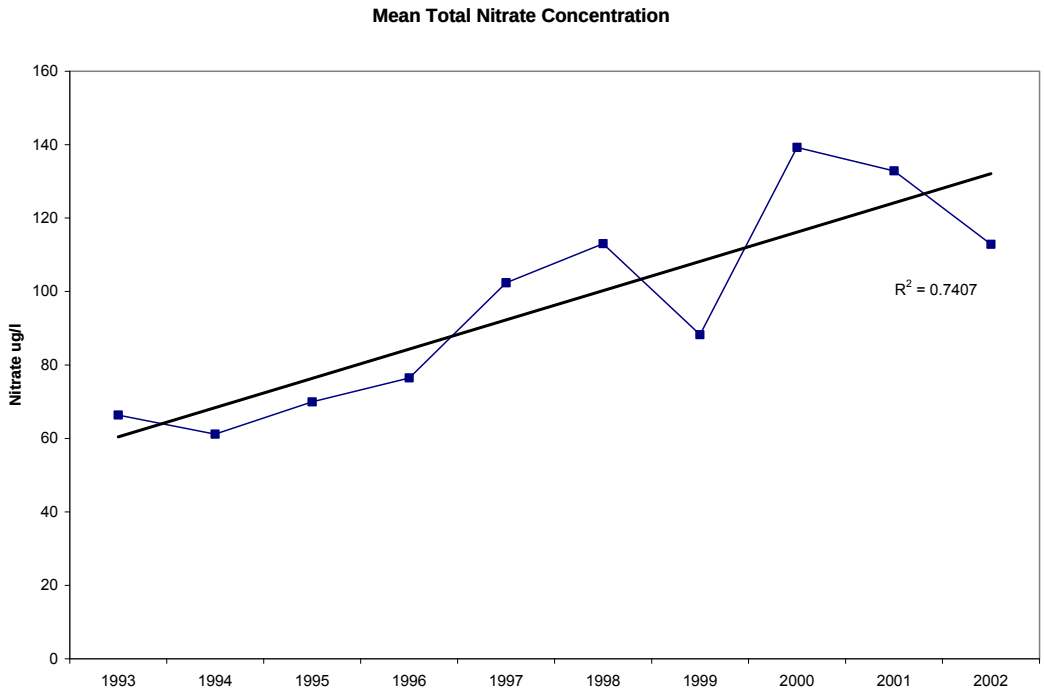


Figure 9. Mean total nitrate concentration 1993-2002.

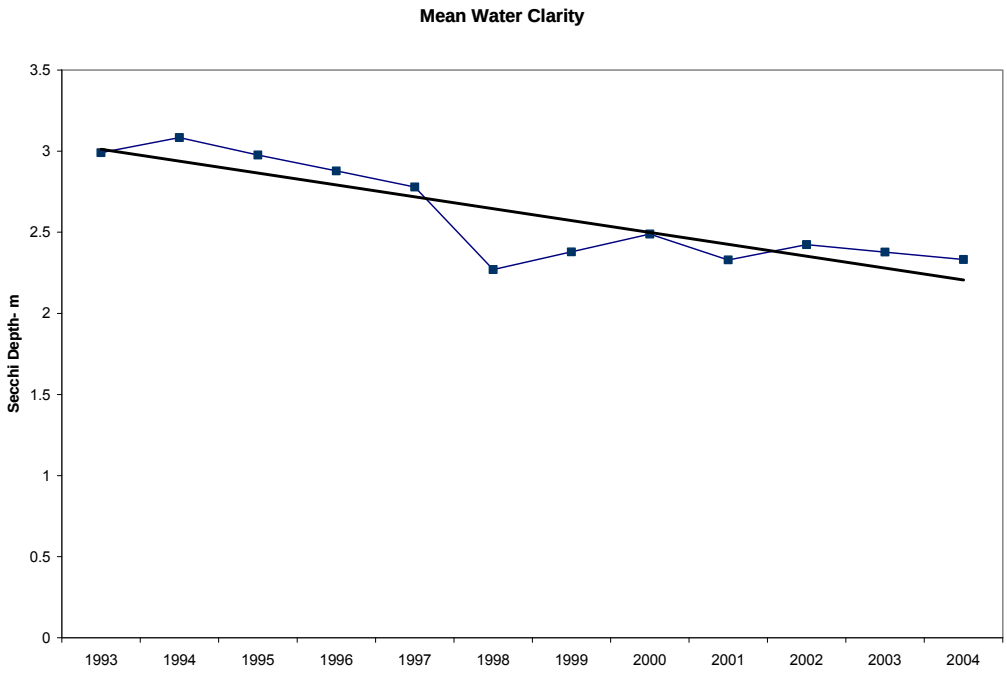


Figure 10. Mean water clarity (Secchi depth) 1993-2004.

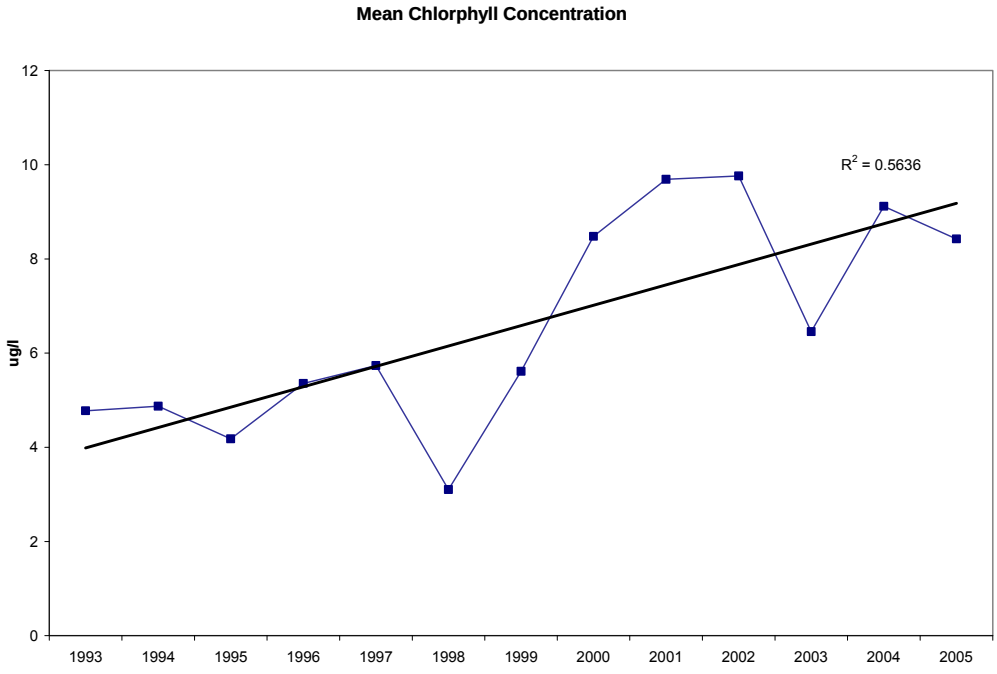


Figure 11. Mean chlorophyll concentration 1993-2005.

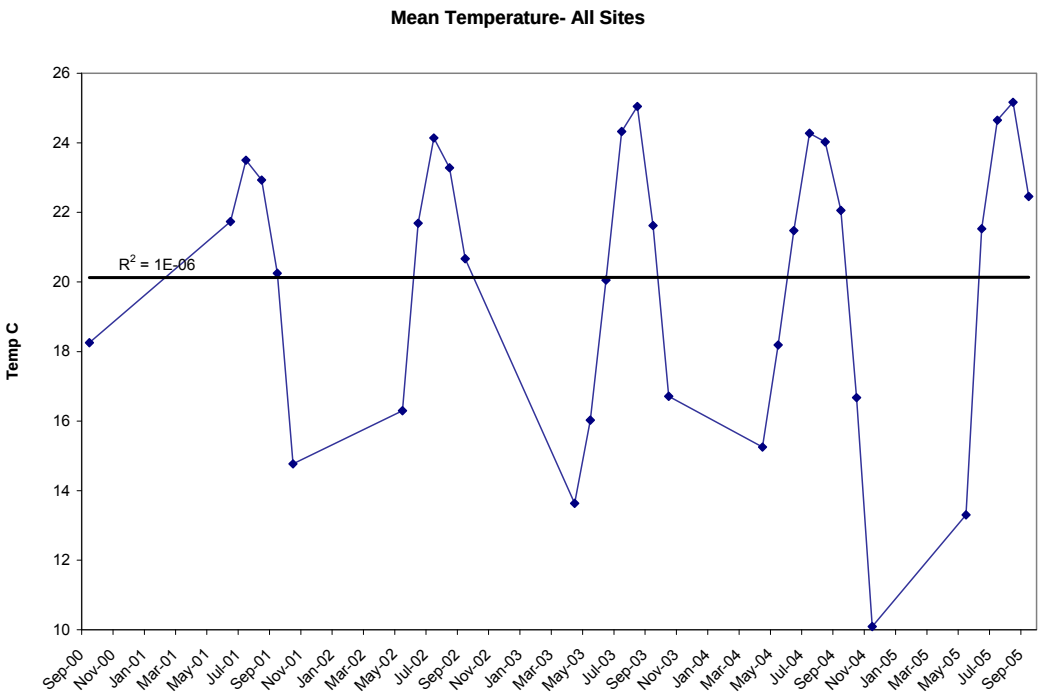


Figure 12. Mean temperature 2000-2005.

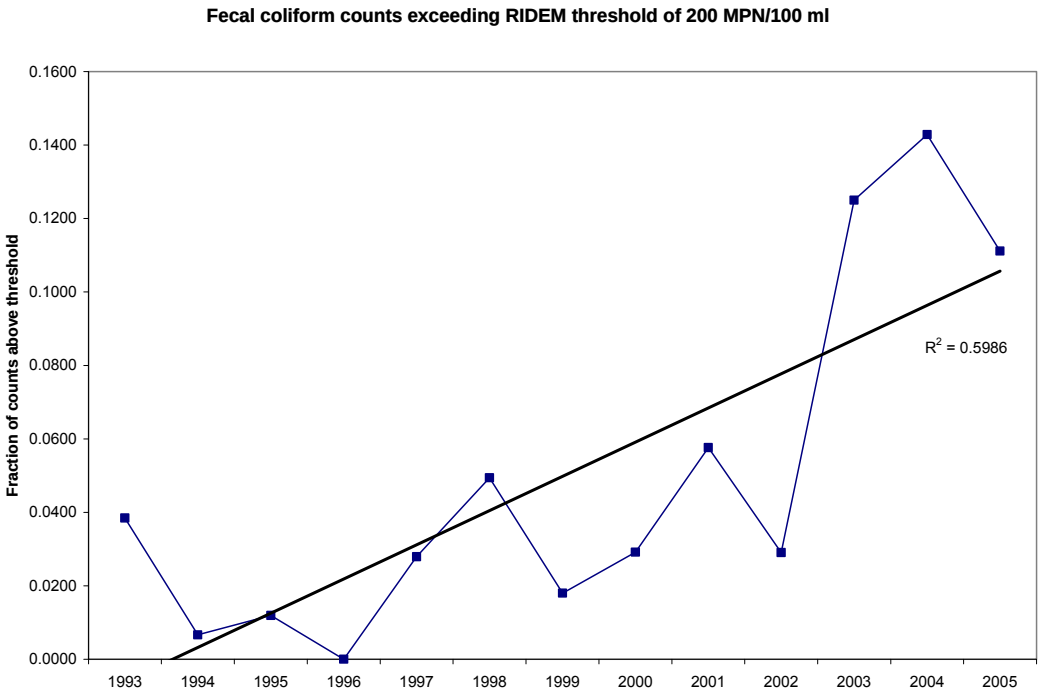


Figure 13. Fraction of fecal coliform counts above RIDEM threshold 1993-2005.

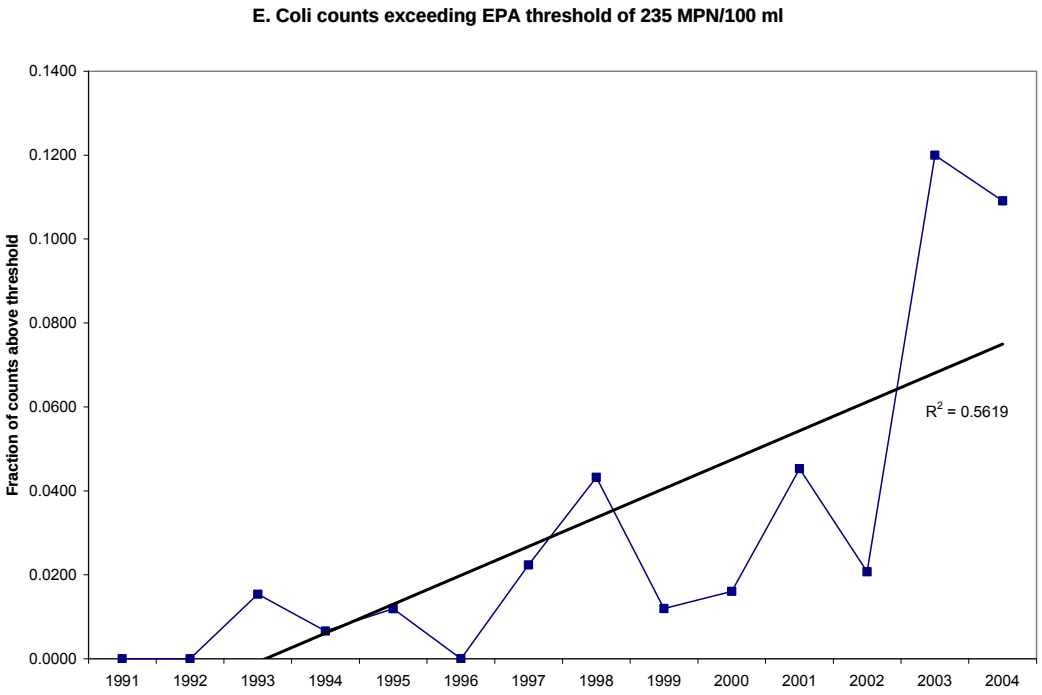


Figure 14. Fraction of E. coli counts above EPA threshold 1991-2004.

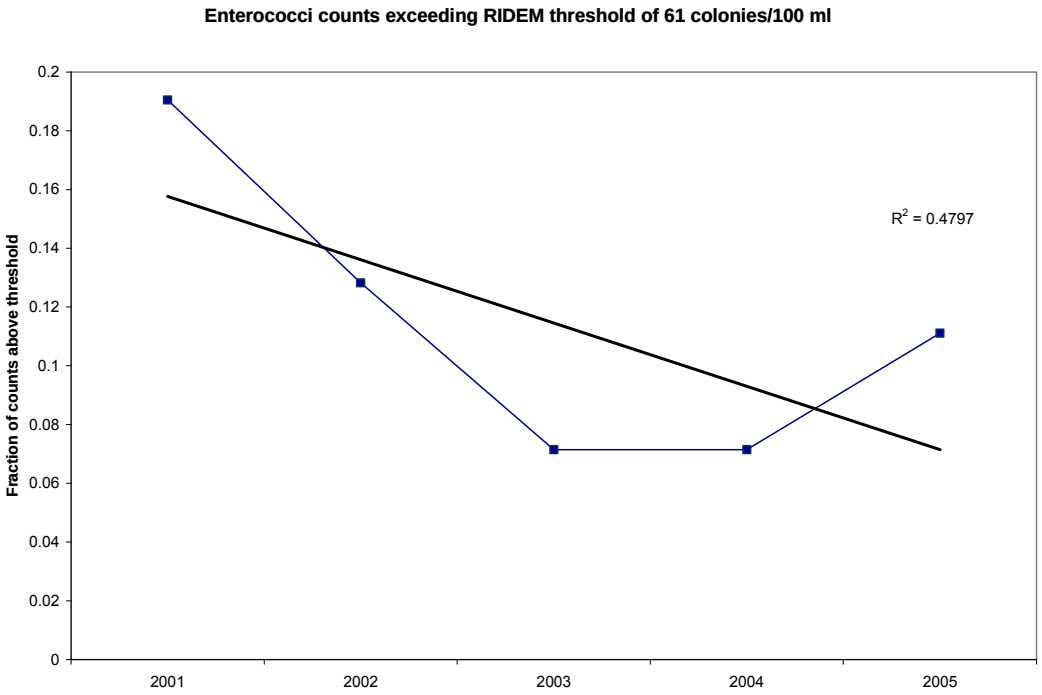


Figure 15. Fraction of enterococci counts above RIDEM threshold 2001-2005.

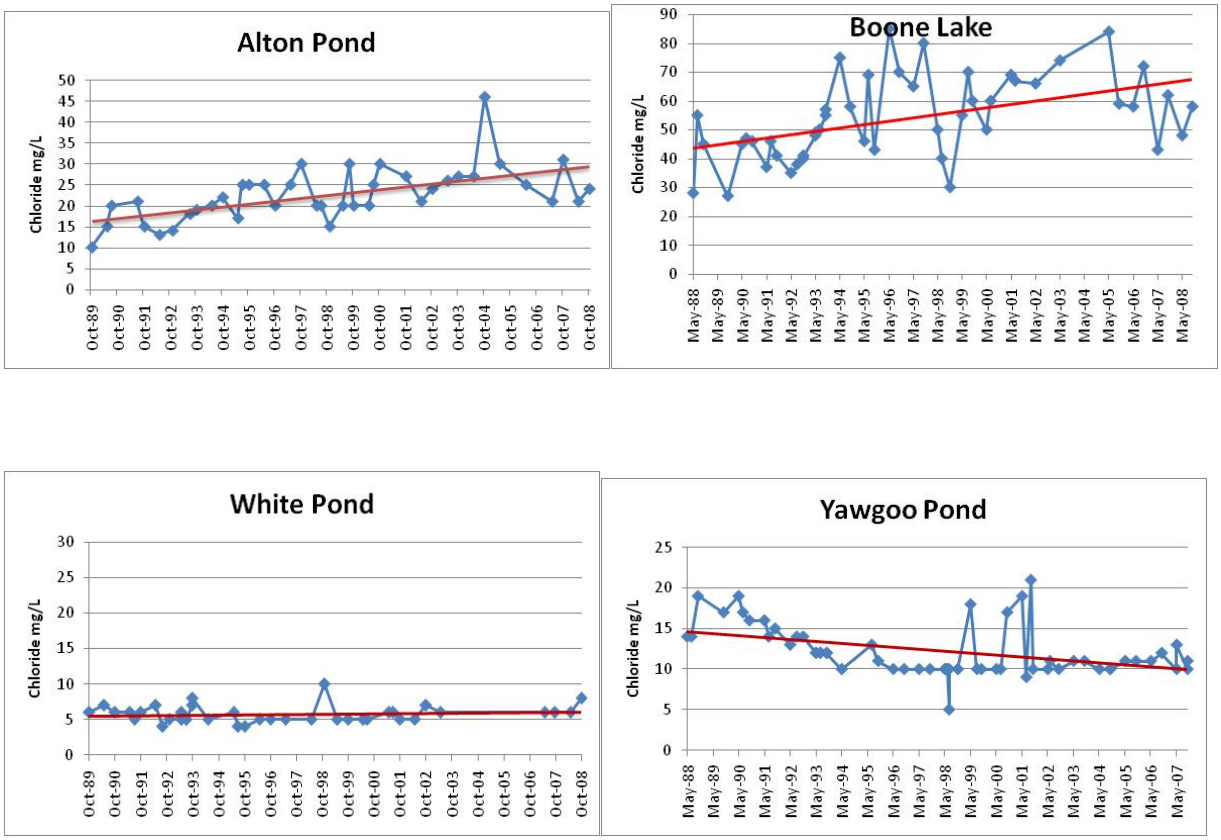


Figure 16. Comparison of annual chloride levels for four sites- a “typical” site (Alton Pond); a site with higher than typical levels (Boone Lake); a “control” site that is relatively far from human activity (White Pond), and an anomalous site that showed decreasing levels (Yawgoo Pond).

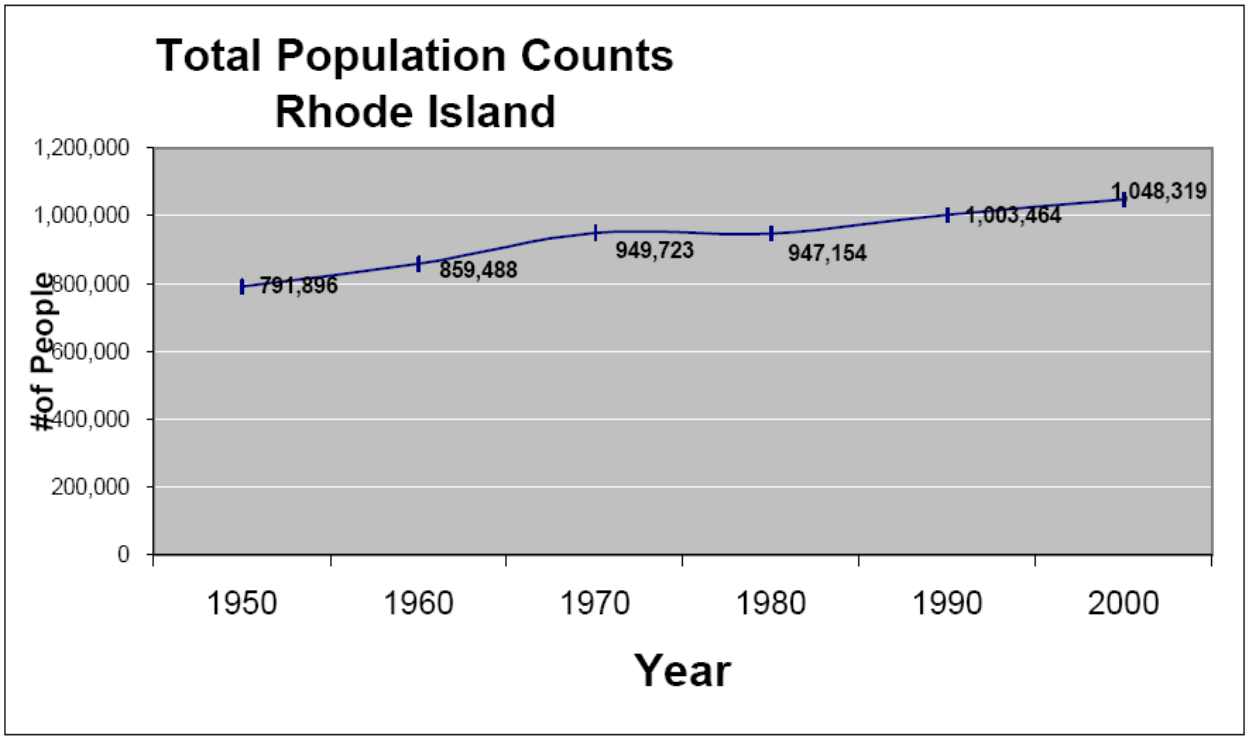


Figure 17. Rhode Island population 1950-2000 (http://www.planning.ri.gov/census/ri2000.htm)

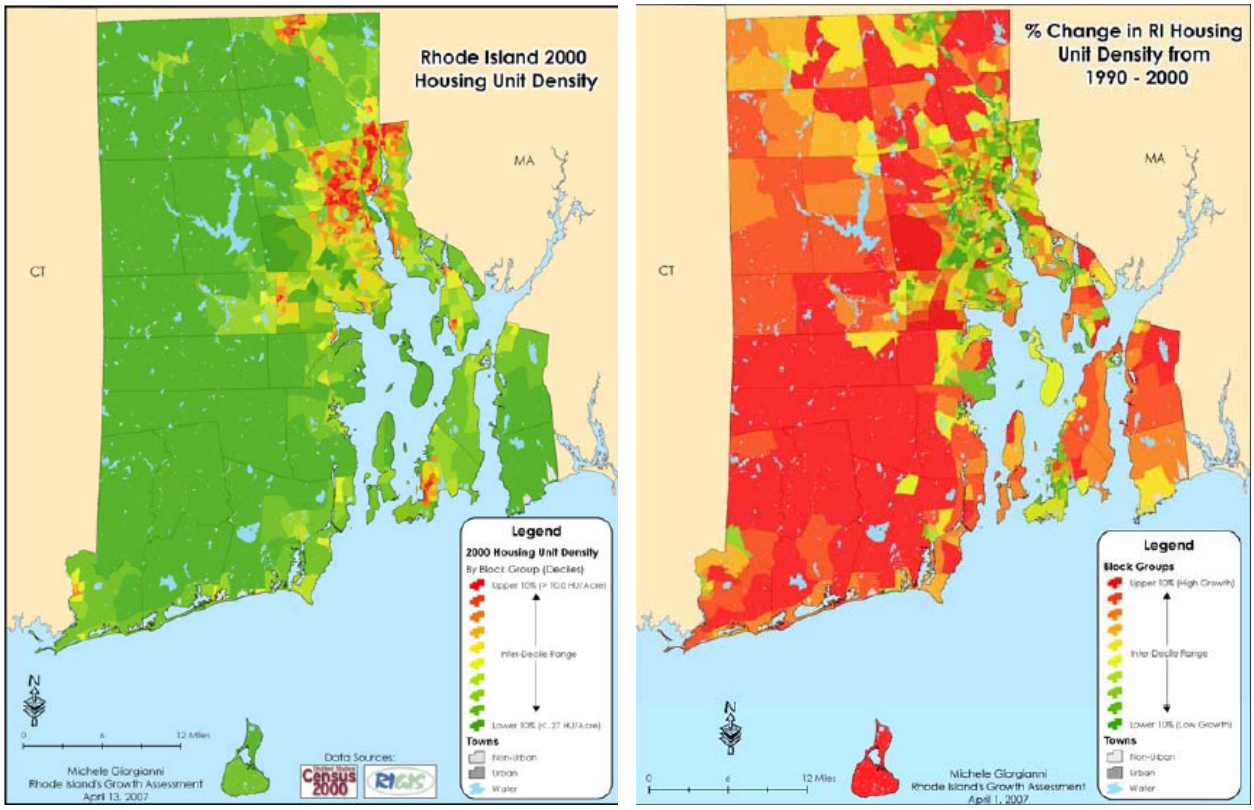


Figure 18. (a) Rhode Island housing unit density in 2000 and (b) percent change in housing unit density from 1990 to 2000.

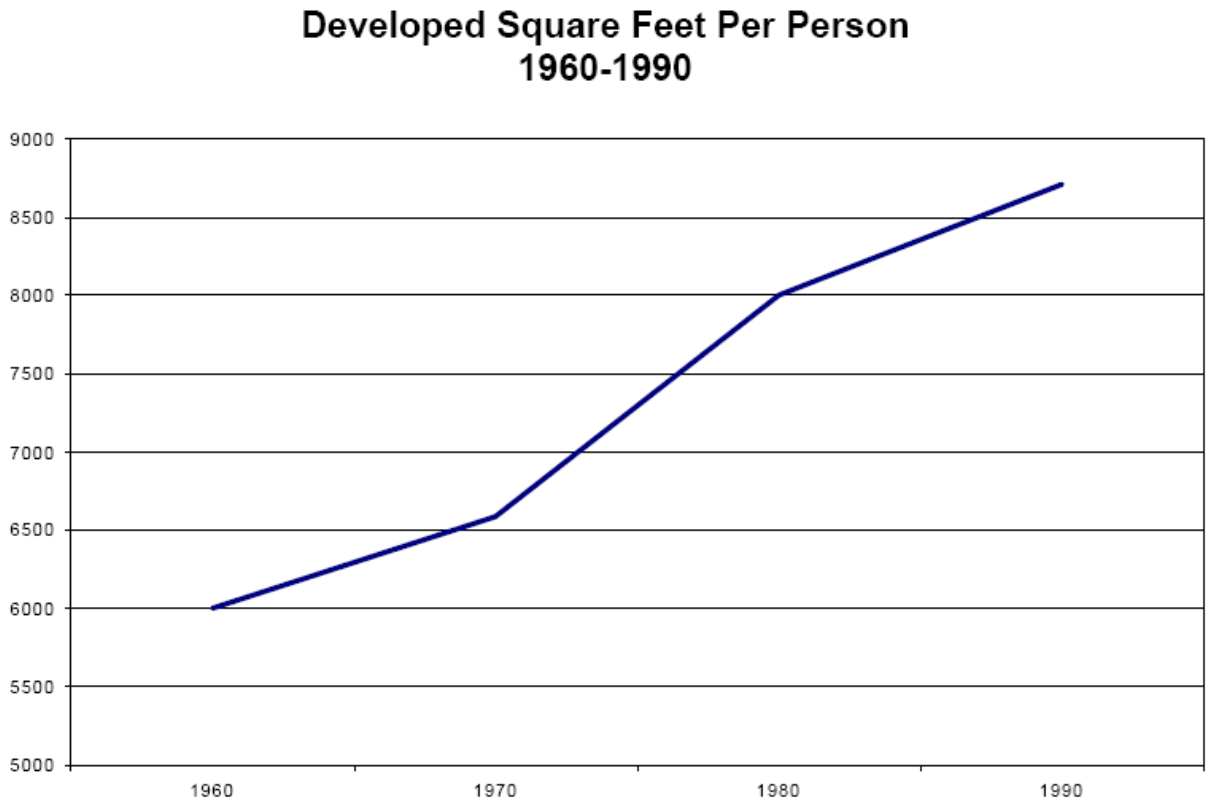
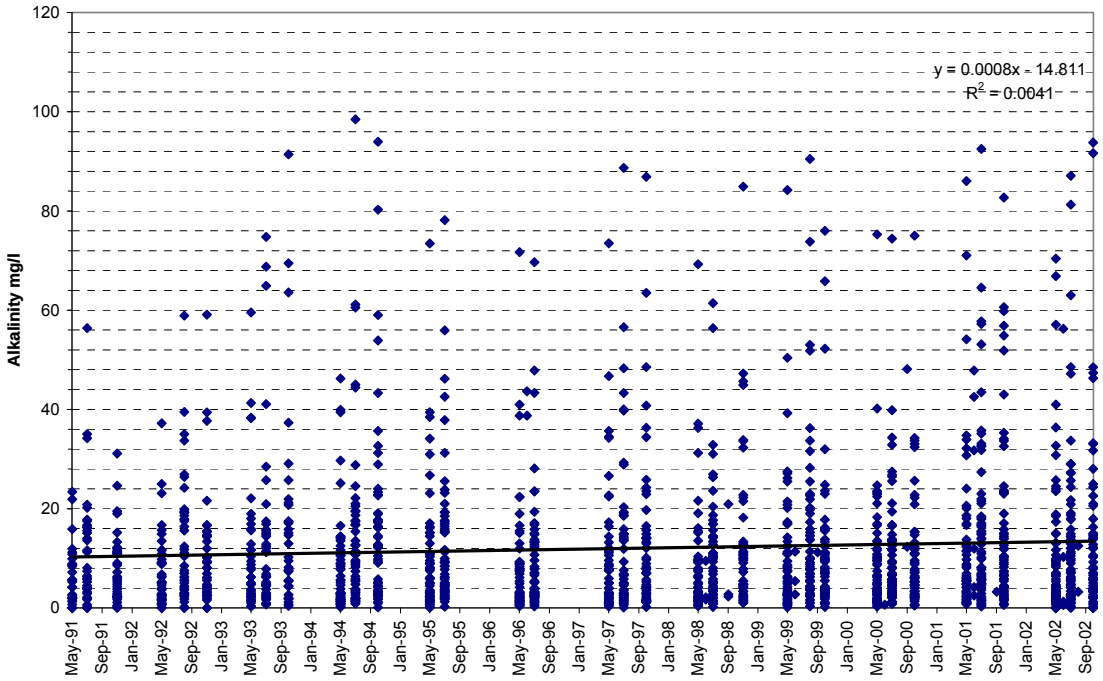


Figure 19. Rhode Island developed square feet per person.

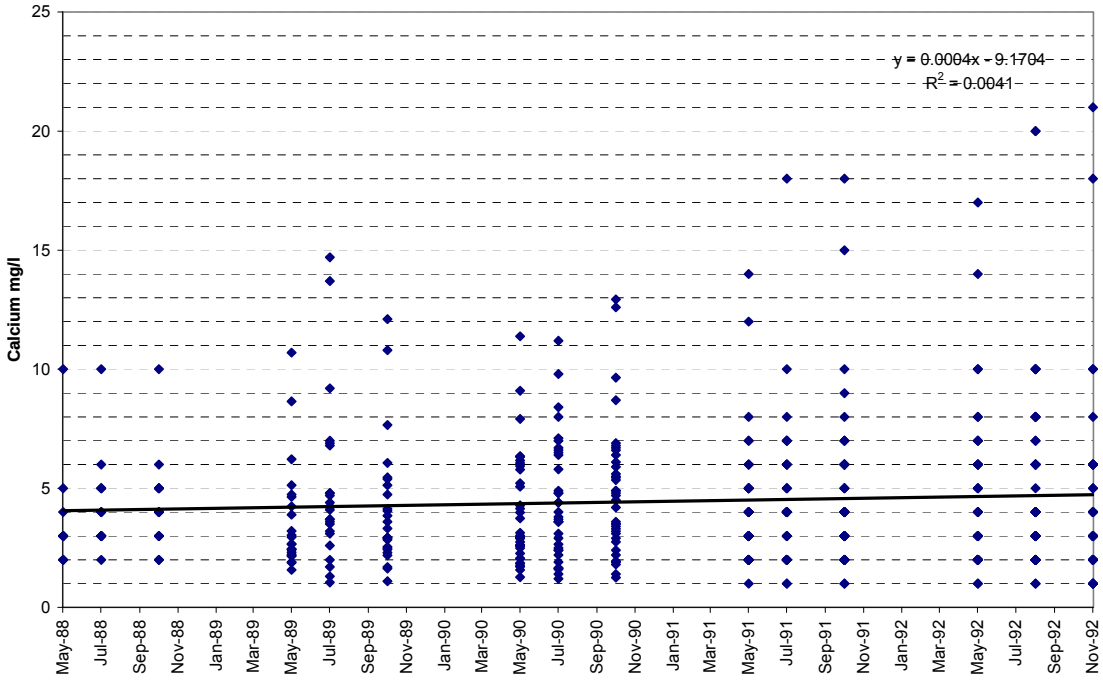
APPENDIX A.

AGGREGATE DATA FROM ALL SITES WITH LINEAR TRENDLINES

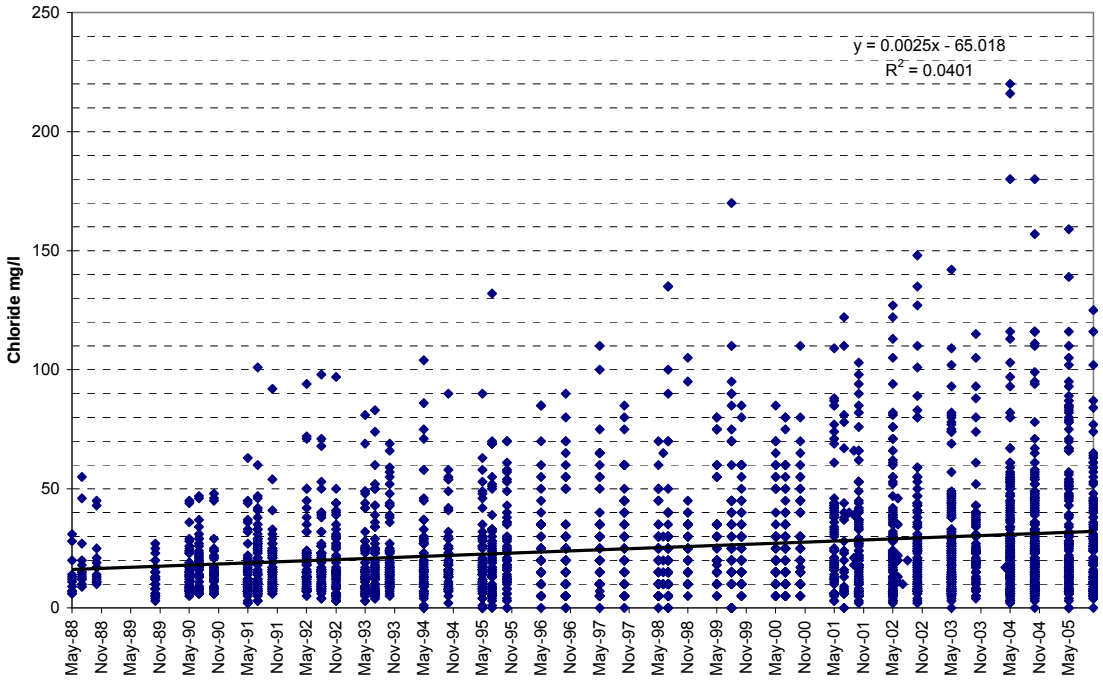
Alkalinity- All SItes



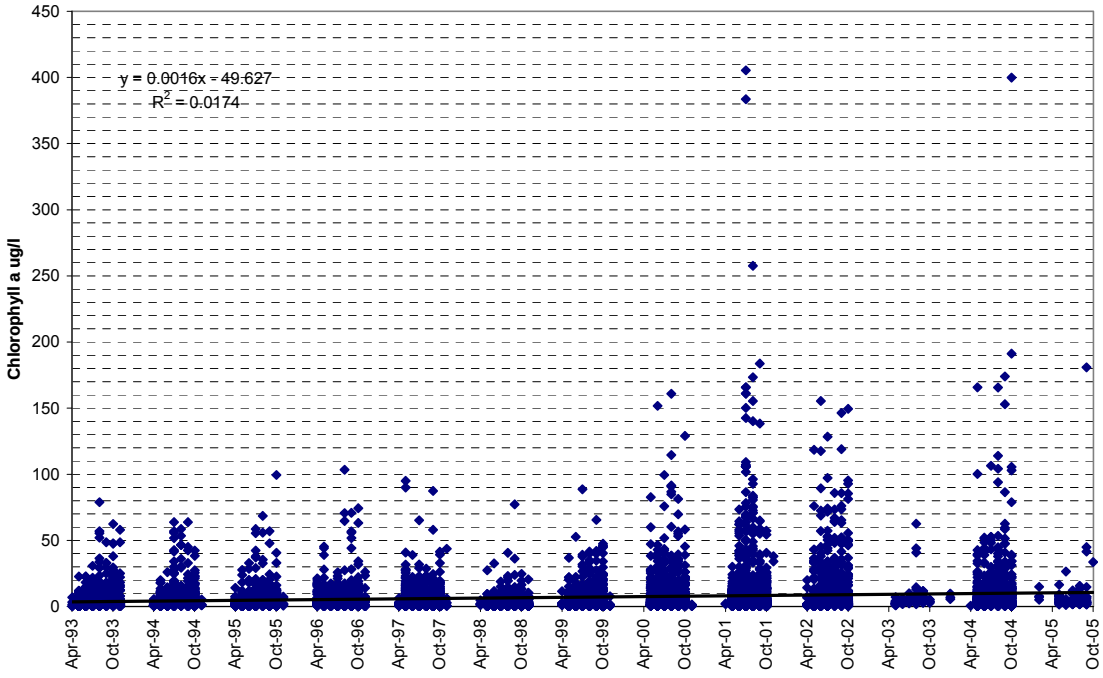
Calcium- All Sites



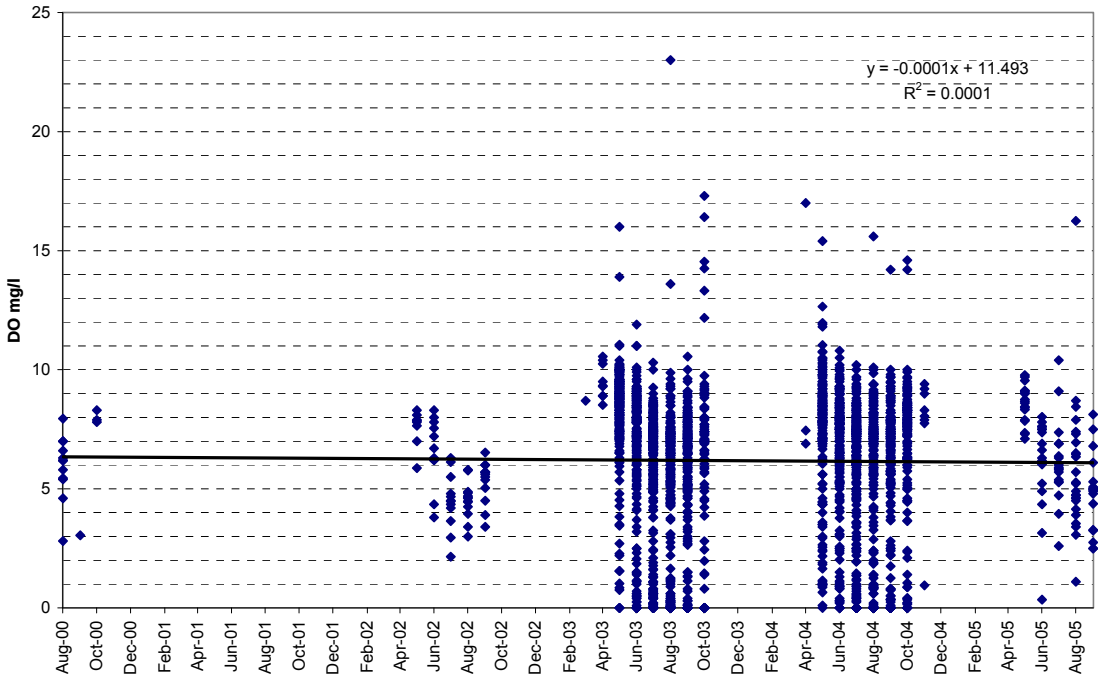
Chloride- All Sites



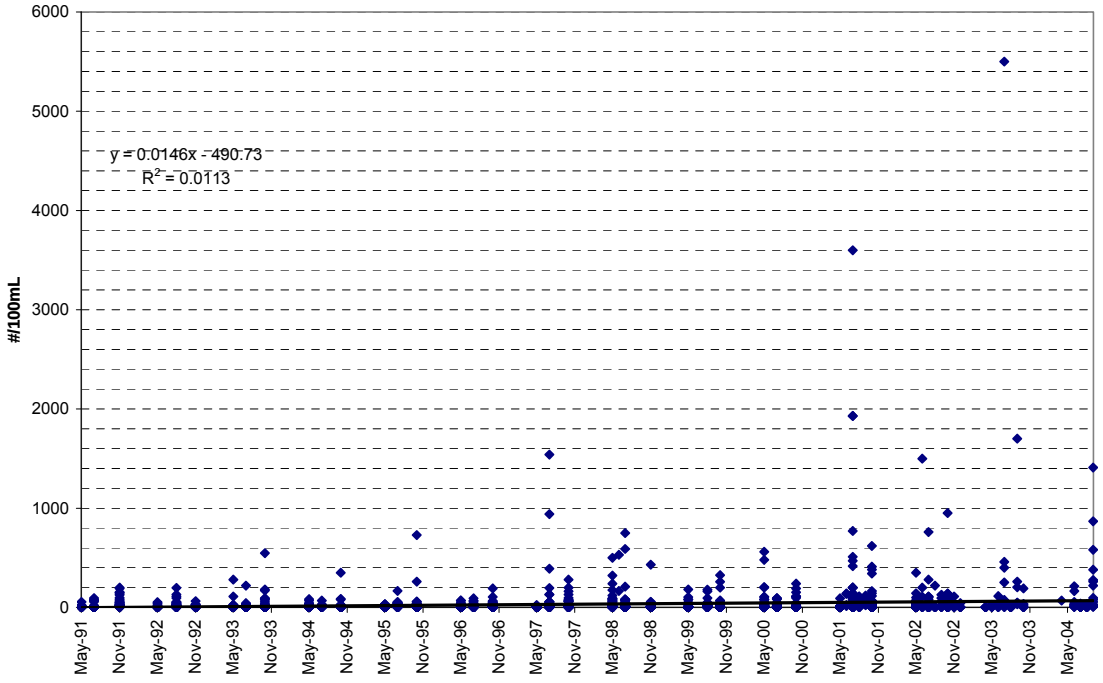
Chlorophyll a - All Sites



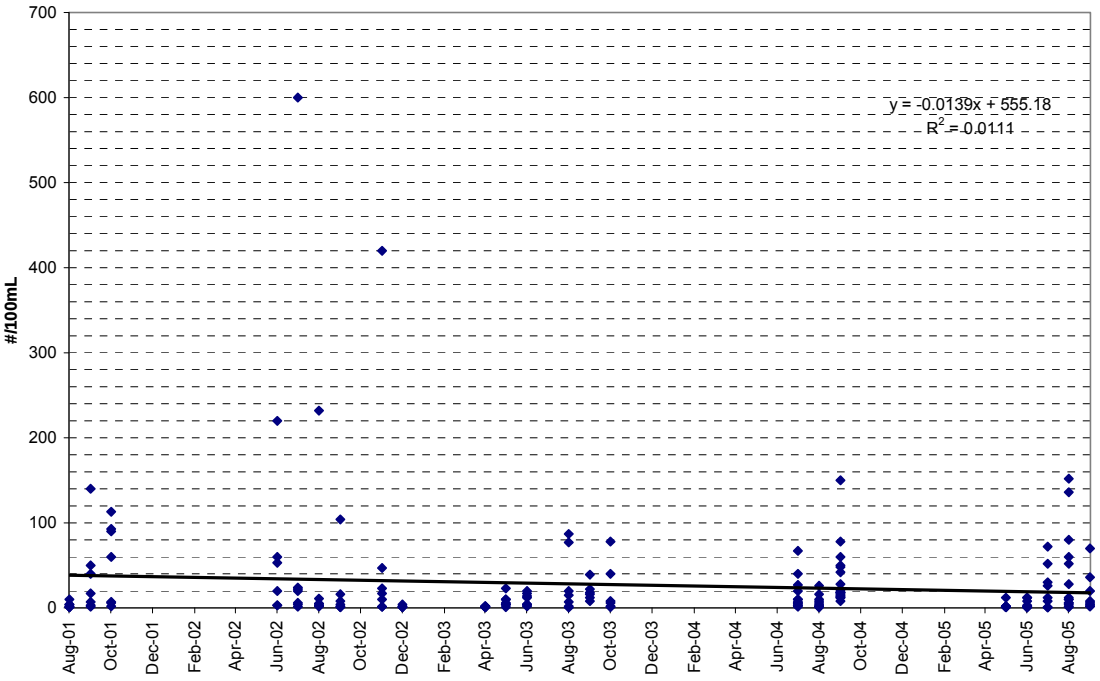
Dissolved Oxygen- All Sites



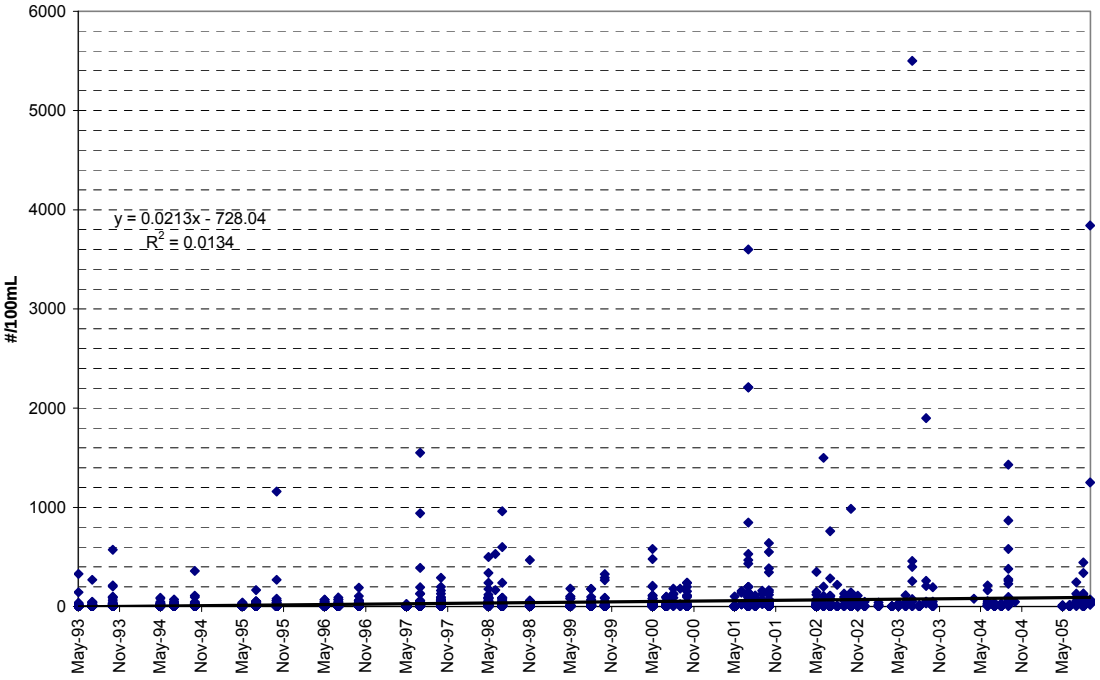
E. coli- All Sites



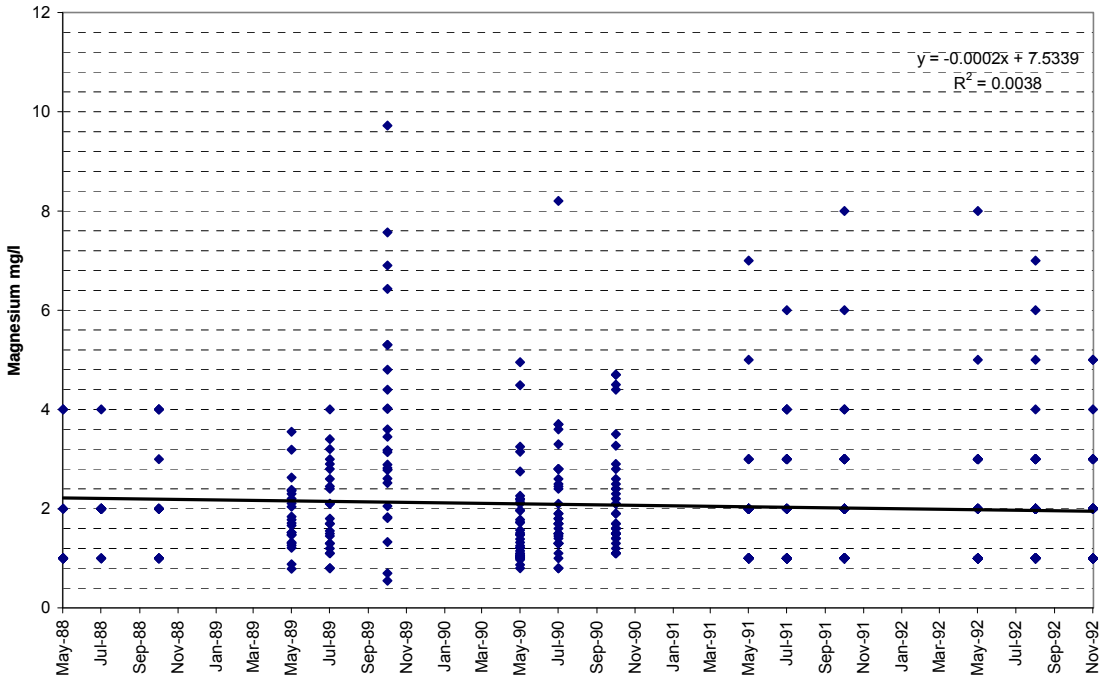
Enterococci- All Sites



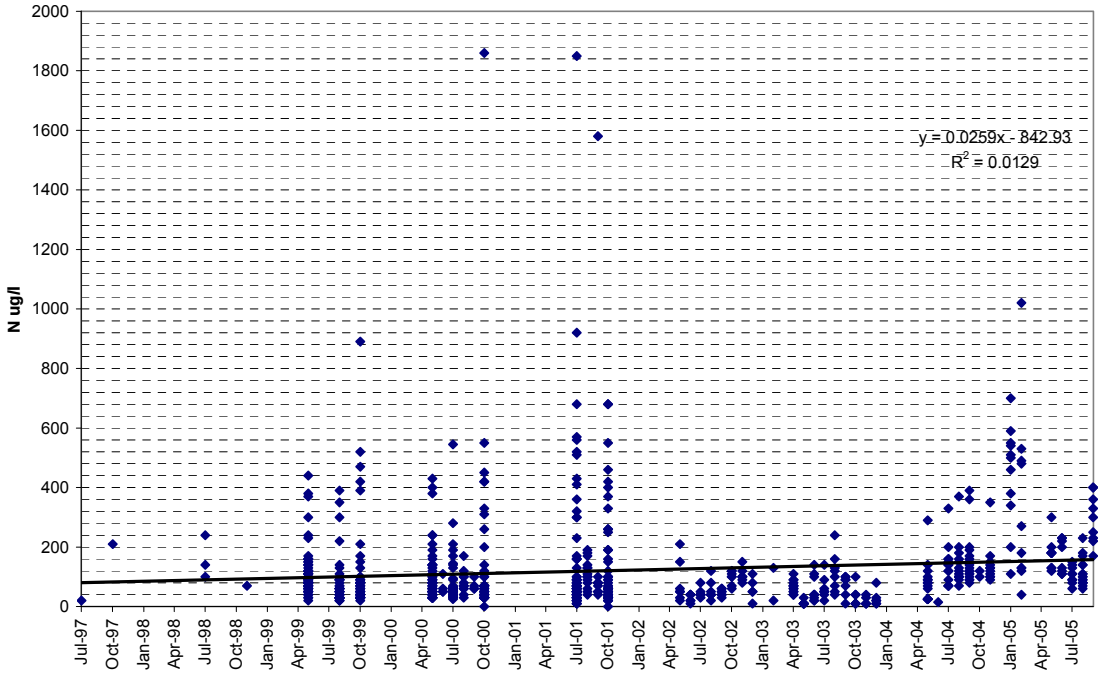
Fecal Coliform- All Sites



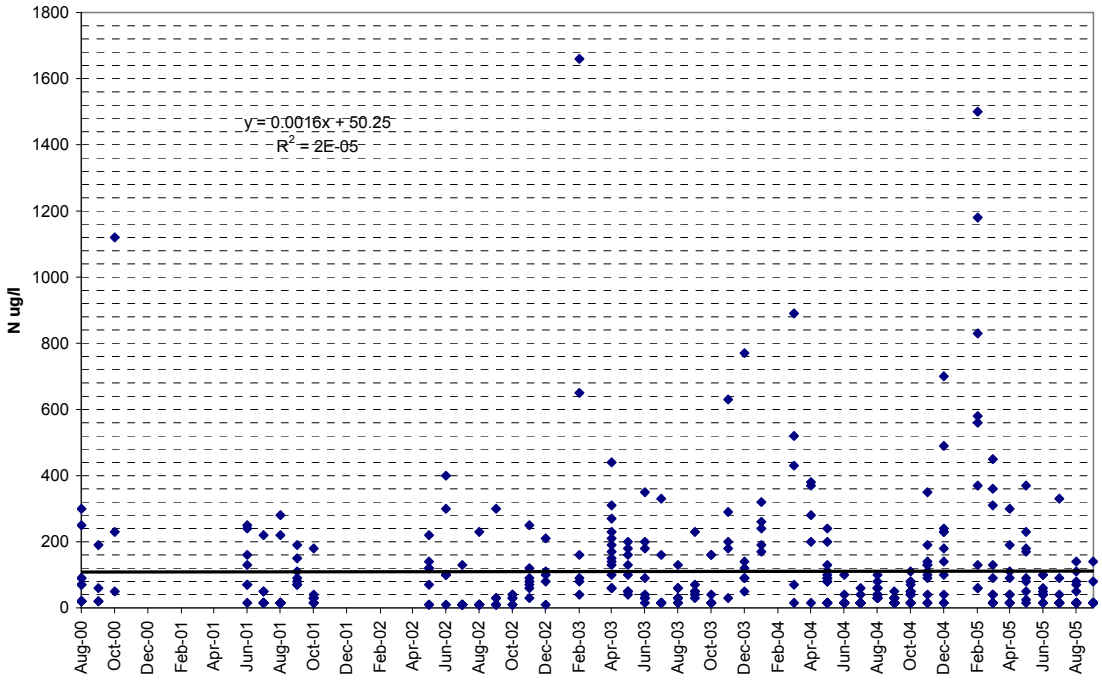
Magnesium



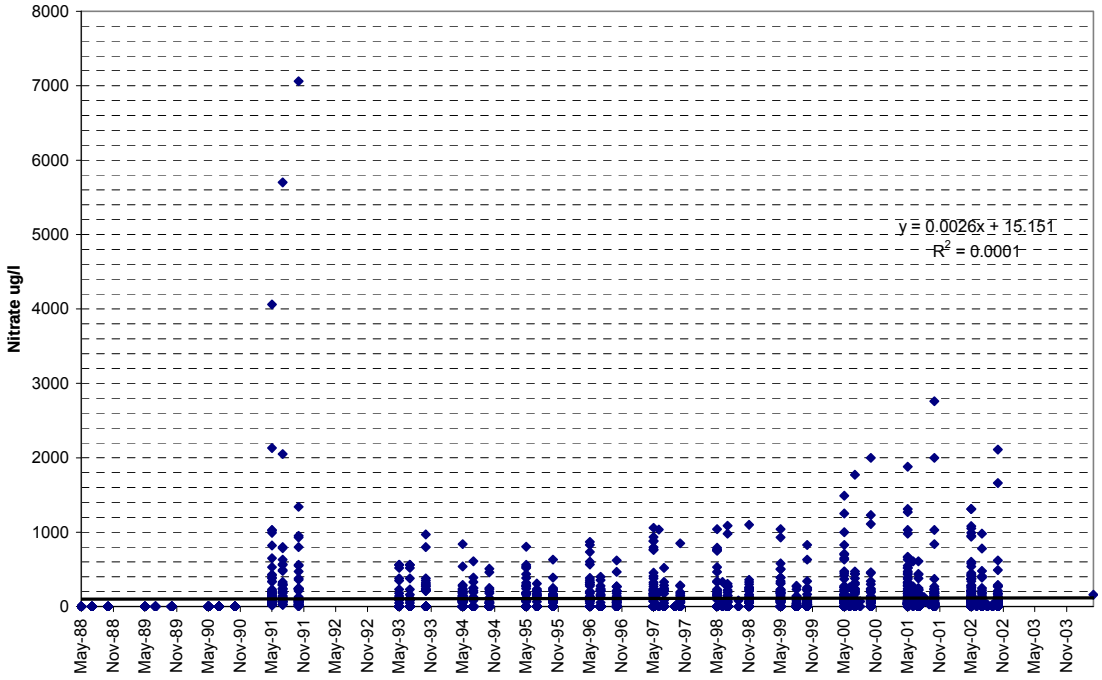
Nitrogen, Ammonia Dissolved as N- All Sites



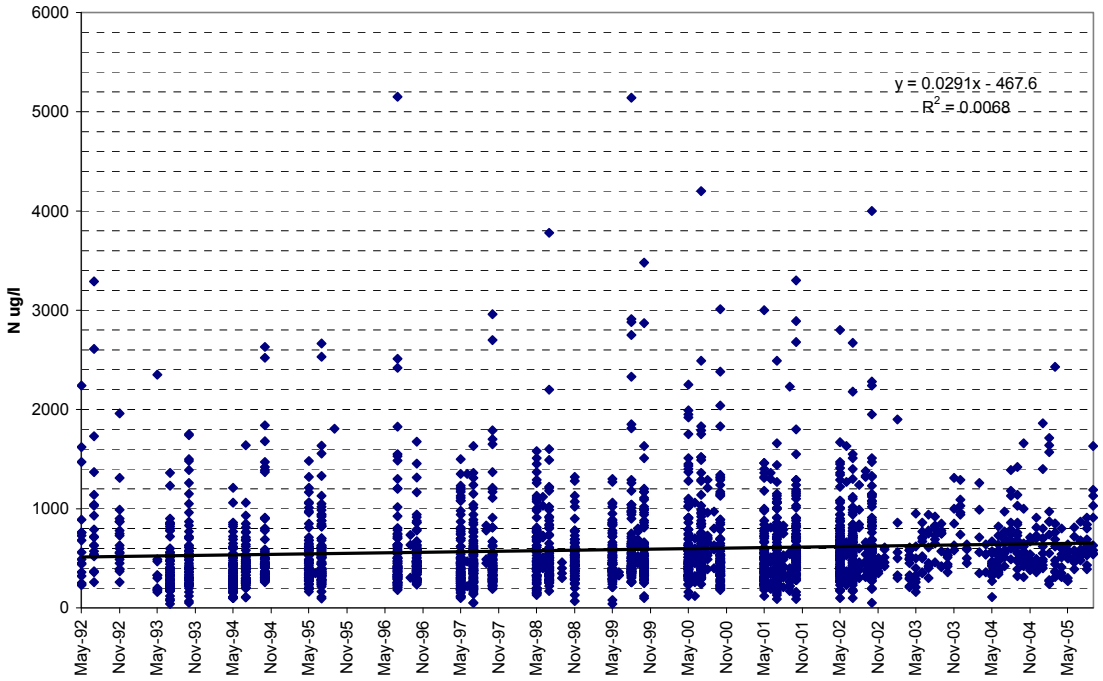
Nitrogen, Nitrate Dissolved- All Sites



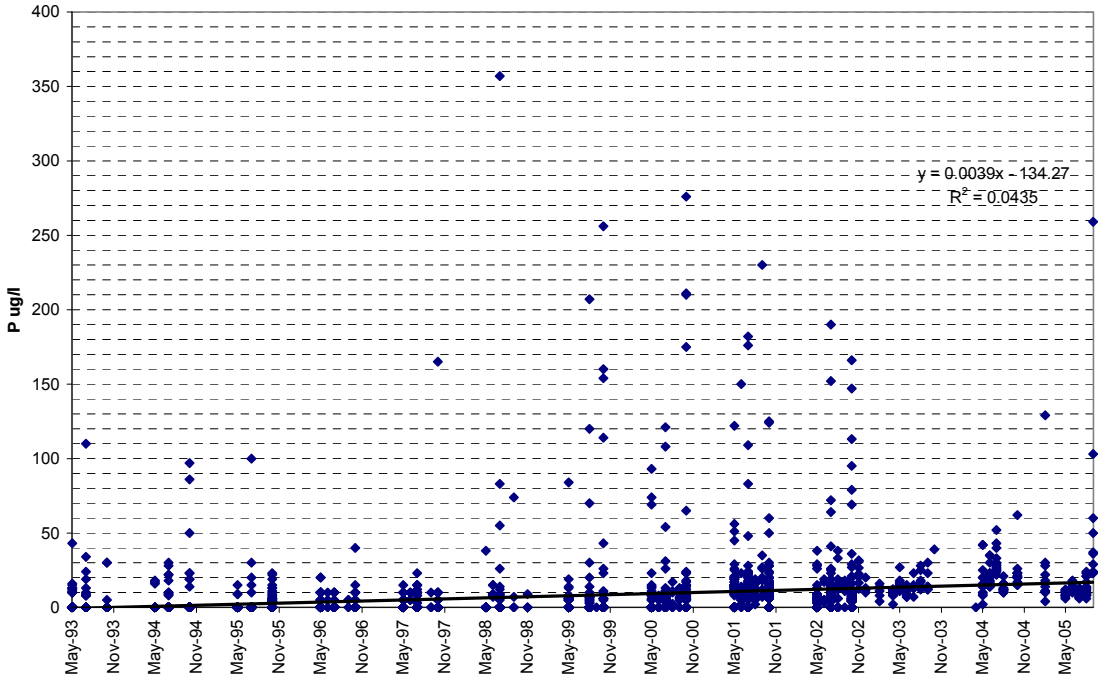
Nitrogen, Nitrate Total- All Sites



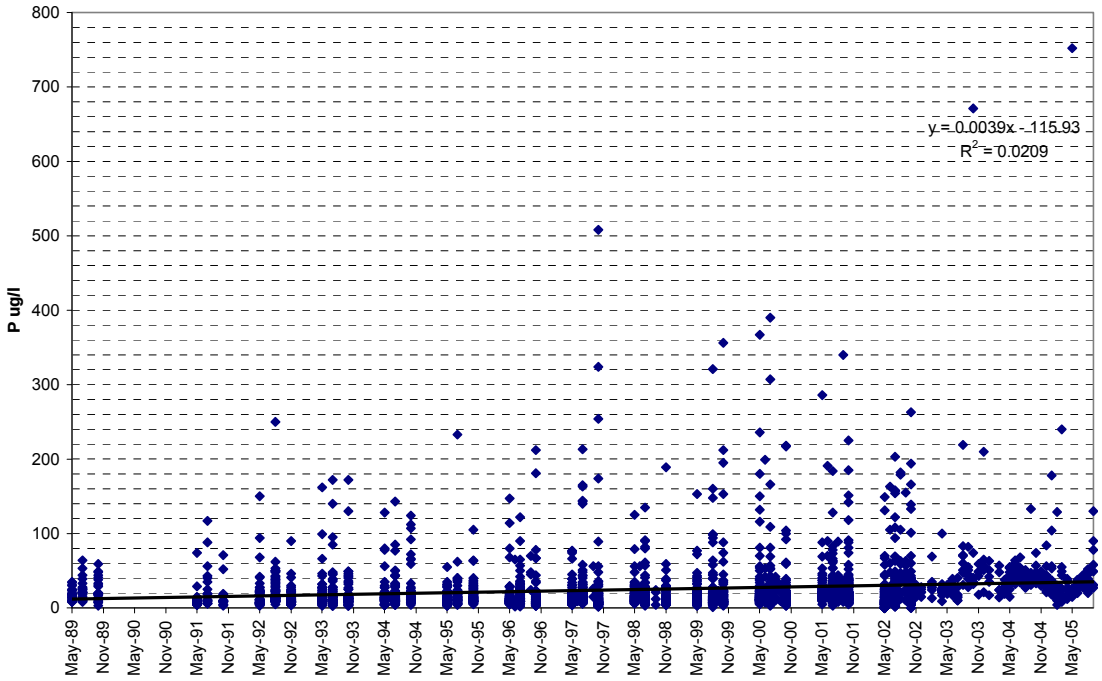
Nitrogen, Total- All Sites



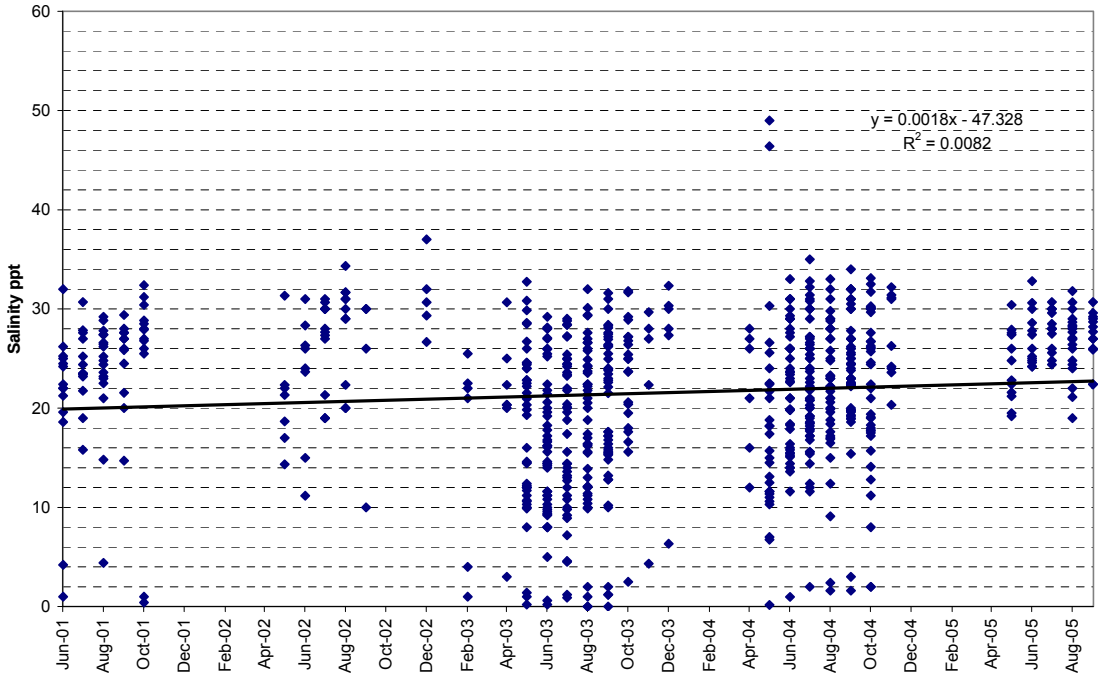
Phosphorus, Dissolved



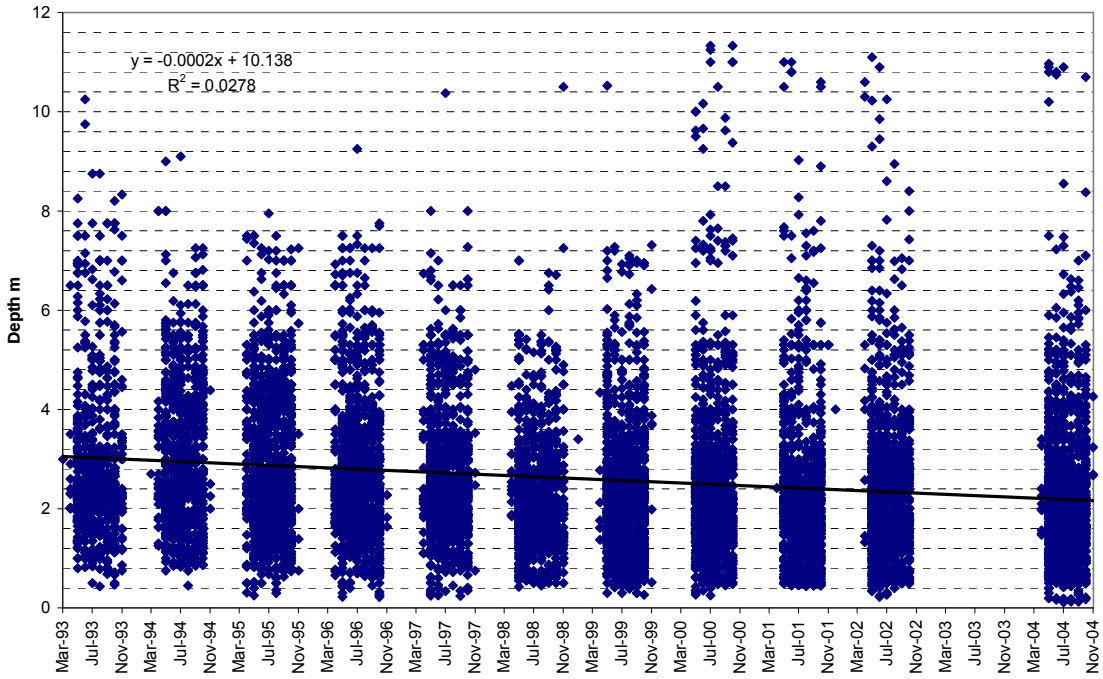
Phosphorus, Total- All Sites



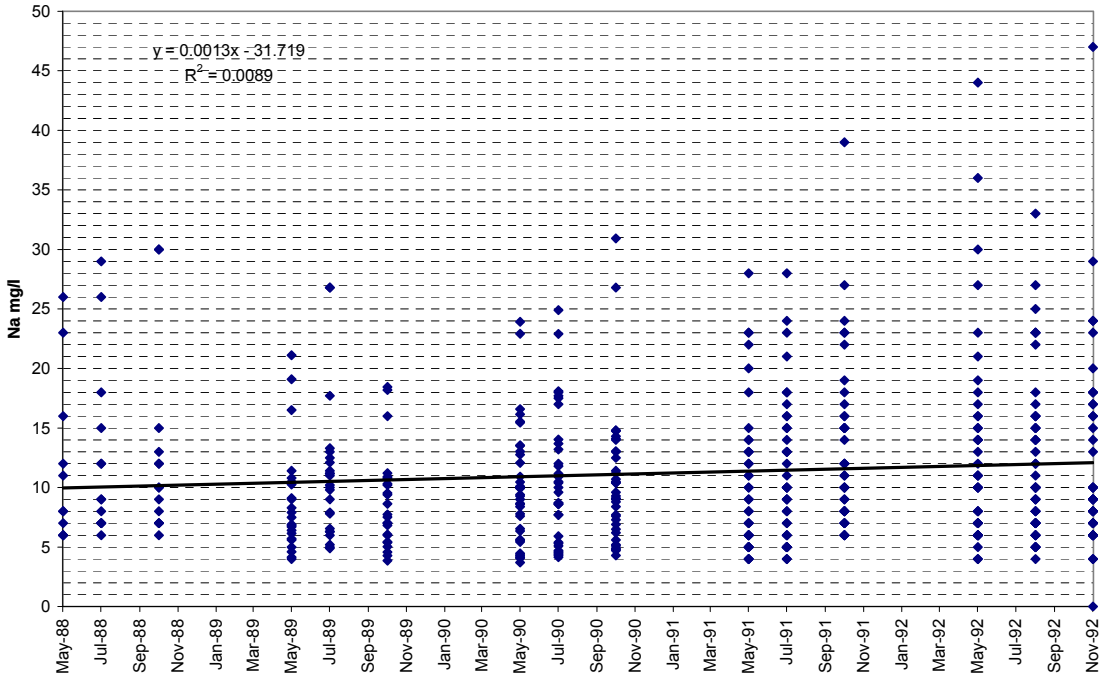
Salinity- All Sites

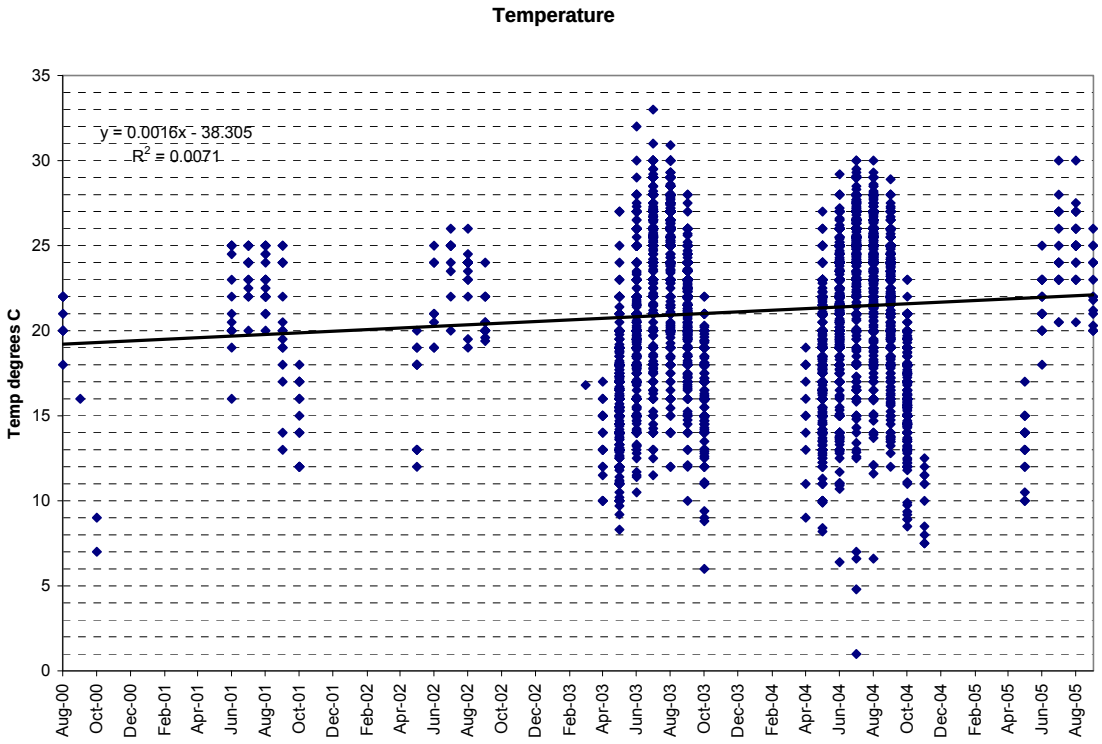


Secchi Depth- All Sites



Sodium, Total- All Sites

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Utilization of Silver Nanoparticles as Chlorine-free Biocide for Water Treatment

Basic Information

Title:	Utilization of Silver Nanoparticles as Chlorine-free Biocide for Water Treatment
Project Number:	2008RI75B
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End Date:	2/28/2009
Funding Source:	104B
Congressional District:	2
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Focus Category:	None, None, None
Descriptors:	None
Principal Investigators:	Vinka Oyanedel-Craver

Publication

1. R. Singer and V. Craver (2009) Silver Nanoparticles for Water Disinfection: Water Chemistry Effect. Disinfection 2009. Water Environmental Federation. Atlanta. Georgia.

Utilization of silver nanoparticles as chlorine-free biocide for water treatment

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University of Rhode Island
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Kingston, RI 02881

ABSTRACT

The objective of this research is to elucidate the main disinfectant mechanism of nanosilver and to evaluate its interaction with the biological, chemical and physical components of natural waters. Silver nanoparticles interact differently with different dissolved and particulate compounds commonly present in drinking water depending upon the disinfectant mechanism.

Our preliminary results show that concentrations of silver nanoparticles below 5 mg/L can achieve removal percentages higher than 99%. Additional results will be presented for silver nanoparticles disinfectant kinetics, and the effects of dissolved inorganic and organic matter in water on the disinfection process.

The results obtained from this research allow the principal investigator to collect data that lead to obtain a National Science Foundation award (CBET # 0854113) which will ensure the continuation of the research started with this grant.

KEYWORDS: Silver nanoparticles, ionic strength, organic matter

INTRODUCTION

Silver and its compounds have been used since the age of the ancient Egyptians, when silver vessels were used to preserve water and wine (Russell and Russell 1995). Before the emergence of antibiotics, silver compounds were widely used during World War I to prevent wound infection. Metallic silver was used to treat surgical prostheses and splints and serve as fungicides. Soluble silver compounds were used to treat a range of diseases from mental illness to gonorrhea (Drake and Hazelwood 2005). Even today, silver sulfadiazine is the standard antibacterial treatment for serious burn wounds (Chen and Schluesener 2008). Recent advances in nanotechnology have demonstrated that nanosize particles of metallic silver have strong antimicrobial properties.

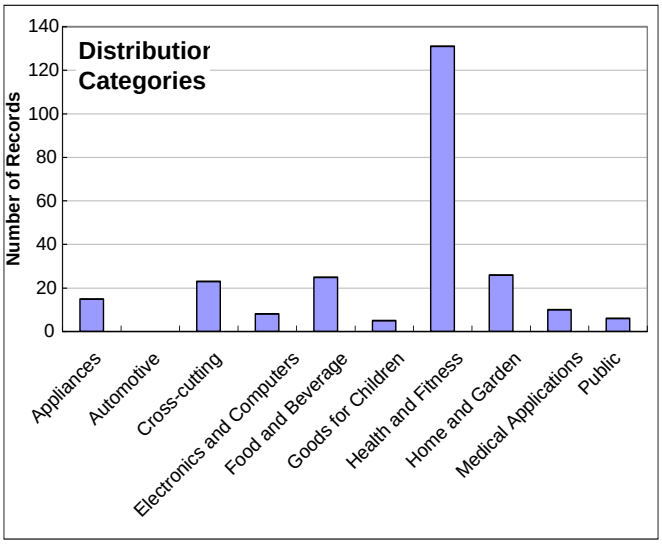
Silver nanoparticles have large surface areas and high reactivities compared with the bulk solid; thus, they exhibit remarkable physical, chemical, and biological properties, such as an increased catalytic activity because of their highly reactive facets (Morones et al. 2005). In addition, there is increasing interest in using nanosilver as a special class of biocidal agents. Sondi and Salopek-Sondi (Sondi and Salopek-Sondi 2004) showed that silver nanoparticles

were an effective bactericide against *E. coli*. Other recent studies have demonstrated the antimicrobial properties of silver nanoparticles against other pathogenic microorganisms such as *Bacillus subtilis* (Ruparelia et al. 2008), *Staphylococcus aureus* (Dubas et al. 2006), *Staphylococcus epidermidis* (Panacek et al. 2006), and HIV-1 (Elechiguerra et al. 2005). Still other researchers have investigated the bactericidal properties of silver nanoparticles supported by polyurethane foam (Jain and Pradeep 2005), a zeolite (Rivera-Garza et al. 2000), alumina (Heinig 1993), activated carbon (LePape et al. 2002; LePape et al. 2004), textiles (Dubas et al. 2006) and ceramic materials (Oyanedel-Craver and Smith 2008).

In April 2005, a partnership between the Woodrow Wilson International Center for Scholars and the Pew Charitable Trusts established The Project on Emerging Nanotechnologies. The Project is dedicated to helping ensure that as nanotechnologies advance, possible risks are minimized, public and consumer engagement remains strong, and the potential benefits of these new technologies are becoming realized. The project maintains an extensive consumer product inventory with more than 800 products, produced by 420 companies, located in 21 countries Silver nanoparticles, the active component of more than 20% of the nanoproducts currently available on the market, are the most commonly cited nanomaterial (Scholars 2008).

Approximately 88% of these products have some form of antibacterial or antimicrobial activity (Fauss 2008). Because of these antibacterial properties, the use of nanosilver products ranges from dietary supplements to spray-on disinfectants to anti-odor textile applications (Figure 1).

Figure 1. Number of silver nanoparticle commercial products separated by categories. From Fauss (2008)



A silver nanoparticle is a fine particle of metallic silver, which has at least one dimension lower than 100 nm. Nanosilver particles exhibit physical properties that are different from both the ion and the bulk material. Because of their strong antibacterial properties, several studies have shown the potential use of silver nanoparticles in biomedical and environmental applications, such as the treatment of wounds and burns (Chen and Schluesener 2008; Furno et al. 2004; Maneerung et al. 2007) and water disinfection (Jain and Pradeep 2005; LePape et al. 2002).

Although a number of recent studies have confirmed the strong antibacterial properties of silver nanoparticles (Chen and Chiang 2008; Cho et al. 2005; Furno et al. 2004; Jain and Pradeep 2005; LePape et al. 2002; Lok et al. 2007; Maneerung et al. 2007; Pal et al. 2007; Panacek et al. 2006; Petica et al. 2008; Ra□ et al. 2008a; Ra□ et al. 2008b; Shrivastava et al. 2007; Sondi and Salopek-Sondi 2004; Zhang et al. 2008), few of them have tested their inactivation effect on viruses (Elechiguerra et al. 2005; Rogers et al. 2008) and, to our knowledge, the disinfectant properties of silver nanoparticles toward protozoan pathogens has never been reported. The antimicrobial properties of silver nanoparticles have been demonstrated in a wide variety of applications from biomedical products (Chen and Schluesener 2008; Furno et al. 2004; Maneerung et al. 2007) to water treatment (Jain and Pradeep 2005; LePape et al. 2004; Oyanedel-Craver and Smith 2008). Most of these studies have focused exclusively in the disinfectant properties of silver nanoparticles; only a few of them have tried to elucidate a disinfection mechanism. Three possible antimicrobial processes have been suggested: (1) direct interaction of the silver nanoparticles with the cell membrane resulting in damage to the membrane and complexation with intracellular components, (2) release of Ag^+ ions and subsequent disinfection, and (3) formation of reactive oxygen species (ROS). None of these mechanisms have been conclusively confirmed, nor has the relative importance of each mechanism in the inactivation of different types of pathogenic microorganisms been elucidated. The majority of these studies were performed under different conditions, which makes their comparison difficult. The objective was to evaluate silver nanoparticles interactions with the biological, chemical and physical components of natural waters.

METHODOLOGY

The effectiveness of silver nanoparticles will be evaluated for *Escherichia coli*. *Escherichia coli* HCB 137 (obtained from R. M. Ford, University of Virginia) will be used to create bacterial suspensions. Bacterial-buffer solutions will be prepared as described by Sherwood et al. (Sherwood et al. 2003) and aliquots will then be added to synthetic water samples to obtain the desired bacterial concentration of approximately 10^8 cfu/ mL.

Manufacture and Characterization of Silver Nanoparticles. Due to the current application of a commercial formulation of silver nanoparticles in the ceramic filters distributed by Potter for Peace, we will characterize and use this product as well in our tests. Proteinate™ is a silver nanoparticle solution developed by Argenol Laboratories (Spain), because of the trademark of this product no information from the manufacturer can be obtained about its particle-size distribution or surface characteristics. Dynamic light scattering (DLS) will characterize the particle-size distribution of synthesized silver nanoparticles. Microscopic observations of silver particles with a transmission electron microscope (TEM) was performed to determine the size and shape of the nanoparticles.

Disinfection Kinetics. Disinfection kinetics will be determined for the four types of silver nanoparticles and the three pathogens selected. Batch tests will be performed at different concentrations and disinfectant-pathogen contact times. The concentration of the microorganisms will be determined in triplicate at the beginning and end of each concentration–contact time (*Ct*) test. This set of experiments will provide the overall rate coefficient for the

disinfection process at three different levels of oxygen concentration for each pathogenic organism.

The following Chick-Watson, Rennecker-Marinas, and Collin-Selleck disinfection models will be used as appropriate to analyze the above-described experimental data:

$$\ln\left(\frac{N}{N_0}\right) = -\Lambda_{CW} \times Ct$$

Chick-Watson

$$\ln\left(\frac{N}{N_0}\right) = \begin{cases} 0 & Ct < b \\ -\Lambda_{CW}(Ct - b) & Ct \geq b \end{cases}$$

Rennecker-Marinas

Collin-Selleck

where N_0 is the initial concentration of microorganism (cfu/L), N is the concentration of microorganism at time t (cfu/L), Λ_{CW} is the coefficient of specific lethality (dimensionless), C is the concentration of silver nanoparticles (mg/L), t is the contact time (min), and b is the lag time (min).

RESULTS

The effect of the ionic strength on the particle size distribution of the nanoparticles is shown on Figures 2, 3 and 4. Table 1 summarized the main parameters determined. The TEM and DLS particles size distribution profiles differ form each other in terms of average particles size distribution about 3 folds. The different results are expected since the TEM analysis is performed in dry samples while DLS determine the actual particle size distribution of the suspension.

Our results show a clear effect of the buffer concentration on the average size of the nano-silver particles. Larger nanoparticles were observed when they were suspended using a high ionic strength solution. The size of the nanoparticles decreased with the decrease of the ionic strength. Similarly the dispersity of the particles decreased with the decrease of the ionic strength. These results indicate that the nanoparticles tend to aggregate when large amount of ions are dissolved in solutions. Additionally the narrow range of small size particle is obtained at low ionic strength. These results agree with the double-layer theory for colloidal particles

QuickTime™ and a
decompressor
are needed to see this picture.

Figure 2. Transmission electron microscopy of silver nanoparticles as dry powder

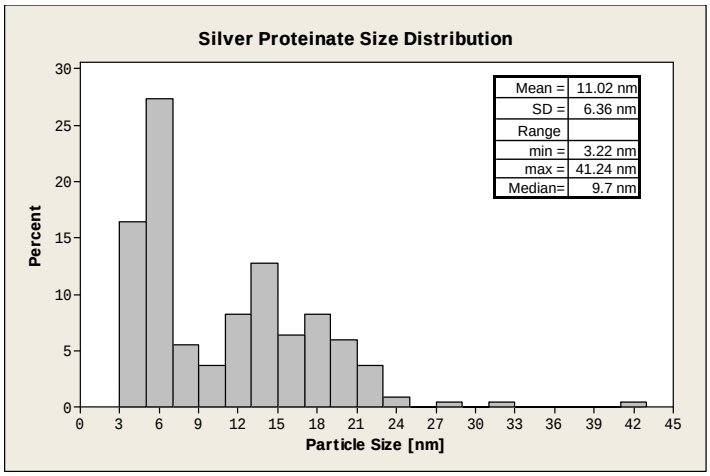


Figure 3. Particle size distribution of silver nanoparticles as dry powder obtained using TEM

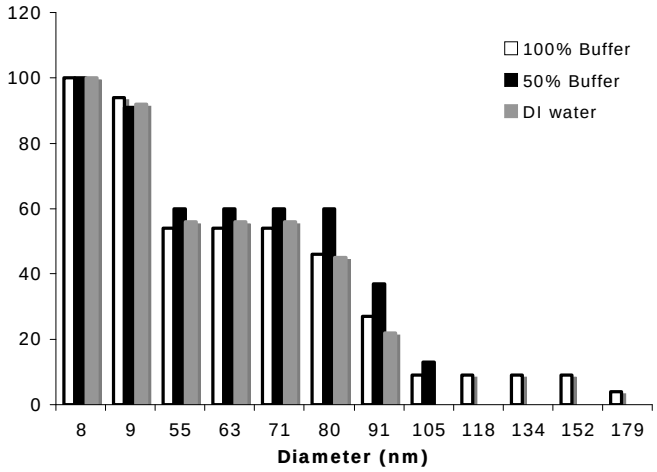


Figure 2. Effect of ionic strength on the nanosilver particle size distribution obtained using a dynamic light scattering equipment

Table 1. Nanosilver particles mean diameter and dispersity values at different ionic strength

	100% Buffer	50% Buffer	DI water
mean diameter (nm)	57	54	50
dispersity	0.39	0.365	0.321

Regarding the disinfection properties of the silver nanoparticles, Figure 3 shows the determination of the optimum contact time for a 2 mg Ag/L concentration of nanoparticles. Figure 3 shows that a higher contact times better disinfection performance is obtained. We determined that 20 minutes is the optimum contact time for the utilization of nanosilver

Figure 4 presents the results obtained for the disinfection kinetics of silver nanoparticles used for the inactivation of *E. coli*. The results showed a clear linear relationship between the *Ct* parameter and the level of disinfection achieved. Chick-Watson seems to be the best model to describe the disinfection performance of silver nanoparticles for E. coli bacteria. From the

results obtained the Chick-Watson coefficient of specific lethality obtained was 0.014 $Lmin^{-1}mg^{-1}$ which is lower than the values obtained for free chlorine (Hoff, 1986).

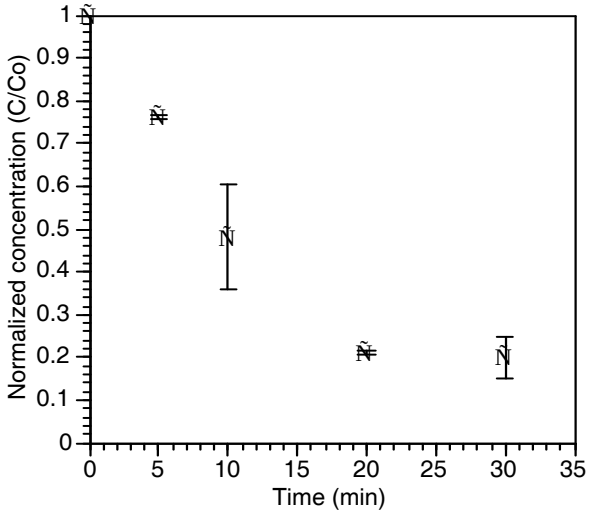


Figure 3. Determination of optimum contact of silver nanoparticles (2 mg/L) for the inactivation of E. Coli.

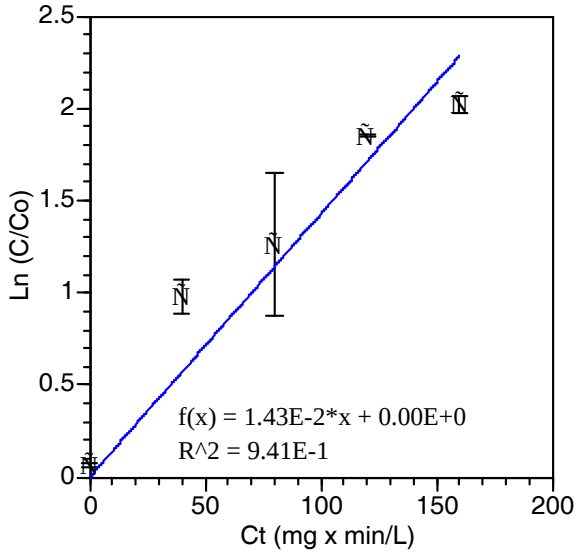


Figure 4. Disinfection kinetics of silver nanoparticles for the inactivation of E. Coli.

Figure 5 presents the results obtained for the disinfection performance of silver nanoparticles at different concentration of dissolved organic matter (DOM). No significant reduction of the removal percentages where observed. This could imply that ROS may not play a big role in the disinfection properties of nanoparticles. If ROS would have a big contribution then the addition of DOM would reduce the disinfection properties since ROS will interact with then instead of the bacteria.

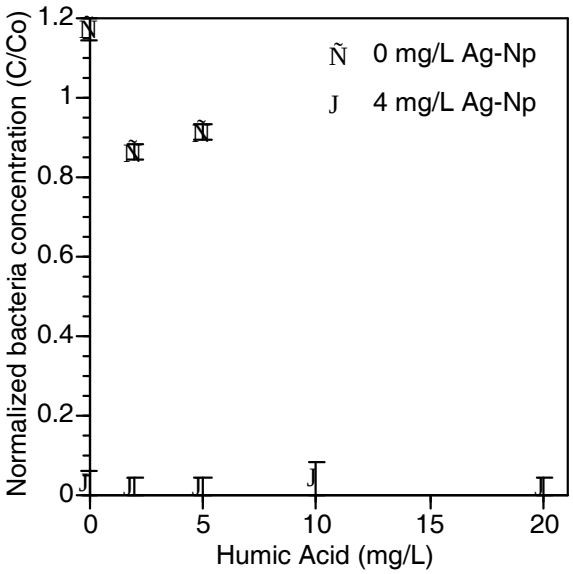


Figure 5. Effect of Humic acid concentration on the disinfection efficiency of silver nanoparticles.

Figure 6 shows the disinfection results obtained at using a concentration of 8 mg/L of silver nanoparticles. Opposite to what we expected, lower ionic strength seems to have a negative effect on the disinfection efficiency. At lower ionic strength silver nanoparticles and bacteria should be less aggregated then silver nanoparticle cluster should be smaller and more reactive. However our results indicate the opposite. One possible explanation is that at lower ionic strength bacteria clusters are smaller or not formed then more bacteria is in suspension individually this will give higher counts of bacteria in our plaque detection methods.

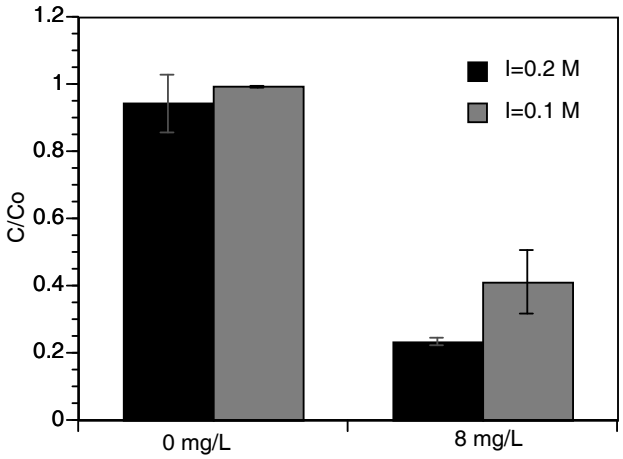


Figure 6. Effect of Ionic strength on the disinfection efficiency of silver nanoparticles.

CONCLUSIONS

Ionic strength affects the particles size distribution of silver nanoparticles. Aggregation and wider size range distribution are obtained at high ionic strength.

Chick-Watson kinetics was obtained for the disinfection of *Escherichia coli* by silver nanoparticles.

Dissolved organic matter dissolved did not affect the disinfection efficiency of silver nanoparticles significantly.

From the results obtained ROS do not have a significant contribution to the overall disinfection process

The culture method used in this research may not be the most accurate method to determine the ionic strength, and therefore water chemistry effect on the disinfection performance of silver nanoparticles.

Further research should be performed to determine more accurately the effect of different ionic solution on the disinfection performance of silver nanoparticles.

FUTURE WORK

Retention of Ag-NPs is critical, not only because of the cost associated with the loss of the reactive material, but mainly because of its potential impacts on human health and ecosystems. For Ag^+ the U.S. EPA maximum contaminant level (MCL) in drinking water is 0.1 mg/L. According to C.R.C. (2000), Ag^+ is a relatively rare metal originating from natural sources and from industrial waste. Its concentration in U.S. drinking waters reportedly varies between 0 and 0.002 mg/l. The only adverse effect resulting from chronic exposure to low levels of silver in animals and humans is a blue-gray discoloration of the skin and internal organs. With regards to Ag-NPs, a number of recent studies have examined its toxicity in cell cultures (rat liver cell; Hussain et al., 2005) and aquatic (*Chlamydomonas reinhardti;* Navarro et al., 2008*)* and terrestrial (Sprague Dawley rats; Sung et al., 2008) organisms. Archer (2008) reported the first case of silver cardiomyopathy in humans due to the ingestion of colloidal silver as a food supplement. These reports provide evidence for the need to develop effective and reliable methods to securely anchor Ag-NPs to surfaces and porous matrices, such as filtration membranes or sediments, and enhance their separation from water solutions. Our literature review indicates that the *direct* production of Ag-NPs on surfaces like clays and silica spheres potentially immobilized the reactive particles (Chen and Chiang, 2008; Jiang at al., 2005).

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Information Transfer Program Introduction

One of the goals of the information transfer program was to encourage high school students to pursue a career in the water resources area by participation in a summer camp. This camp involved lectures, hands-on laboratory experiences and field trips to water and wastewater treatment plants. In addition, the second Clean Water Conference was held with the goal of sharing current water research with undergraduate and graduate students as well as water resource professionals.

Clean Water Technology for Rhode Island

Basic Information

Title:	Clean Water Technology for Rhode Island
Project Number:	2008RI72B
Start Date:	3/1/2008
End Date:	2/28/2009
Funding Source:	104B
Congressional District:	2
Research Category:	Not Applicable
Focus Category:	Education, Conservation, None
Descriptors:	
Principal Investigators:	Harold Knickle

Publication

Clean Drinking Water in Rhode Island

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Kingston, RI 02881

ABSTRACT

The objective of this project was to promote the transfer of information, technology and education. This was accomplished by two major outreach activities, a clean water technology conference aimed at water professionals and educators and a hands-on summer workshop targeted to middle and high school students. to promote interest in clean water careers.

KEYWORDS: water quality, information transfer, education

INTRODUCTION

Summer Workshop on Clean Water for Middle and High School Students

Middle and High school students were recruited with the help of high school teachers' encouragement to participate in a week of lectures, lab activities and field trips that focus on clean water. The students were recommended by teachers, guidance councilors or other school administration. Many students came from inner schools with limited science resources.

The participants in the Summer Workshop met Monday to Friday during the week of July 7, 2008. Students arrived at 9:00 am and left at 3:30 pm.

Scheduled activities included lectures, hands-on laboratory experiences and several field trips. The lectures (given by University of Rhode Island faculty) included presentations of the water cycle, chemistry of water, water quality and treatment, sewage treatment using biological technology, runoff and storm water, industrial water pollution, pollution prevention, filtration and adsorption, health effects and the location and quality of major source of drinking water in Rhode Island.

The laboratory exercises were designed to teach current water quality and sampling techniques by designing several hand-on laboratory experiments. All experiments were either conducted at the URI engineering laboratories or in the field. Some examples of experiments included water sampling and testing, pH and dissolved oxygen measurement, pollutant indicating bacteria culturing, conductivity measurement, acid rain testing, and typical water treatment processes including aeration, carbon adsorption and filtration. All of the experiments were facilitated by utilizing analytical and bench and pilot-scale treatment equipment in the Environmental Laboratory.

The final component of the Summer Workshop was to demonstrate treatment processes and field sampling by scheduling a series of field trips. This component was designed to introduce the students to the collection of water samples from various locations such as water and wastewater treatment facilities as well as water bodies.

At the conclusion of each experiment the students wrote a brief laboratory report which was graded. The creation of the laboratory reports served to enhance both writing skills and data collection and analysis skills.

METHODOLOGY

The actual schedule for the summer program follows.

Summer 2008

Clean Water Engineering & Science Academy

July 7-July 11

9:00 AM to 3:30 PM

Session 1: Monday July 7

- Introduction and Survey
- Intro to Water Cycle
- Intro to Water Chemistry
- Drinking Water Sample Collection
- Water Quality Treatment
- Drinking Water Testing
- Laboratory Report

Session 2: Tuesday July 8

- Introduction to Sewage Treatment
- Introduction to Biology Technology
- Introduction to COD and BOD
- Oil Spill Laboratory
- Field Trip to Sewage Treatment Plant East Greenwich
- Laboratory Report

Session 3: Wednesday July 9

- Introduction to Water Runoff and Storm Water
- Pond water Sampling
- Dissolved Oxygen, pH, and Hardness
- Introduction to Aeration
- Laboratory Continued
- Laboratory Report

Session 4: Thursday July 10

- Introduction to Health Effects Associated With Water Quality
- Introduction to Pollution Prevention.
- Introduction to Chemical and Physical Adsorption
- Field Trip to Water Treatment Plant

Session 5: Friday July 11

- Introduction to Blackstone River Clean Up
- Introduction to Point and non-Point Sources
- Blackstone River Samples
- Adsorption Experiments
- Laboratory Report
- Laboratory Report
- Post Assessment Survey
- Certificates

An example of a typical experiment is shown below.

Oil Spill Laboratory

Goal: What is a surfactant and how does it influence water quality?

Work in Teams

Procedure – Part 1

1. Aluminum Pans
   Fill to about one inch
2. Small ketchup cup
   Fill half way with light oil (SAE10W30)
3. Pour oil in corner of aluminum pan (Weigh Oil)
   Carefully to try not touch the pan with the oil
4. Measure the distance spread with time using a ruler at different times
   Measure the longest distance from the corner of the pan

Part 2

1. Fill an eye dropper with liquid soap (surfactant)
   Dishwashing soap is OK
2. Place a drop from the eye dropper in the pan near the edge of the spread
   What happens?
3. Repeat with more drops
   Describe in words what has happened.

Part 3

1. Use EXCEL to graph the experimental spread of oil in the aluminum pan
   Use the computers in the Engineering Computer LAB
2. Use the proper procedures in making the graph
   Title: include information about the experiment
   X Axis: This is time and include the units of time
   Y Axis: This is distance and include the units of distance

Part 4

1. Calculate the spread of oil with time from a theoretical equation
   Graph this calculation on the same graph as the experimental data
2. Describe the differences in the results
3. Any explanations?

RESULTS

Eighteen students signed up for the summer workshop. College mentors provided encouragement to the high school students to complete the laboratory assignments.
The students were highly motivated and their performance enabled to complete each laboratory assignment. The students especially liked these hands-on laboratory assignments.
The plant visits were well received. These included a modern wastewater treatment plant in East Greenwich, Rhode Island. That plant is typical of wastewater treatment plants in their primary treatment. In their secondary treatment they use rotary filters and for their final step before discharging into Narragansett Bay the use ultraviolet lams to kill any bacteria left in the discharge stream. Another important plant trip was to visit the University of Rhode Island fresh water system. This included the pond which supplies the aquifer from which water is pumped. These steps are followed by the addition of lime to neutralize the water. The water is then pumped up to a large storage tank followed by gravity feed to the academic buildings. A notable plant trip included the Scituate Reservoir and the Providence Water Supply Board Water treatment plant. The plant provides water to more than 60% of the residents of the State of Rhode Island. The water treatment plant includes a number of import steps including settling, aeration and chlorination. The plant visits were enhanced with lecture and laboratory experiences which are outlined in the summer workshop schedule. A series of photographs follows.

The following pictures are from the Scituate Reservoir and Providence Water Supply Treatment Plant field trip.

Section of the Scituate Reservoir Dam

The Phillip Holton Water Treatment Plant

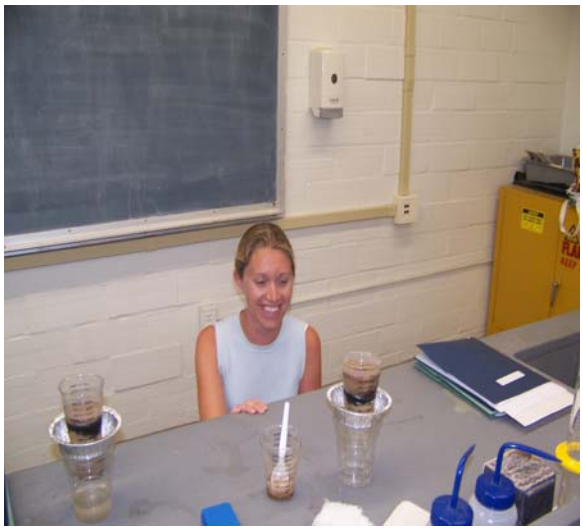
Fountain Aerators

Small Chemical Addition Pumps

Treatment Plant Control Room

Analytical Control Laboratory

The following pictures depict lab experiments with sand and activated carbon filtration.



Observation of Sand Filter Performance

Students Working in Teams

A Successful Experiment !

Laboratory Filter Representative of a Full-Scale Water Treatment Filter

Sharing Laboratory Data

The following pictures depict components of the URI drinking water system.

30 Acre Pond Adjacent to Well

Building Containing Well

Collecting Water Samples From 30 Acre Pond

Lime Addition for pH Adjustment

Clean Drinking Water Conference

March 5, 2009
Thursday

The presentations have been posted to www.wrc.uri.edu/

12:45 to 1:00pm Registration

1:00 Welcome: Dr. Thiem, Dr.Knickle

Session 1

1:15pm to 2:00 pm

- **Conservation and ReUse**
  Harold Mantius, Ocean Spray, Senior Process Engineer

COFFEE BREAK

Session 2

2:15 to 3:00 pm

- **Industrial Perspective**
- Brackish Water Technology
  Brian Hernon, VP Engineering,
  Seven Seas Water

Session 3

3:00 to 3:45 pm

- **Water Treatment**
- **MIOX System**
  Chris Duhamel, DiPrete Engineering
  Westerly Town Council

4:00 pm ADJOURN

At the meeting and workshop the guest lecturer, Harold Mantius, and keynote speaker was from the Ocean Spray Cranberry Cooperative and its expansion. He discussed the reduction in usage of fresh water in production plants. Following the keynote speaker was a discussion of recycling, conservation and changing processing methods.

USGS Summer Intern Program

None.

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	3	0	0	0	3
Masters	3	0	0	0	3
Ph.D.	2	0	0	0	2
Post-Doc.	0	0	0	0	0
Total	8	0	0	0	8

Notable Awards and Achievements

Based upon the data generated from the Rhode Island Water Resources Center funding, PI Vinka Craver applied for and received the following grant.

Collaborative Research: The Antimicrobial Properties of Silver Nanoparticles: Mechanisms and Water Chemistry Effects Principal Investigator: V. Craver. National Science Foundation (36 months, $227,274) (CBET#0854113)

Publications from Prior Years