Water Resources Research Center
Annual Technical Report
FY 2006

Introduction

Fiscal Year March 2006 - February 2007

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Prepared by the Arizona Water Resources Research Center, the University of Arizona, Tucson, Arizona

Research Program

Forward and Inverse Transient Analytic Element Models of Groundwater Flow

Basic Information

Title:	Forward and Inverse Transient Analytic Element Models of Groundwater Flow
Project Number:	2004AZ68G
Start Date:	9/1/2004
End Date:	8/31/2007
Funding Source:	104G
Congressional District:	7th
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Hydrology, Models
Descriptors:	Ground-water, Hydrology, Models
Principal Investigators:	Shlomo P. Neuman

Publication

1. Kuhlman, Kristopher L. and Shlomo P. Neuman. Recent advances in Laplace transform analytic element method (LT-AEM) theory and application to transient groundwater flow, In Computation Methods in Water Resources, Volume XVI, 2006.
2. Kuhlman, K.L. and S.P. Neuman, Recent advances in Laplace-transform analytic element method (LT-AEM) theory and application to transient groundwater flow, Proc. XVIth Intern. Conf. Computational Methods in Water Resources XVI (CMWR XV), June 2005, Copenhagen, Denemark, 2006.

Progress Report

Mr. Kris Kuhlman, a doctoral student in the department of Hydrology and Water Resources, has been working as Research Associate on this project. The work described below has been accomplished by him under the supervision of the PI in consultation with our USGS co-PI, Dr. Paul A. Hsieh.

The project focuses on developing and implementing a novel transient extension to the analytic element method (AEM), by posing the transient problem in Laplace space. A general numerical Laplace transform inversion method is used to compute the approximate solution in the time domain to a high degree of accuracy. The resultant Laplace transform AEM (LT-AEM) provides accurate solutions to transient groundwater flow problems which are far more general than most transient analytic solutions (e.g., flow to a well) and far less complex than fully gridded flow simulation codes such as MODFLOW.

To date, Kris derived and implemented active and passive elliptical elements in addition to circular and point LT-AEM elements. Finite line segments are implemented as degenerate ellipses (the line connecting the two foci of the ellipse), allowing much greater flexibility and accuracy than other attempts to implement analytic expressions for transient line sources.

To implement ellipses and line segments in Laplace space, a special algorithm was developed to compute radial and angular Mathieu functions of a complex parameter. The algorithm is general and works in almost all cases of interest.

Kris implemented an improved direct solution method that alleviates common convergence problems arising from the previously used fixed-point iterative scheme. In the case of complex geometries the direct solution method is much faster than the iterative scheme, which is now used primarily as an option to obtain added accuracy.

The LT-AEM is now implemented using modern platform-independent Fortran-2003 programming (utilizing modules, intrinsic vector / matrix operations and overloaded procedures). The program is being made modular to admit a variety of element types and numerical Laplace transform inversion algorithms.

Current work is focusing on adding intersecting elements (e.g., the union of two overlapping circles) and approximate rectangular elements to the list of available elements in LT-AEM. An important role of rectangular and polygonal elements would be to allow coupling our LT-AEM program with grid-based codes to allow (a) an easy treatment of far-field conditions in these codes without explicitly extending the solution mesh and (b) the treatment of domain within which the flow equations are nonlinear. The coupling can be iterative or, in the case of gridded models operating in the Laplace domain, directly (e.g., by incorporating the LT-AEM into the stiffness matrix of a finite element model).

In a separate program Kris is planning to implement some simple three-dimensional LT-AEM elements for which he has already developed the requisite mathematics.

Kris has completed his graduate coursework and plans to complete his doctoral comprehensive exams this Spring Semester 2007.

In June 2006 Kris presented a paper based on his research at the XVI-th International Conference on Computational Methods in Water Resources (CMWR XVI) in Copenhagen, Denmark. The paper is available on the conference permanent website under the title

Kuhlman, K.L. and S.P. Neuman, Recent advances in Laplace-transform analytic element method (LT-AEM) theory and application to transient groundwater flow, Proc. XVIth Intern. Conf. *Computational Methods in Water Resources XVI* (CMWR XV), June 2005, Copenhagen, Denemark, 2006.

In March 2007 Kris presented a talk based on his research at the annual Dia del Agua workshop of the University of Arizona Department of Hydrology and Water Resources. He received the coveted Earl Montgomery Prize for best presentation at the workshop.

Kris' work will be the focus of an invited paper in the Journal of Engineering Mathematics that we plan to prepare over the summer.

Pharmaceutically Active Compounds: Fate in Sludges and Biosolids Derived from Wastewater Treatment

Basic Information

Title:	Pharmaceutically Active Compounds: Fate in Sludges and Biosolids Derived from Wastewater Treatment
Project Number:	2004AZ70G
Start Date:	9/1/2004
End Date:	8/31/2007
Funding Source:	104G
Congressional District:	Arizona #7
Research Category:	Water Quality
Focus Category:	Groundwater, Non Point Pollution, Toxic Substances
Descriptors:	Wastewater, Pharmaceuticals, Sludge
Principal Investigators:	David Matson Quanrud, Robert Arnold, Jon D Chorover, Gail Cordy, Wendell Ela

Publication

Progress Report

The two main objectives of this project are to (1) perform measurements of endocrine disrupting compounds (EDCs) and pharmaceutically active compounds (PhACs) in sludges/biosolids obtained at selected wastewater treatment plants using different sludge digestion processes and (2) examine the fate of biosolid-associated EDCs and PhACs in soils at land application sites receiving biosolids.

During the third year of the project, tasks performed to satisfy project objectives included the following:

1. Liquid and sludge/biosolid samples were obtained from four wastewater treatment plants in Arizona to compare EDC removal efficiencies by different treatment processes. Sampling points included influent, effluent, and digested sludges to support overall mass balance calculations at each treatment facility.

2. As part of the knowledge transfer objective of the project, PhD students from the environmental engineering program at the University of Arizona (UA) visited Edward Furlong's USGS laboratory to learn LC-MS and GC-MS analytical techniques for PhACs and EDCs. Two PhD students (Otakuye Conroy, Sondra Teske) visited in April 2006 for a one-week training session. During summer 2007, another PhD student (Bing Feng Dong) will receive similar training at the USGS lab and will assist with analysis of soil samples from a land application research field site near Tucson.

3. Leachate and soil samples obtained from three 1-m long stainless steel columns set up to simulate land application were sent to Dr. Furlong's laboratory for analysis of PhACs and EDCs. The analytical measurements at Dr. Furlong's laboratory were conducted in part by the graduate students from UA in April 2006. The analytical measurement work is ongoing.

4. A new focus was made on the emerging contaminant polybrominated diphenyl ether (PBDE). The fate of PBDEs has been examined during conventional wastewater treatment in trickling filter and activated sludge facilities, effluent polishing during soil aquifer treatment, and biosolid application onto agricultural land research sites in Arizona and Washington State.

5. A second comparison of sample extraction techniques (microwave assisted extraction, MAE; accelerated solvent extraction, ASE) is underway. A series of digested sludge samples were extracted using both procedures and are being analyzed for 21 PhACs and 61 wastewater compounds using liquid chromatography-mass spectroscopy (LC-MS) and gas chromatography-mass spectroscopy (GC-MS) at Edward Furlong's USGS laboratory in Denver, Colorado. In addition, parallel work is underway at UA to measure estrogenic activity on all extracts. A peer-reviewed Technical Note will be prepared summarizing results of the comparison.

Planned Activities:

During the final few months of the study, planned activities include:

1.Data analysis including mass balance calculations on contaminant flux rates at the Ina Rd wastewater treatment plant (activated sludge process).

2. Analysis of soil samples from a local land application site for a suite of organic wastewater contaminants. A UA graduate student will conduct this work during a visit this summer to the USGS analytical laboratory in Denver under the direction of Ed Furlong.

3. Compilation of analytical results to support conclusions on efficacy of wastewater treatment unit processes and land application practices for attenuation of solid-bound PhACs and EDCs.

4. Preparation of final project report.

Chemolithotrophic denitrification: The missing link in the biogeochemical cycle of arsenic

Basic Information

Title:	Chemolithotrophic denitrification: The missing link in the biogeochemical cycle of arsenic
Project Number:	2005AZ114G
Start Date:	9/1/2005
End Date:	8/31/2008
Funding Source:	104G
Congressional District:	AZ05
Research Category:	Biological Sciences
Focus Category:	Toxic Substances, Groundwater, Non Point Pollution
Descriptors:	Denitrification, Arsenic, Non Point Pollution
Principal Investigators:	Reyes Sierra, James Field, Ronald S Oremland

Publication

1. Sierra-Alvarez, R., W. Sun, P. Rowlette, I. Cortinas and JA Field. 2005. Anoxic Oxidation of Arsenite Linked to Denitrification. Eighth International In Situ and On-Site Bioremediation Symposium. June 6-9, 2005. Baltimore, MD. (Conference proceedings).

Progress Report

Microorganisms are important in catalyzing conversions of arsenic between its two common oxidation states, arsenate (As(V)) and arsenite (As(III)). Recent evidence indicates that nitrate-reducing bacteria can oxidize As^{III} in anoxic environments. The objective of this study is to evaluate the importance of chemolithotrophic denitrifying bacteria in the biogeochemical cycle of arsenic. The proposed research will examine the direct microbial oxidation of As(III) with nitrate as electron acceptor, as well as the microbial oxidation of Fe(II) with nitrate and subsequent adsorption of As(V) by the iron oxides formed. The central question addressed in this proposal is whether anoxic oxidations of As(III) and Fe(II) are ubiquitous process in groundwater and surface waters controlling the mobility of arsenic.

Inocula from different sources were tested for their ability to support the anoxic oxidation of As(III) with nitrate as the electron acceptor. Pond sediments and wastewater sludges were found to be capable of this reaction. The results indicate that chemolithotrophic denitrification utilizing As(III) as an energy source is a ubiquitous process in anaerobic environments. The microbial reactions could be sustained for long periods of time in upward flow anaerobic sludge bed reactors (in which biomass is immobilized as granular biofilms). An example of continuous reactor operation is shown in Figure 1 by the formation of As(V) from As(III). The reactor was able to tolerate up to 5 mM As(III); however when 7.5 mM As(III) was applied, there was a steady decline in activity that was corrected by lowering the influent As(III) concentration back to 3.75 mM. The molar ratio of As(V) formed compared to nitrate consumed (corrected for background removal by the endogenous substrate) was found to be 2.45. This is close the theoretical stoichiometry of 2.5 for complete denitrification as shown in equation 1 below:

$$5AsO_3H_3 + 2NO_3^- + 2H^+ \rightarrow 5AsO_4H_3 + N_2 + H_2O \qquad [1]$$

To confirm that N_2 was indeed the end product of the reaction, a batch experiment was conducted with acclimatized continuous reactor sludge to test for N_2 production from NO_3^- with and without As(III) addition as electron donor. The results shown in Figure 2 indicate that N_2 gas was formed in response to As(III) addition. The ratio of As(V) formed to net NO_3^- consumption (corrected for endogenous nitrate consumption) was found to be 2.65, which was close to the theoretical value for complete denitrification (eq. 1). The molar yield of N_2-N compared to NO_3^--N consumed was 94.3%. This constitutes the first direct evidence that As(III) oxidation is linked to complete denitrification.

Several enrichment cultures have been developed from the original inocula or from biomass from the continuous reactors. Enrichments were made by repeated transfers (once every 3 weeks) into basal mineral medium with 0.5 mM As(III) and excess nitrate. Presently, three enrichment cultures are maintained as follows: 1) originating from an anaerobic biofilm from a reactor treating distillery wastewater; 2) originating from pond sediments; and 3) originating from biofilm from one of our continuous reactor converting As(III) to As(V) linked to denitrification. Although As(III) is readily used as an electron donor by the enrichment cultures, it is nonetheless an inhibitory compound. In batch experiments, rates of As(III)-linked denitrification are observed to increase with decreasing As(III) concentrations due to the lower inhibitory effect at lower concentrations.

As(III) is generally considered to be more mobile in the environment compared to As(V). The basis for this claim is that As(III) is less strongly adsorbed by certain common metal oxides such as aluminum oxides. Adsorption isotherms of both As(III) and As(V) shown in Figure 2, illustrate that As(III) is less strongly adsorbed by activated alumina (AA) compared to As(V). This information taken in combination with the fact that NO_3^- is used by microorganisms to oxidize As(III) led us to the following hypothesis. Nitrate can potentially be used to oxidize As(III) in groundwater to decrease the mobility of arsenic. The As(V) formed would be more strongly retained by metal oxides in soil. We set out to test the hypothesis using columns packed with activated alumina. The columns (0.42 L) were continuously fed with approximately 500 μg/L of As(III), column either in the presence of nitrate (column S1) or absence of nitrate (column S2). The columns were inoculated with an As(III) oxidizing-denitrifying enrichment culture. Figure 4 shows the release of arsenic (measured as total arsenic) was greater in S2 compared to S1 in accordance with the expectation. Column S2 broke-through on day 200; whereas in the same time period, only half the arsenic entering the column S1was released. The differences in the release of arsenic from the two activated alumina columns could be attributed to the difference in speciation of arsenic resulting from the microbial oxidation of As(III) to As(V) by chemolithotrophic denitrifiers in column S1. Figure 5 illustrates the average speciation of arsenic in the influent and effluent of reactors S1 and S2 during days 202 to 215. The graph demonstrates that the arsenic in the influent and the effluent of S2 was predominately composed of As(III); whereas the effluent of S1 contained only As(V). There was incomplete recovery of As(V) in the S1 effluent due to its continued adsorption by activated alumina. The results taken as a whole suggest that microbial oxidation of As(III) linked to denitrification decreases the environmental mobility of arsenic.

In the coming period, we will test the impact of nitrate in reducing the mobility of arsenic in sand sediment columns fed with a mixture of Fe(II) and As(III), which would represent the species of iron and arsenic in anoxic groundwater. The expectation is that the oxidation of iron by chemolithotrophic denitrifiers will form iron oxides that can adsorb both As(III) and As(V).

In conclusion, the research so far has demonstrated that the anoxic oxidation of As(III) by chemolithotrophic denitrification is a relatively ubiquitous process that can be enriched from inocula in anaerobic sludges and sediments. The evidence indicates that As(III) oxidation is linked to the complete denitrification of NO_3^- to N_2 gas. The change in speciation from As(III) to As(V) by this anoxic process was shown to lower the mobility of arsenic in a model sediment column packed with aluminum oxides.

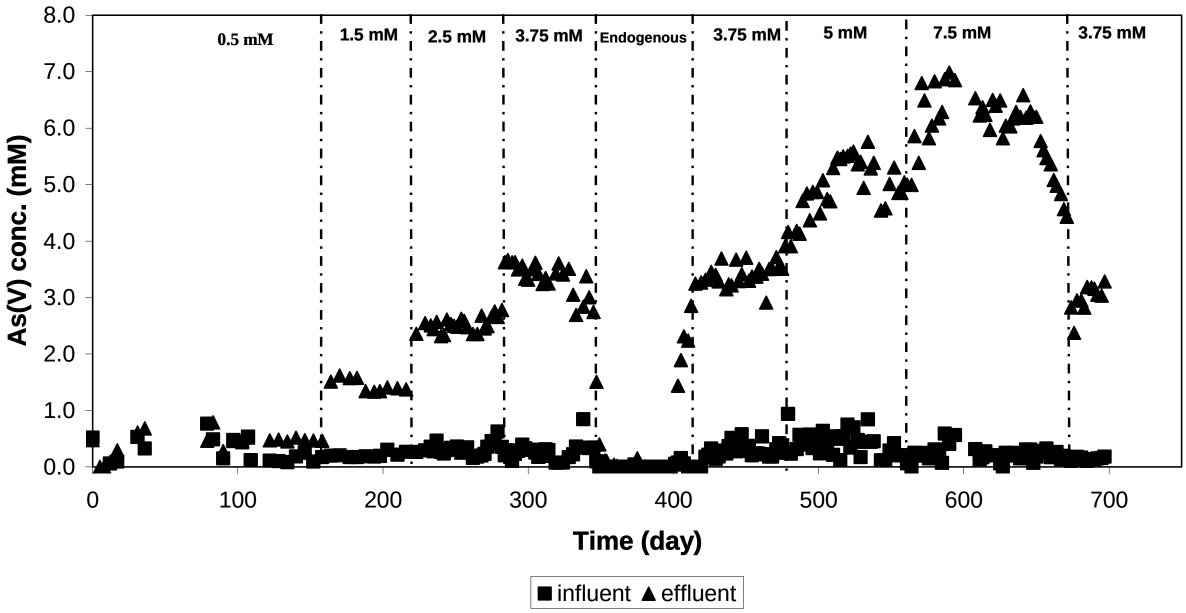

Figure 1. Influent and effluent concentrations of As(V) during the operation of a 2-L laboratory-scale upflow anaerobic sludge blanket reactor inoculated with 27 g volatile suspended solids/L of granular anaerobic biofilm from a full scale anaerobic reactor treating distillery wastewater (Nedalco). The reactor was fed with basal mineral medium and As(III) as the sole energy source and nitrate as the sole electron acceptor, the As(III) concentrations added in influent are indicated in the graph (endogenous means no addition of any electron donor). The hydraulic retention time was maintained at 1 day.

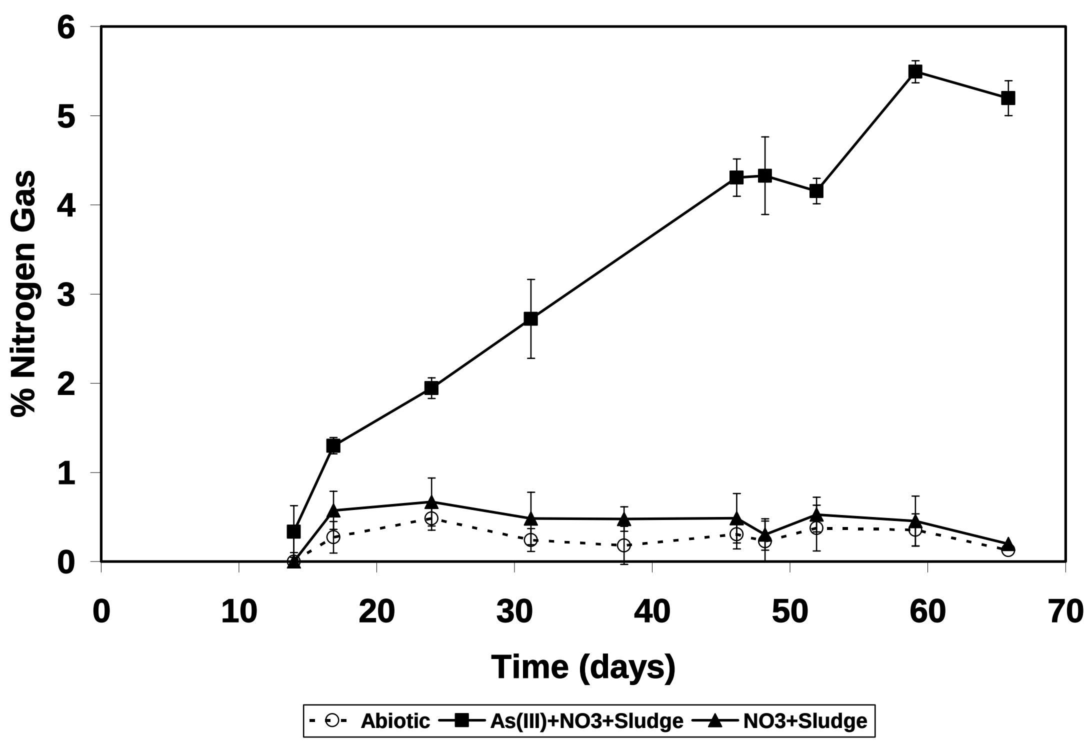

Figure 2. Formation of N_2 gas from the oxidation of As(III) linked to denitrification. Bottles were incubated with 3.5 mM As(III) with 0.6 g volatile suspended solids/L

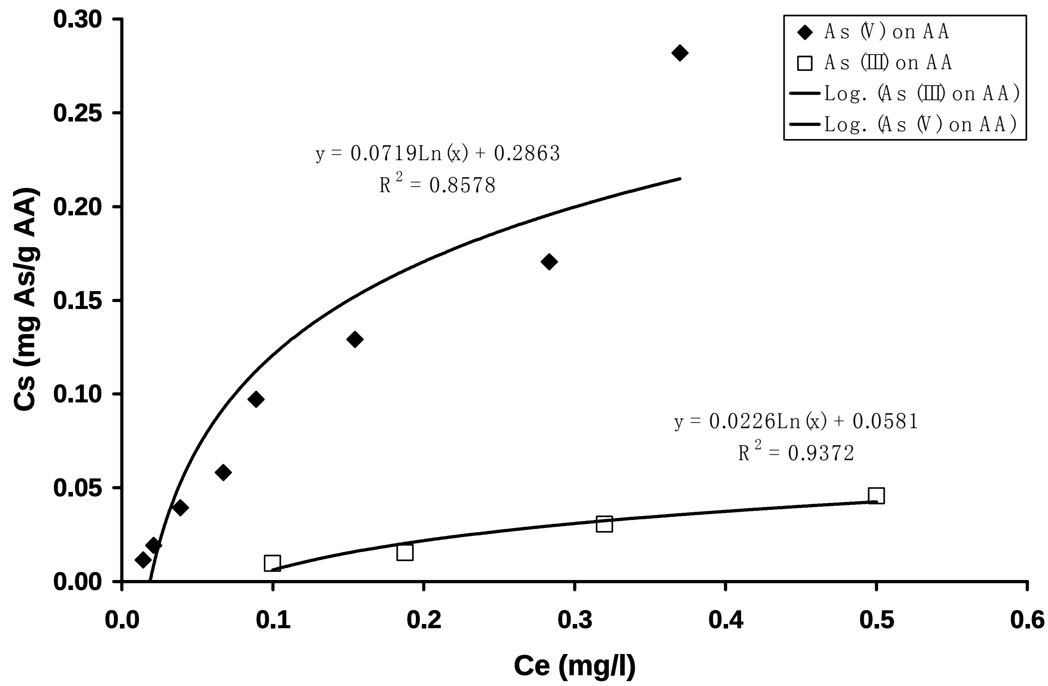

Figure 3. Adsorption isotherms of As*V) and As(III) on activated aluminum.

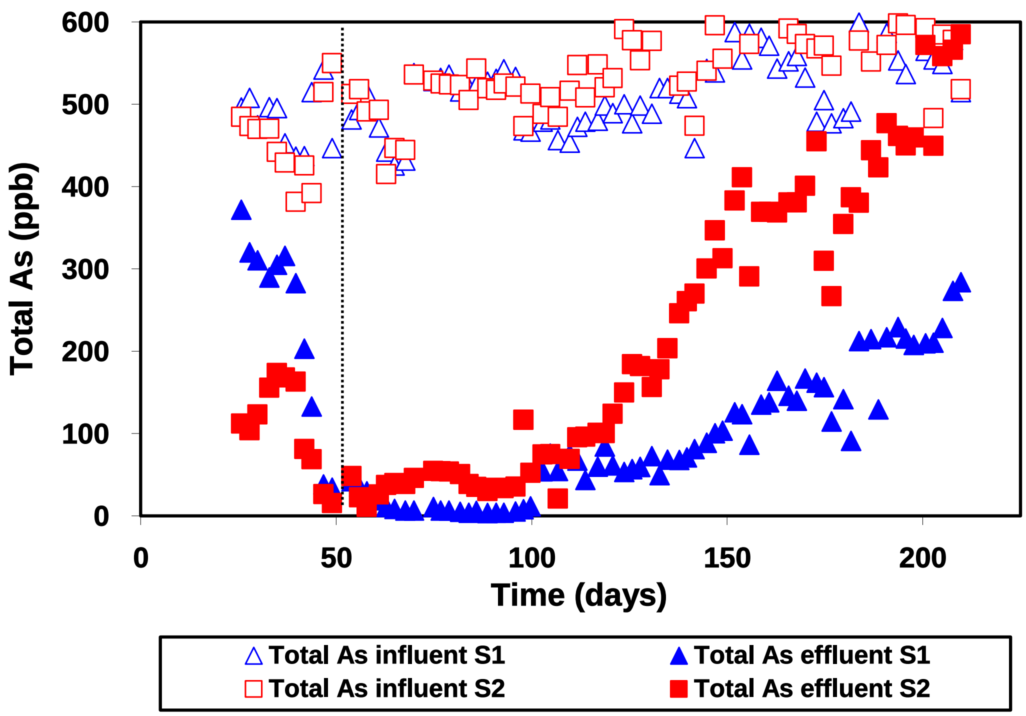

Figure 4. Influent and Effluent concentrations of total arsenic entering activated alumina packed bed columns S1 (with NO_3^-) and S2 (without NO_3^-). The vertical line on day 50 indicates the time point, after which the pH was controlled around 7.5, prior to day 50 the pH was alkaline (8 to 10).

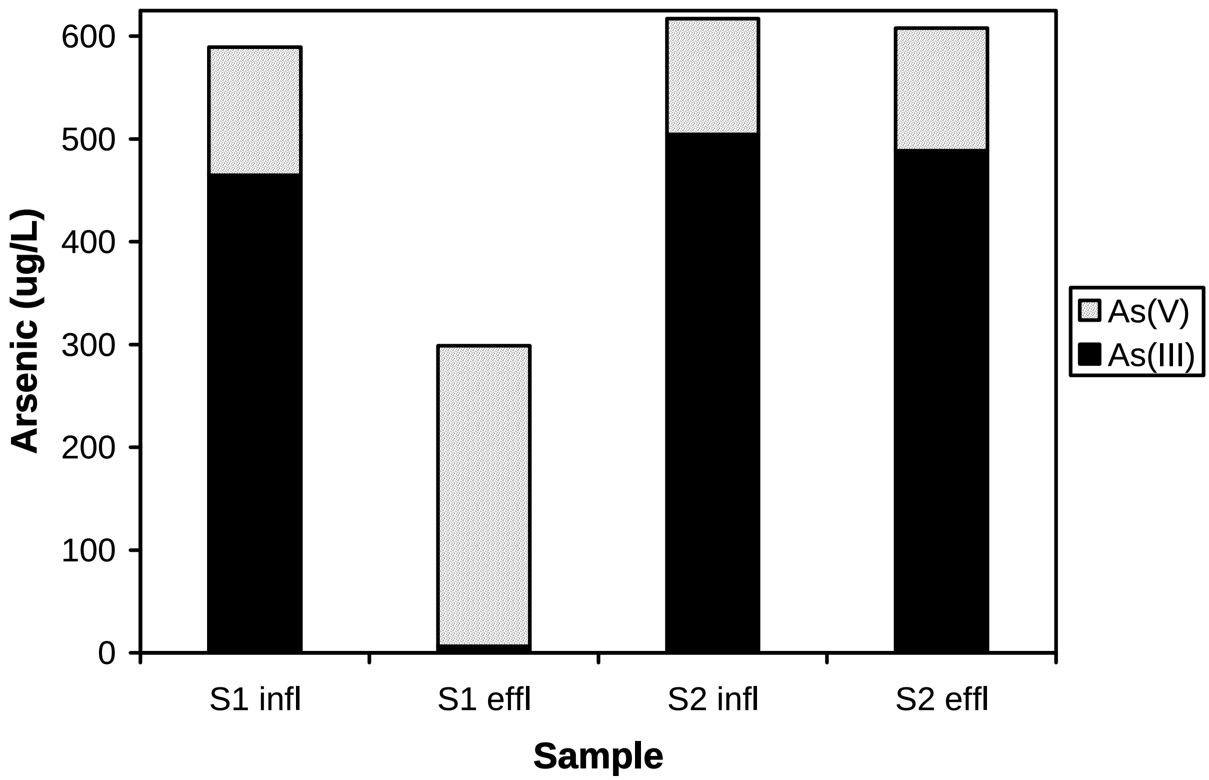

Figure 5. Speciation of arsenic in influent and effluent samples of activated alumina packed columns containing NO_3^- (S1) or lacking NO_3^- (S2).

Student Support

PhD Student:

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Student Training, Research, and Participation in Water Harvesting Design and Implementation

Basic Information

Title:	Student Training, Research, and Participation in Water Harvesting Design and Implementation
Project Number:	2006AZ131B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	Arizona 7th District
Research Category:	Engineering
Focus Category:	Conservation, Education, Management and Planning
Descriptors:	None
Principal Investigators:	James Joseph Riley, Jim Walworth

Publication

1. Brill Duisberg, Emilie, G. McCormick, J. Riley, and P. Virdee, 2006, Presentation: Collaborative Water Harvesting at the University of Arizona, in Association for the Advancement of Sustainability in Higher Education (AASHE) Conference on: The Role of Higher Education in Creating a Sustainable World, Arizona State University, Tempe, AZ, USA, October 4-6, 2006
2. Brittain, Richard and J. Riley, 2006, Relative Cistern Water Quality at 12 Sites Capturing Rainwater in Tucson, Arizona, in Looking Ahead: Managing Stormwater and Harvesting Rainwater for Conservation, Tucson, AZ, October 27-28, 2006.
3. Yoklic, Martin R., J.J. Riley, D. Confer, J. Robinson, B. Lancaster, A. Phillips, and K. Kroesen., 2006, "Water Harvesting Potential in an Arid City: A quantity Assessment for Tucson, Arizona", in Looking Ahead: Managing Stormwater and Harvesting Rainwater for Conservation, Tucson, AZ, October 27-28, 2006.
4. Riley, James J., E. Casey, C. Phillips, S. Lippel, E.Brill Duisberg, E. Feirstein, and R. Bark. 2006, A University of Arizona Rainwater Harvesting Project: Integrating Student Initiative with Campus Cooperation, Poster at Looking Ahead: Managing Stormwater and Harvesting Rainwater for Conservation, Tucson, AZ, October 27-28, 2006.

A. Problem and Research Objectives

Rainwater harvesting has long been used in the arid southwest for agriculture and sustenance. Human populations including early settlers and native peoples have utilized harvested rainwater, but modern societies have been slow to take advantage of this vital resource. In a region of increasing water scarcity, knowledge of rainwater harvesting techniques remains scarce as well. Population growth in southern Arizona continues to depend upon groundwater and transported surface water. When the volume of rain that falls on the metropolitan Tucson area annually is approximately equal to the to the annual municipal residential water use, there is clearly a need for research and education on the topic.

The University of Arizona Comprehensive Campus Plan 2003, approved by the Arizona Board of Regents, states clear objectives for the sustainable management of limited land and water resources at the university, yet these objectives remain purely theoretical, with the specific techniques for sustainable, efficient resource management in need of development.

As an institution of higher education in an area of resource scarcity and frequent drought, the University of Arizona is ideally situated to provide research and education on water harvesting to both campus and greater metropolitan communities. Yet thus far, the opportunity to create a learning laboratory for more sustainable water management techniques has not been taken advantage of at the university level. Few water harvesting techniques have been employed on campus, and the few that have do not serve any explicit educational purpose.

There is an urgent need for leadership on water issues, and this need promises to grow in importance with the growth of human populations in the region. In addition, well-managed harvested rainwater has the potential to replace a significant percentage of groundwater pumping for landscaping and other non-potable purposes at the university, decreasing the university's draw on threatened groundwater reserves and thus reducing the magnitude of land subsidence in the Tucson Basin. The further need exists to develop and model more sustainable, efficient water management techniques for application elsewhere in the region and familiarize a broader segment of the population with possible approaches.

Water harvesting can ameliorate flooding by retaining or detaining runoff water. Additionally, water harvesting can provide an alternative source of water at a time when long-term drought may lead to a reduction in the amount of Colorado River water available to the Tucson Community. The University of Arizona should take a lead role in addressing these problems and teaching how to incorporate water harvesting into the long-term community water plans.

The purposes of this study are to develop the methodology needed to apply rainwater harvesting on the campus of the University of Arizona in keeping with the water management objectives stated in the Campus Comprehensive Plan, 2003, and to provide training and experience to undergraduate students in project design and implementation, disseminating both practical skills and a working knowledge of water scarcity concerns to a broader swathe of the student community. By involving University Faculty, Risk Management and Safety Staff and Facilities and Planning Staff it is hoped that the water harvesting lessons learned can be institutionalized and applied elsewhere on campus. Interventions at the McKale Memorial Center are intended to reduce the risk of flooding a highly visible facility while maintaining more water on campus and thereby reducing stormwater flood levels on City of Tucson streets.

Research Plan

The following techniques will be among those addressed by and considered for the project:

- Close observation, mapping, calculation, and monitoring of water quantity and surface flow patterns across walkways and landscape areas surrounding the McKale Memorial Center sports complex.
- Design and installation of earthen contour swales and berms to divert rainwater into landscaping areas and away from existing buildings.
- Terracing of naturally occurring slopes to slow water flow and erosive power and allow for infiltration.
- Design of a walkway cut, cement berm, drainage pipe or channel, fountain, and catchment basins to interrupt a flow pattern currently causing flooding of the lower level offices at McKale Center.
- Mulching and planting of native vegetation mimicking that found along ephemeral arroyos of the Sonoran Desert.
- Redesign of sidewalk and roadway features to facilitate water flow into catchment basins, swales, and planted beds.
- Design of drainage and/or storage tank facilities for water above the utilization capacity of landscape features.
- Labeling of all installations to provide information on the importance of rainwater harvesting to the campus and metropolitan communities

The maximum quantity of rainwater available for harvesting will be calculated, and existing surface water flow patterns across project areas will be mapped before new installations are considered. Multiple design options will be examined for each project area and collaborative rainwater management plans will be developed. Consultation with regional water harvesting authorities and site visits to relevant projects will occur before adoption of a plan to be implemented in the vicinity of McKale Center. Other consultations may occur with members of the campus Surface Water Working Group, the departments of Soil, Water, and Environmental Science (SWES), Landscape Architecture, and the Campus Arboretum. Once structural and landscape alterations are made, close monitoring will occur to identify necessary changes and improvements both at the site and in future projects elsewhere on campus. The following tables illustrate the original project plan and for comparison the actual implemented plan:

Original	2006	2006	2006	2006	2007
Task	Jan-Mar	Apr-May	Jun- Sep	Oct-Dec	Jan-Mar
Class(es) on Water Harvesting			Tentative		
Study of Harvesting Principles					
Initial Site Evaluations: Flooding/Harvesting					
Map McKale sub-watershed					
Students contributions to designs					
Development of rainwater harvesting plan for McKale					
Implementation of water harvesting plans					
Report with photo documentation					

Actual	2006	2006	2006	2006	2007	2007
Task	Jan-Mar	Apr-May	Jun-Sep	Oct-Dec	Jan-Mar	Apr-Jun
Class(es) on Water Harvesting						
Study of Harvesting Principles						
Initial Site Evaluations: Flooding/Harvesting						
Map McKale sub-watershed						
Students contributions to designs						
Development of rainwater harvesting plan for McKale						
Implementation of water harvesting plans AME and Meinel Buildings						
Report with photo documentation						

B. Methodology

The Surface Water Working Group composed of University staff directly responsible for the management of water on the campus, has invited undergraduate representation to their deliberations. Also, they have offered to work with the project to involve additional students in assisting them in designing solutions to the flood problem at McKale Memorial Center that have a water harvesting component. This combination, of students, faculty, and staff is intended to be a precedent setting model for transforming the campus into an example of good water management in an arid environment.

A solution to the flooding problems at McKale has been included in the SWWG budget and will be completed with or without project input. The opportunity proposed herein is to make that fix an example of holistic planning that will serve as an example for future planning and take a step toward making the University of Arizona an example for other aridlands institutions.

C. Principal Findings and Significance

The funding enabled us to offer an experimental course on water harvesting by James J. Riley, Ph.D. during spring 2006 at The University of Arizona. There were 12 undergraduates and 5 graduate students enrolled. In the spring 2007 there were 19 undergraduates and 5 graduate students. With the funding provided, Mr. Brad Lancaster, author of the text used in the course, "Rainwater Harvesting for Drylands, Volume1" and Richard Brittain, College of Architecture and Landscape Architecture, were able to provide practical instruction in the design of water harvesting systems with emphasis on sites on the campus of The University of Arizona and put them in context of international practices. The enthusiasm and dynamics of the class were impressive. Often times it was necessary to force the student to leave the classroom because the room was going to be used by another class. This grant has enabled us to establish the water harvesting course and to initiate an active water harvesting program on-campus with the assistance of the Surface Water Working Group.

The 2006 class analyzed the McKale Memorial Center grounds as the building floods in severe rains for a class project. We proposed a number of potential interventions to apply water harvesting on the building and on the surrounding area to reduce the flooding. Some of these required evaluation and implementation by the University Facilities Staff others were to be done by students, using the funds provided in the grant to pay their wages. Unfortunately the primary activity for students could not be implemented as some electrical cables were in the way of a proposed channel that would carry runoff water to trees.

With the help of the Surface Water Working Group of the University we were able to identify another project which was implemented during the summer 2006 by the students. It was on the grounds of the Aerospace and Mechanical Engineering (AME) Building along Speedway Boulevard, a highly visible location for pedestrian and vehicular traffic. The objective was simple, direct water from 6 downspouts to 6 trees; but the implementation took about 4 hours per day for six weeks during the summer months with an average of 6 students per day participating. Faculty members, staff of Facilities Management, and other volunteers joined the project from time to time. Facilities Management provided technical support in terms of the hydrology, landscaping, grounds, and planning. Facilities Management staff provided materials, transportation, equipment, and tools as required.

Rains that occurred during the project implementation facilitated evaluation of the project in terms of capturing and directing water runoff on the site as well as adjusting the plans to make it more effective.

When it was completed, a dedication ceremony was held with attendance from departments involved in the construction as well as students and administration representatives. Local and University television interviewed students and participants for local shows. Facilities Management erected a sign acknowledging the contribution of PARASOL, the principal participating student organization in developing the water harvesting at the AME site.

While the major project was under construction, Facilities Management asked the students to participate in the landscaping for passive water harvesting on the grounds of the Meinel Optical Sciences Buildings. Berms were constructed to hold water on the site for infiltration following which the UA Grounds planted the area. This area is highly visible as it is on the University mall and adjacent to the public bus stop. A slide show presented to an AASHE conference is appended to more clearly demonstrate the project's accomplishments.

The 2007 class continued to focus on water harvesting mostly on the UA campus but with some exceptions. The table below summarizes the semester's projects:

Title	**Description**	**Accomplishments**
Development of a Water Harvesting GIS Layer for the UA campus	Students working with Facilities Planning and the Office of Arid Lands Studies will develop a GIS layer(s) to facilitate the implementation of water harvesting on campus.	The project was still in the planning stage by the end of the semester, but sufficient work was completed that it should enable the establishment of a Water Harvesting GIS layer for the campus by the end of Summer 2007.
Visitors Center	Students attended planning meetings for the Phase I of the project which will include the installation of active and passive water harvesting on the UA visitors center as well as the demonstration of electrical solar energy generation. Students developed Phase II of the project to utilize the runoff from the parking lot on an infiltration/garden feature.	At the end of the semester these projects had approached the advanced planning stage and are intended to be implemented in the Summer 2007.
Applying Water	Students spent some time on determining how water harvesting might	The intent of this project was more of a translational

Harvesting to a golf course	be used on a golf course and then found one course willing to work with them.	nature in that the basic information and site for a possible demonstration project was identified.
Water Harvesting Display at the Tucson International Airport (TIA)	Students worked with staff from the TIA and the Environmental Research Lab to develop a design for a display case (donated by TIA for one year) which will highlight the benefits of water harvesting.	The students completed the design for the display and liaised with the TIA on the selection of the display location and the content. The display should be completed by July 2007.
Tree of Life	Students worked with staff from the Tree of Life (TOL) organization, 2 of who attended the class, to develop an active and passive water harvesting plan for the TOL grounds in Patagonia, AZ.	The plan was completed during the class and several students, faculty and volunteers joined the TOL staff in initiating the implementation of the design during the semester.
SE corner of FCS Building	In January 2006, the landscaping on Southeast corner of the Family and Consumer Sciences Building was modified to direct the water from two downspouts to existing and newly planted vegetation. During the summer of 2006 it was observed that the area needed some modifications to be more effective.	Students developed a plan which was implemented by students during the semester with the assistance of a faculty member.
Controlling irrigation in water harvesting areas	One of the troubles with the implemented water harvesting projects on the UA campus is that the existing irrigation system continues to function in the same manner as prior to the completion of the projects. This project explored the selection and demonstration of appropriate water controllers in cooperation with the UA Grounds staff.	By the end of the spring semester a controller whose delivery of irrigation water is governed by soil moisture content was selected and is intended to be installed on the Visitors Center site in the near future.
West Stadium water interception	Some of the reclaimed irrigation water runoff and rainfall runoff flow from the campus on to East 6th street, a city street. The intent of this project was to see if these flows could be intercepted on campus and used for campus landscape irrigation via passive water harvesting.	The students made good progress in the analysis of the problems and selection of proposed interventions. However, it was learned that the areas of implementation were soon to be destroyed for the construction of other campus buildings and

		features. So this group joined in the work on the Visitors Center.
Utilization of ECE ultra-pure water discharges	Initially the student team was working to evaluate the feasibility of using stored runoff water from the Integrated Learning Center for irrigation. However, in their investigations they learned about the discharge of ultra-pure water from the Electrical and Computer Engineering Building at a rate of 3,000-5,000 gallons per day. The students then re-focused on how to use this water.	The students liaised with Facilities Management, ECE Engineers, and the faculty of the nearby Architecture Building. They developed several ideas on how the water could be used in the landscaping of the Architecture Building and in the future in a planned courtyard of a library building in the vicinity. Students will continue to track the progress of the implementation of their ideas.

The work of the students in the Water Harvesting class inspired UA Grounds staff to apply water harvesting principals in other locations. The prime example is a site of flooding on the tennis courts where drains were installed to direct the excess water to nearby vegetation.

The students who participated in this project have gone on to take a larger role in developing a more sustainable and environmentally aware campus by establishing a new organization: ECOalition, and taking a more active role in Focus the Nation and the Association for the Advancement of Sustainability in Higher Education, AASHE.

Perfluorinated Chemicals in Municipal Wastewater Treatment Plants in Arizona

Basic Information

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Publication

1. Ochoa, Valaria, 2006, Processes for the Removal of Perflurooctane Sulfonate (PFOS) from Semiconductor Effluents, MS Dissertation, Department of Chemical and Environmental Engineering, Univ. of Arizona, Tucson, Arizona.

A. Problem and Research Objectives

A.1. Statement of critical regional or state water problems

Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and related PFCs are emerging environmental pollutants. These compounds have come under increased scrutiny due to recent reports of their detection in environmental and biological matrices as well as concerns regarding their persistence and toxicity. Recent studies indicate that wastewater treatment plants are point sources of PFCs (Boulanger *et al*., 2004; Higgins *et al.,* 2005). The fluorochemicals may enter the environment through effluent discharge or land application of biosolids.

Little is known about the fate of PFCs in municipal wastewater treatment systems. Sewage sludge is suspected to be the main sink of perfluorinated compounds in municipal wastewater treatment plants as these compounds are expected to partition into biosolids due to their high bioaccumulation potential. There is presently no data on the occurrence of PFCs in environmental samples nor in municipal wastewater treatment plants (WWTP) in Arizona, yet PFCs are extensively used in the growing semiconductor industry sector in the State, in (forest) fire fighting operations, and in a wide variety of other industrial, commercial and consumer applications. Data regarding the presence of PFCs in municipal wastewaters will be useful to understand the potential role of municipal WWTPs as indirect sources of PFCs emissions. As Arizona's population centers expand and the demand for water increases, reuse of treated wastewater is expected to become more prevalent, which could increase the potential for environmental contamination with PFCs. Information on the occurrence of PFCs in sewage sludge is also of importance for Arizona because biosolids are used as soil amendments throughout the State.

Safe water resources are of strategic importance for Arizona to meet the rapidly increasing demand for potable water. Understanding the occurrence and fate of these emerging pollutants in Arizona's wastewater treatment plants could be critical to protecting our water supplies. Utilities and government agencies will be able to utilize information gained from this study to determine the need for implementing measures to prevent the spread of PFCs in the environment.

A.2. Background information

PFCs are emerging pollutants that have been used for over the last 50 years in a wide variety of industrial processes and consumer-based products. Among these chemicals, PFOS and PFOA (Figure 1) are the most studied fluorinated alkyl surfactants due to their world-wide distribution, environmental persistence and bioaccumulation potential. Studies show that PFOS has been detected in human blood samples (Olsen *et al.*, 2003; Kannan *et al.*, 2004; Calafat *et al.*, 2006), in wildlife tissues collected worldwide, including biota from pristine areas (Giesy and Kanan, 2001; 2002; Martin *et al.*, 2004a) and in environmental matrices such as sewage sludge (Higgins *et al.*, 2005). In response to these concerns, regulatory agencies in numerous industrialized countries have initiated studies to quantify the use of perfluorinated chemicals, assess their potential risks, and consider regulations restricting or banning their use (Martin *et al.,* 2004b).

Little is known about the occurrence and fate of perfluorinated compounds in municipal WWTPs. A study conducted by 3M in 2001 revealed that PFOS concentrations in sewage sludge in Alabama, Tennessee, Georgia and Florida were in the range of 58 to 3,120 ng/g (3M, 2001). Higgins *et al* (2005) quantified PFC levels in sewage sludge and in sediments impacted by sewage discharges in California. The survey detected total PFCs levels ranging form 55 to 3,370 ng/g in domestic sludge. Loganathan and coworkers (2006) reported PFOS and PFOA at concentrations of 62 – 990 ng/g in sludge samples obtained from a municipal WWTP in Kentucky.

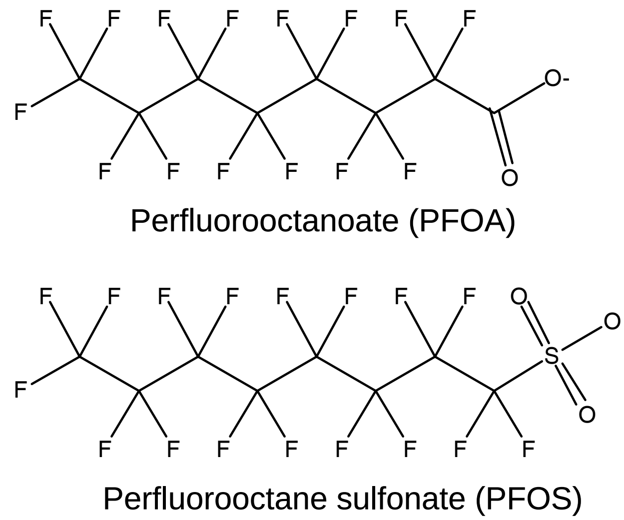

Fig.1. *Chemical structure of the most ubiquitous perfluoro alkyl surfactants in the environment.*

Research on the fate and transport of PFCs in the environment has been hampered by a lack of analytical capability (Martin *et al.,* 2004b). Compound specific quantitative methods for the analysis of PFCs became first available in the year 2001, when a procedure consisting of liquid solvent extraction, solid-phase extraction cleanup, and analysis by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) was described for the analysis of PFCs in biological matrices (Hansen *et al.,* 2001). Methods for the determination of perfluoroalkylsulfonates and perfluroalkylcarboxylates in aqueous samples, sludge and sediments by LC-MS/MS have also been described recently (Boulanger *et al*., 2004; Higgins *et al.*, 2005; Moody *et al.*, 2001). LC-MS/MS is the method of choice for the quantification of PFCs constituents in environmental samples and biological matrices, both because of its sensitivity and selectivity (Martin *et al.*, 2004b; Schultz *et al*., 2003). Quantitative analysis of perfluoroalkylsulfonate anions in water has been accomplished by direct injection MS, without prior chromatographic separation (Hebert *et al.*, 2002). Direct injection MS is less expensive and time consuming than LC-MS/MS and could offer an interesting alternative for samples that do not cause interfering matrix effects.

A.3. Objectives

The objective of this study is to conduct a preliminary evaluation of the significance of PFCs in discharges from municipal wastewater treatment plants by: *1)* developing analytical methods for the detection and quantification of PFCs in wastewater treatment sludge; *2)* assessing PFCs levels in sludge samples obtained from selected municipal wastewater treatment plants; and *3)* evaluating the importance of biosorption processes on the fate of fluorinated compounds during biological wastewater treatment.

B. Methodology

B.1 Chemicals

Perfluorooctane sulfonic acid potassium salt, PFOS (98%), was purchased from SynQuest Laboratories (Alachua, FL). Perfluorobutane sulfonic acid potassium salt or PFBS (98.2%) was kindly provided by the 3M Company (St. Paul, MN). Sodium perfluoro-1-hexane sulfonate, PFHXs (98%), sodium perfluoro-1-decanosulfonate, PFDS (98%) and perfluoro-n-decanoic acid, PFDA (98%) were obtained from Wellington Laboratories (Ontario, Canada). Perfluorooctanoic acid, PFOA (96%) and sodium fluoride (99%) were obtained from Sigma-Aldrich (St. Louis, MO). Solid phase extraction (SPE) cartridges, 3ml, 500 mg ODS-C18 were supplied by Agilent Technologies (New Castle, DE). Methanol (HPLC grade) was purchased from Burdikc & Jackson (Muskegon, MI). Acetic acid, glacial (ACS grade) was obtained from EMD chemicals (Gibbstown, NJ). Sulfuric acid (95-98% ACS grade) was purchased from Sigma-Aldrich (St. Louis, MO), acetonitrile (99.8 % HPLC grade) and boric acid (99.5%, ACS grade) were obtained from Mallinckrodt Chemicals (Phillipsburg, NJ). All chemicals were used as received.

B.2. Analytical Methods

*C.2.1. Suppressed conductivity ion chromatography quantification***.** PFOS and related compounds in aqueous samples were analyzed by ionh chromatography with suppressed conductivity detection (Dionex ICS-3000 system). The chromatograph was equipped with an autosampler (injection volume 5 µl), a pump, a degasser, a guard column and a separation column (Acclaim Polar Advantage II, C18, 4.6mm i.d., 25 cm length) operating at 35ºC. A mixture of 20 mM boric acid (pH 8.0) and 95% acetonitrile was used as the mobile phase at a flow rate of 1ml/min. The ratio of boric acid to acetonitrile varied with linear gradient program 0 min: 75:25 v/v to 13.2 min: 45:55 v/v. Blanks were continuously run to assure that the column was clean and that traces of the analyte were not carried over between samples.

The total concentration of perfluorinated compounds in aqueous samples was obtained by linear calibration curves ($r^2 > 0.99$) using known concentrations of PFOS ranging from 0–150 mg/l. The detection limit of PFOS was 0.5 mg/l.

C.2.2. LC-MS/MS: Mass spectrometry analysis was conducted by a method described by Higgins *et al.* (2005). LC-MS/MS measurements were performed on a Magic 2002 (Michrom Biosciences, Inc.) ThermoFisher (Finnigan) LCQ Classic HPLC-MS system. Chromatographic separation was conducted on a MagicMS C18 micobore column (5 µm, 200A, 1x150 mm). Two solutions were used as a mobile phase: (A) buffer (10mM NH_4OAc in H_2O) and (B) methanol. A gradient program with 5% B to 90% B in 35 min was used to elute the components of the samples with a flow rate of 50 µl/min, temperature 40ºC and injection volume 25 µl. Negative ionization was employed to detect fluorinated sulfonates and carboxylates. Selected ion monitoring (SIM) was used to improve detection limit for the perfluorinated compounds. Standard solutions were run first to determine peak intensity ratios for the selected ions (m/z 399, 413, 499, 513, and 599). A m/z window of +/- 3 around the selected m/z value was used in the SIM experiments. Tandem MS/MS was also applied to get structural information on selected ions (e.g., on m/z 499, $CF_3(CF_2)_7SO_3^-$). He was used as a collision gas and a 35% relative collision energy was applied in the MS/MS experiments. MS/MS spectra were recorded within a mass range of m/z 75-1000 using a scan time of 0.2 s. Blanks samples were used to monitor instrument background and were continuously run after three sludge samples.

Blanks samples were used to monitor instrument background and were continuously run after three sludge samples.

B.3 Sewage sludge extractions

Sludge extractions were conducted according to the method described by Higgins *et al.* (2005). Anaerobically digested sewage sludge (ADS) from two different municipal wastewater treatment plants in Tucson, Arizona (Ina Road and and Roger Road treatment plants), were evaluated in this study. ADS samples were dried in an oven at 70ºC overnight and air-dried for 1 day. Samples were ground and homogenized using a mortar and pestle. Homogenized sludge (100 mg) was transferred to a Nalgene bottle and 7.5 ml of 1% acetic acid solution was added. Each sample was vortexed for 10 min and sonicated for 30 min at 60ºC. Following sonication, samples were centrifuged (10,000 rpm, 25 min) and the wash was decanted in a second Nalgene flask. A volume of 1.7 ml of a methanol/1% acetic acid (90/10, v/v) solution was added to the original vial to extract PFCs. Before centrifugation, samples were vortexed for 10 min and then sonicated for 30 min at 60ºC. The extract was decanted in a third Nalgene flask. This procedure was conducted two more times and all washes and extracts were combined. Ina Road ADS was also extracted using a modified procedure. Briefly, 75 ml of 1% acetic acid solution was added to 6,000 mg of homogenized air-dried sludge followed by 20 ml methanol/1% acetic acid (90/10, v/v) extraction mixture. All wash and extract vials were centrifuged (10,000 rpm, 25 min) to avoid clogging of the SPE column. Each sludge sample was extracted and analyzed in triplicate.

B.4 Sample cleanup

Solid phase extraction (SPE) was conducted to preconcentrate and cleanup wash and extract samples. SPE cartridges (3 ml, 500 mg ODS-C18, Agilent Technologies, DE) mounted on a vacuum manifold were conditioned with 6 ml MeOH, followed by 6 ml of 1% acetic acid solution. The desired volume of wash or extract was loaded at 1 ml/min. SPE cartridges were rinsed with 4 ml of deionized water and then centrifuged (4,000 rpm, 25 min) prior elution. Analytes were eluted with 4 ml methanol and collected in clean Nalgene flasks. The eluent was concentrated 8-fold under N_2. In the second extraction when significant amounts of Ina Road ADS were employed, the sample was loaded in 3 different columns and each column was washed with 20 ml of deionized water. All eluents were combined and finally concentrated 10-30-fold under N_2. The extracts were stored at 4°C. Prior to analysis, the samples were diluted 10-fold to reduce matrix interferences and bring concentration in the right LC-MS/MS ranges.

B.5 Quantification

Selected ion monitoring (SIM) was employed to enhance sensitivity during quantification. Standards of the perfluorinated compounds were run in parallel to validate the analysis. Since chemical characteristics influence the ionization process, PFDS was used as an internal standard for PFOS. The latter compounds belong to the perfluoroalkyl sulfonate family and chemically are very similar.

Samples were spiked with a known concentration of the internal standard, PFDS, 0.5 mg/l. Peaks were averaged and the areas were calculated by multiplying the height by the peak width at the half-height. Quantification was possible by relating the area of the PFOS peak to the area of the internal standard. The ratio of areas of PFOS and PFDS in an equimolar standard solution was employed to correct for the differences in response factors of the compounds. The precision of the method was determined by analyzing sludge samples in triplicate and calculating the standard deviation.

B.6 Biosorption assays

Sorption assays were conducted to study the partitioning of PFOS between the aqueous phase and sludge obtained from municipal WWTPs. Three different types of wastewater treatment sludge were employed in this study, anaerobic granular sludge, aerobic activated sludge (RAS) and anaerobically digested sewage sludge (ADS). The anaerobic granular sludge was obtained from an industrial anaerobic reactor treating wastewater from recycle paper manufacturing (Eerbeek, The Netherlands). The samples of RAS and ADS were obtained from the Ina Road municipal WWTP in Tucson, Arizona.

Sorption isotherm experiments were performed in duplicate using Nalgene flasks supplied with aqueous samples containing known concentrations of PFOS (0 to 100 mg/l) in 3 mM phosphate buffer (pH 7.2). In the case of the anaerobic granular sludge, each flask received 100 ml of solution and an amount of sludge that ranged from 0 to 1 gram. For the RAS and ADS samples, the amount of sludge added varied from 0 to 50 ml and the solution volume ranged from 50 to 140 ml. Flasks were shaken in an orbital shaker at 150 rpm overnight at 30ºC. Control flasks in which no sludge was added were run in parallel to correct for possible removal of PFOS by other mechanisms than biosorption. Removal of PFOS from solution was determined using suppressed conductivity ion chromatography following centrifugation and filtration of the samples to remove insoluble matter.

The adsorptive capacity of the various wastewater treatment sludge samples over a range of different concentrations was determined by fitting the sorption results to Langmuir and Freundlich models.

The Langmuir isotherm is defined by:

$$C_s = \frac{a \cdot b \cdot C_e}{1 + b \cdot C_e}$$

where C_s is the concentration of the solute in the solid phase (mg PFOS/g sludge organic matter), C_e is the equilibrium concentration of the solute in solution (mg PFOS/l), a and b are Langmuir adsorption constants; a represents the maximum achievable surface concentration of the solute and b is the equilibrium constant for the sorption reaction.

The Freundlich isotherm is defined by:

$$C_s = K_F \cdot C_e{}^{n}$$

where K_F is the Freundlich adsorption constant or capacity factor and n is the Freundlich exponent. When n =1, the isotherm is linear; when n < 1, the isotherm is concave downward and when $n > 1$, the isotherm is convex upward.

C. Principal Findings and Significance

C.1. Analytical methods for the detection and quantification of PFOS and related compounds

Analytical methods relying on HPLC with suppressed conductivity detection and LC-MS/MS have been successfully developed to monitor PFOS and related compounds in aqueous and solid environmental matrices. The results and discussion will be presented below.

C.1.1. PFC quantification by ion chromatography. An analytical method that relies on suppressed-conductivity ion chromatography has been developed to separate and detect aqueous PFOS and related perfluoroalkyl compounds. Figure 2 shows a chromatogram obtained for a sample containing 12.5 mg/l PFOS. Well resolved peaks and reproducible results were achieved by this chromatography method. The peak at 15.60 min is assigned to PFOS anion and the two little peaks eluting before the major peak at 14.91 min and 15.15 min correspond to PFOS impurities. These impurities have been identified elsewhere as structural isomers of PFOS which are compounds that have the same molecular weight as PFOS but are branched perfluoroalkyl sulfonates (Langlois and Oehme, 2006), by-products with geminal diperfluoromethyl groups and perfluoromethyl substituted compounds (Longanathan *et al.*, 2006).

The quantitative determination of low-ppm concentration of aqueous PFOS was effectively conducted by HPLC suppressed-conductivity ion chromatography as described in the *Materials and Methods* section. A calibration curve for PFOS in aqueous samples is shown in Figure 3. Linear calibration ranges of 0.5 to 100 mg/l PFOS were obtained. The detection limit was 0.5 mg/l PFOS. These results are consistent with those obtained by Hori *et al* (2004) utilizing a different HPLC method in which linear response up to 100 mg/l PFOS and detection limit of 0.66 mg/l PFOS were reported (Langlois and Oehme, 2006).

The use of a reverse-phase C18 column provided good resolution of perfluorinated alkyl substances. A mixture of PFBS, PFOA and PFOS in a 1:1:1 molar ratio was successfully separated as shown in Figure 4. Standard samples of each fluorinated compound studied were run in parallel to identify the retention times of the various compounds. The peaks eluted based on number of carbons and molecular weight. PFBS, a 4-carbon compound with a molecular weight of 299.1 g/mol, appeared first followed by PFOA, a 8-carbon compound with a molecular weight of 414.1 g/mol, and finally PFOS, a 8-carbon compound with a molecular weight of 499.1 g/mol. The response factors of these perfluorinated compounds were significantly different, namely, 0.099, 0.064, and 0.034, for PFBS, PFOA and PFOS, respectively. The response factor was calculated by dividing the area of analyte by the concentration of the analyte.

Ion chromatography is a simple, rapid and efficient method for the separation and detection of perfluorinated compounds. This technique is less expensive than LC-MS/MS and could be commonly applied for monitoring low-ppm amounts of ionic perfluorinated compounds on a routine basis in aqueous solutions. An inherent limitation of the technique is its inability to detected non-ionic compounds.

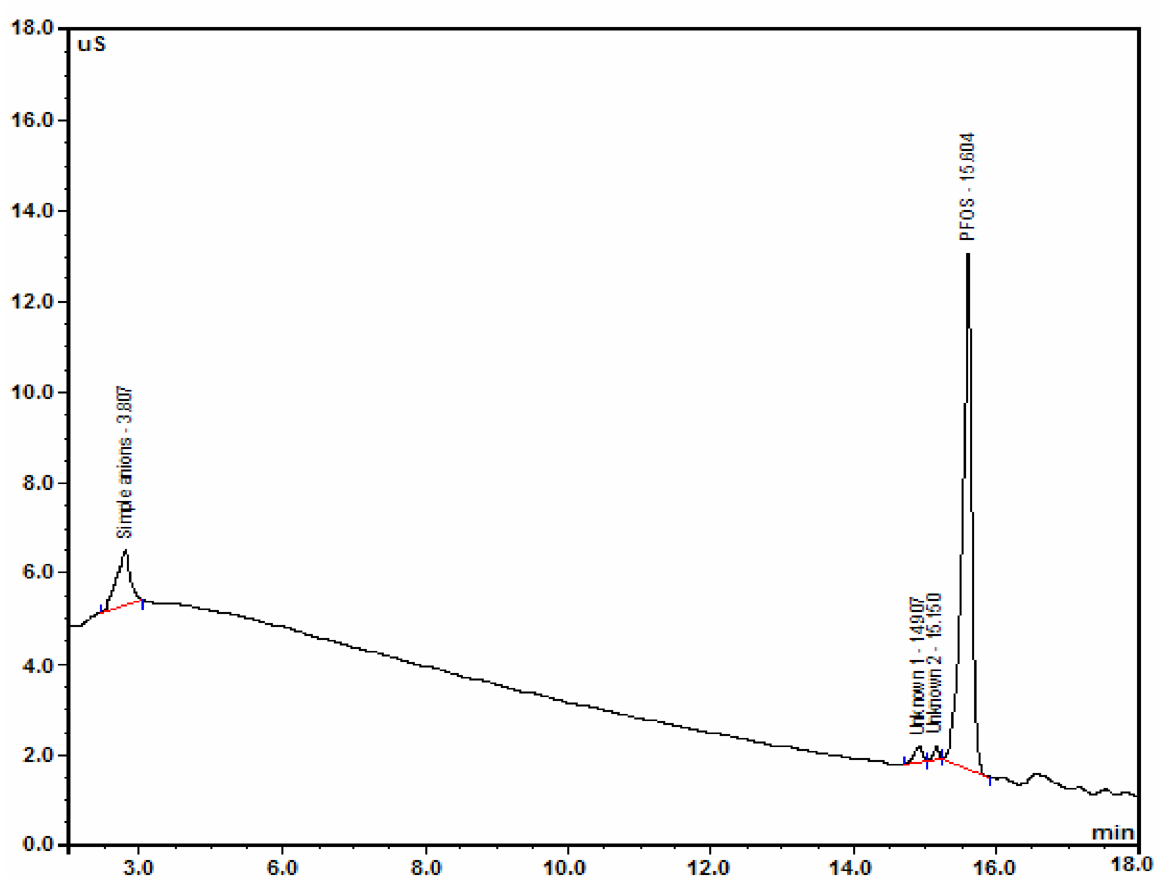

Fig. 2. Detection of aqueous perfluorooctane sulfonate (PFOS) using HPLC-suppressed conductivity ion chromatography.

C.1.2. HPLC with electrospray tandem mass spectrometry. A method based on reverse-phased high-performance liquid chromatography with negative electrospray tandem mass spectrometry (LC-MS/MS) described by Higgins *et al* (2005) was employed to detect PFCs in aqueous and solid environmental matrices. Figure 5 shows a chromatogram obtained for a mixed standard solution containing 5 mg/l of PFHXs, PFOA, PFOS, PFDA and PFDS in methanol. The MS/MS spectra of the same mixed standard solution are shown in Figure 6.

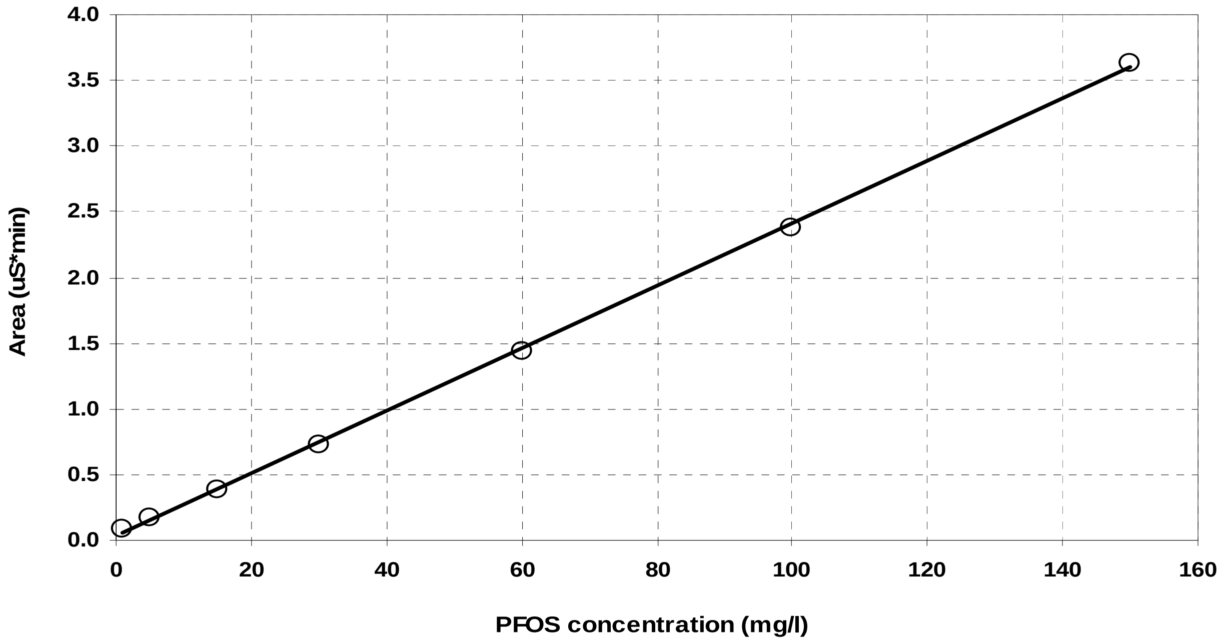

Fig. 3. Calibration curve of aqueous PFOS by HPLC suppressed-conductivity ion chromatography.

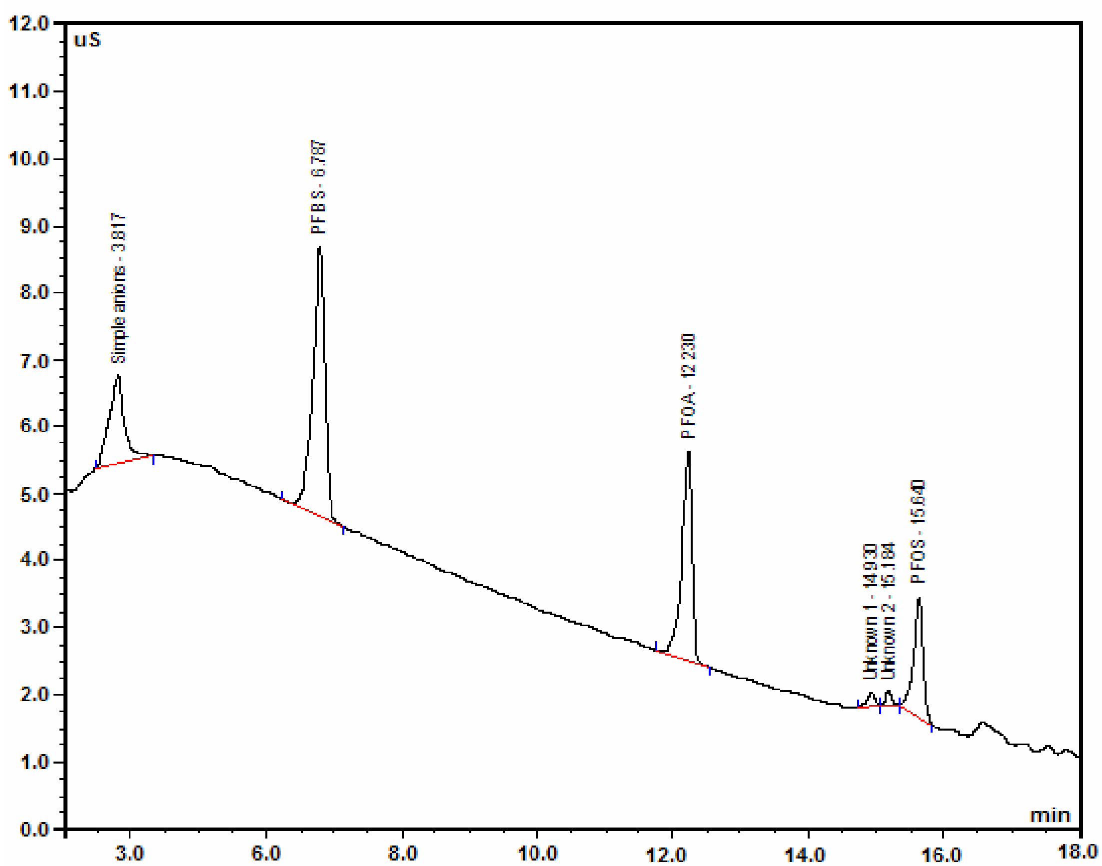

Fig. 4. HPLC-suppressed conductivity ion chromatograph of a solution containing PFBS, PFOA and PFOS.

As expected for a reverse-phased C18 column, perfluorinated chemicals were separated based on the perfluoroalkyl chain length. Distinct peaks are evident for the mixed standard solution of the perfluorinated chemicals (Figure 5). PFHXs (C_6, 399.10 g/mol) eluted first, followed by PFOA (C_8, 413 g/mol), PFOS (C_8 499.12 g/mol), PFDA (C_{10}, 514.09 g/mol) and last PFDS (C_{10} 599.13 g/mol). The response factor of perfluorinated compounds was calculated by dividing the peak area by the concentration of the analyte. The response factor of PFHXs, PFOA, PFOS, PFDA and PFDS were calculated to be 15, 21, 32, 14 and 14, respectively. The response factors of perfluorinated sulfonates and carboxylates with chain lengths of 6 and 10 carbons were the same. However, in the case of PFOA and PFOS (8-carbon chain), these values were higher and significantly different among compounds and within their families. The detection limits of the PFCs chemicals evaluated in this study differ among compounds. The estimated detection limit based on a signal-to-noise ratio of 3 was calculated to be 0.05 mg/l for PFOS, PFDA and PFDS as compared to 0.2 mg/l in the case of PFHXs and PFOA.

LC-MS/MS is a valuable technique to analyze PFCs chemicals in aqueous and solid environmental samples. The precision, accuracy and high sensitivity of the technique make this method ideal for the quantitative determination of PFCs in low-ppb levels (μg/l range). However, ionization suppression effects and matrix interferences such as coelution of other chemicals present in the samples can compromise the quantitative analysis of environmental samples, sewage sludge.

C.2. Assessment of PFCs levels in wastewater treatment sludge

The presence of perfluorinated chemicals in anaerobically digested sewage sludge (ADS) in two different municipal wastewater treatment plants from Tucson, Arizona was evaluated in this study. LC-MS/MS quantification of PFCs in sewage sludge was performed according to the protocol described in the *Materials and Methods* section. Briefly, an acid wash-solvent extraction cycle followed by a SPE sample cleanup and concentration procedure were conducted to assess the levels of PFCs in municipal sludge. Two extractions were carried out, the first one employing 100 mg and a second one using 6,000 mg of dried sewage sludge. In both cases, the wash and the extract were analyzed. In the first extraction, no PFCs were detected, either in the wash or in the extract of ADS from the Ina Road and Roger Road treatment plants, suggesting that the compounds were not present or their concentrations were lower than the detection limits. In the second extraction using 6,000 mg of Ina Road ADS, PFOS was measured in the extract, but PFCs were not detected in the wash. The analytical results obtained in the second extraction are presented below in more detail.

Higgins and collaborators reported that high-molecular weight perfluorinated compounds (> 499 g/mol) are the predominant compounds detected in municipal sewage sludge (Higgins *et al.,* 2005) . PFOS, PFDS, FOSAA (perfluorooctanesulfonamidoacetate), *N*-MeFOSAA (2-(N-methyl-perfluorooctanesulfonamido) acetate), *N*-EtFOSAA (2-(N-ethylperfluoro-octane-sulfonamido) acetate) and PFDA were detected in WWTP discharges in San Francisco Bay Area (Higgins *et al.,* 2005) at concentrations ranging from 176 to 3,390 ng/g. Based on this report, selected ion monitoring (SIM) was employed to analyze PFHXs, PFOA, PFOS, PFDA, *N*-MeFOSAA, *N*-EtFOSSA and PFDS in the extract obtained following extraction of sewage sludge.

Figure 7 shows a LC-MS chromatogram and MS/MS spectrum obtained under SIM analysis of an extract sample spiked with 0.5 mg PFDS/l. PFOS was the only perfluorinated compound detected under the experimental conditions evaluated in this study. PFOS concentration in Ina Road ADS was 77 $\pm$ 5 ng/g sludge dwt. The levels of PFOS determined here are within the range of those determined in related studies around the country (3M, 2001; Loganathan *et al.*, 2006). PFOS appears to be the dominant PFC in sewage sludge samples. Data collected by 3M in 2001 indicated that PFOS concentrations in municipal sludge from Alabama, Tennessee, Georgia and Florida exceed PFOA and FOSA (perfluorooctanesulfonamide) concentrations by one order of magnitude (3M, 2001). In sewage sludge samples from Kentucky, PFOS concentrations were 2 to 5-fold higher than those of PFOA (Loganathan *et al.,* 2006). These results are also consistent with previous work on the presence of perfluorinated chemicals in the environment. In wildlife samples throughout the world, PFOS was the only compound detected (Giesy and Kanan, 2001; 2002; Martin *et al.,* 2004a). PFOS concentrations in human sera samples from a global study were 2-fold greater than those of PFOA and about one order of magnitude higher than PFHXs concentrations (Kannan *et al.,* 2004).

Unlike the results reported by Higgins *et al* (2005), PFOS was the only compound detected in the sewage sludge samples analyzed in this study. This could be attributed to several aspects, inefficient extraction recoveries, inadequate retention or elution times during SPE cleanup, instrument limitations and most likely matrix-derived analyte signal suppression effects (Ferguson *et al.*, 2000; Higgins *et al.*, 2005). In electrospray LC-MS/MS the intensity of an analyte ion signal is a function of both the concentration of the analyte and the total ions present in solution. In heterogeneous matrices such as sewage sludge, the variability and amount of organic matter present can result into suppression effects of the analyte signal (Ferguson *et al.,* 2000). In fact, in the extraction with 6 g of sludge, linear alkylbenzene sulfonates surfactants co-eluted with high molecular weight PFCs (*N*-MeFOSAA, *N*-EtFOSAA and PFDS) in significant concentrations (Figure 7). Therefore, it could be possible that these perfluorinated chemicals might be present however due the matrix interferences they cannot be detected.

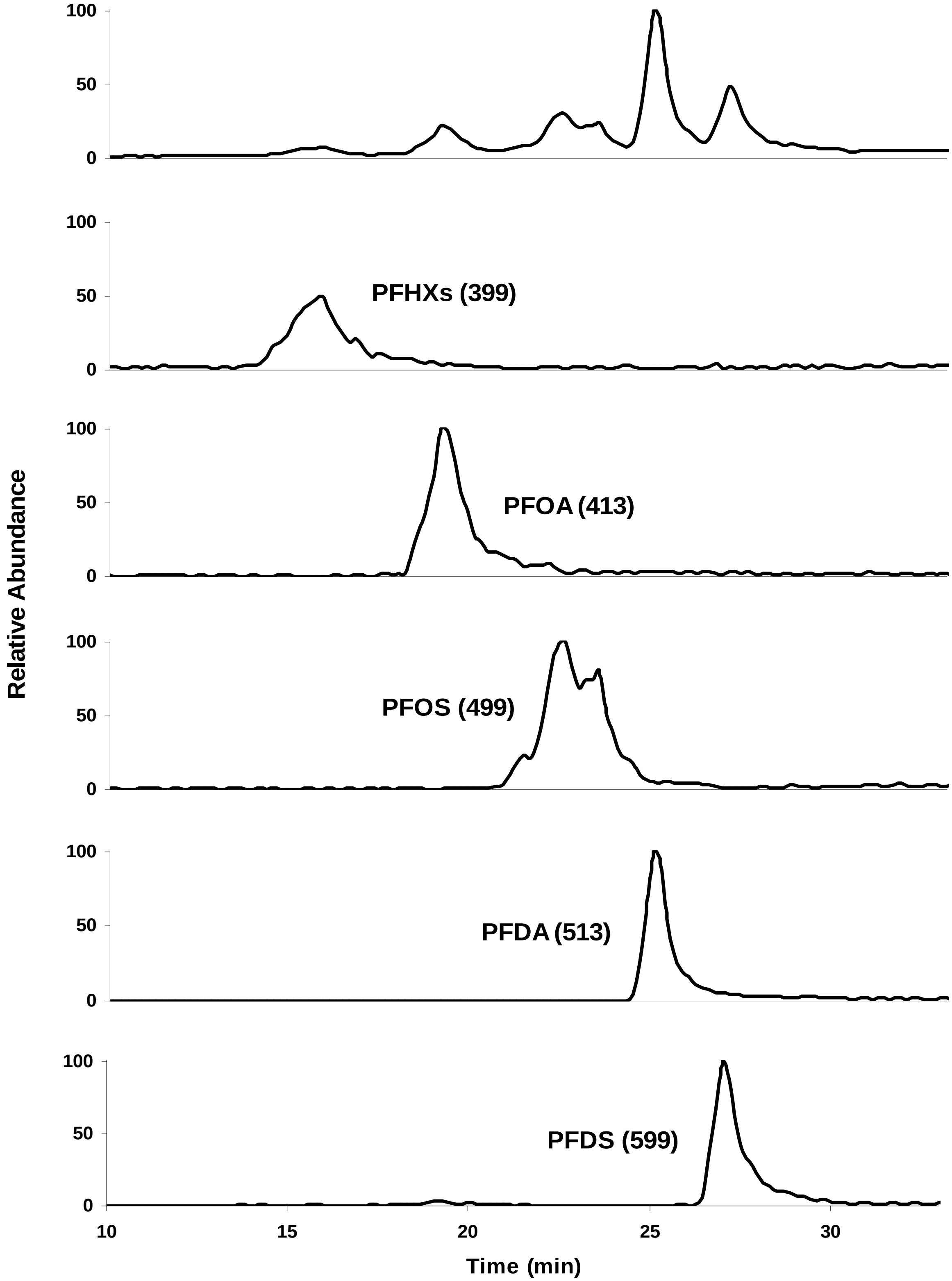

Fig. 5. LC-MS chromatogram of a mixed standard solution containing 5 ppm of PFHXs, PFOA, PFOS, PFDA and PFDS.

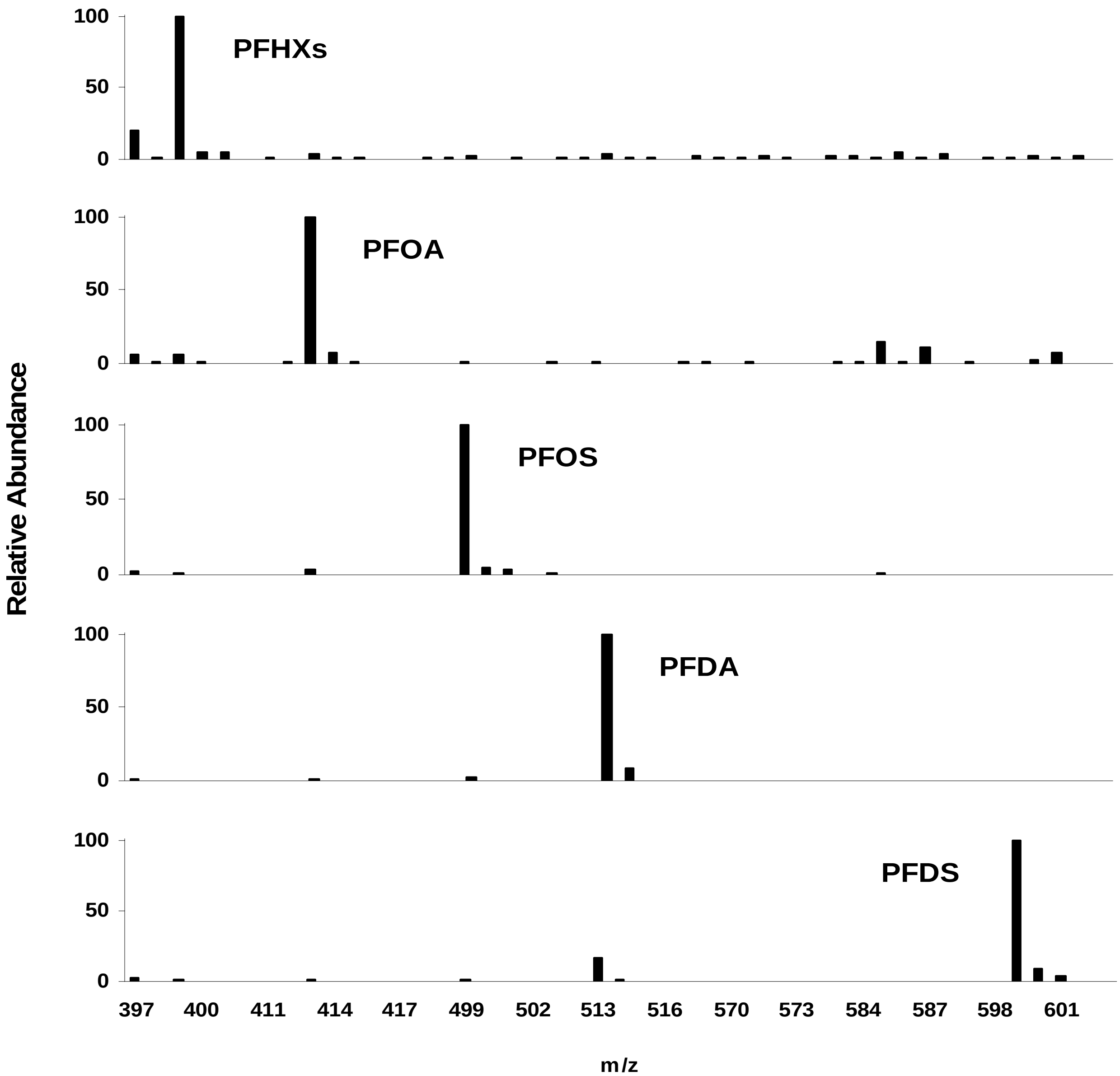

Fig. 6. Negative ESI/MS spectra of a mixed standard solution containing 5 mg/l of PFHXs, PFOA, PFOS, PFDA and PFDS obtained under SIM analysis.

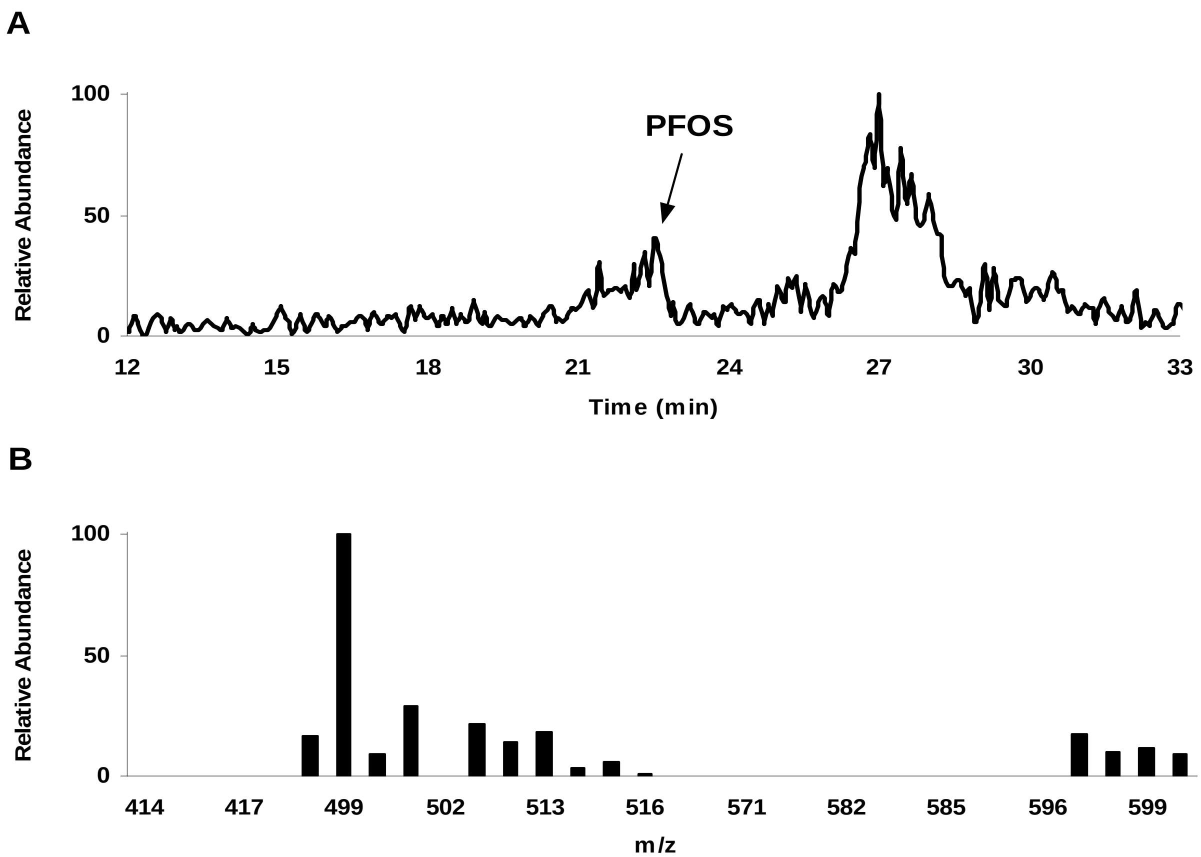

Fig. 7. SIM analysis of a sewage sludge sample in Ina Road WWTP from Tucson, Arizona. A) Typical LC-MS chromatogram and B) MS/MS spectrum of extract sludge sample spiked with 0.5 mg/l of PFDS.

C.3 Adsorption of PFOS onto wastewater treatment sludge

The sorption of PFOS from aqueous solutions onto wastewater treatment sludge was examined in batch experiments at 30ºC and pH 7.2 under well defined conditions according to the protocol described in *Materials and Methods* section. Three different types of sludge obtained from industrial wastewater treatments plants, anaerobic granular sludge, aerobic activated sludge (RAS) and anaerobically digested sewage sludge (ADS) were evaluated in this study. The adsorption isotherms obtained for the various sludge tested are shown in Figure 8.

The experimental isotherms obtained show the concentration of PFOS sorbed to the wastewater treatment sludge (C_s, expressed as mg PFOS per gram sludge organic matter) as a function of the equilibrium concentration of the contaminant in solution ($C_{e,}$ in mg PFOS/l). The organic matter content in the sludge was measured as volatile suspended solids (VSS). The VSS content of the anaerobic granular sludge, RAS sludge and ADS were 13.7%, 1.0% and 11.8% based on the weight if the wet sludge, respectively. The isotherms were fit to the Freundlich and Langmuir models (Table 1).

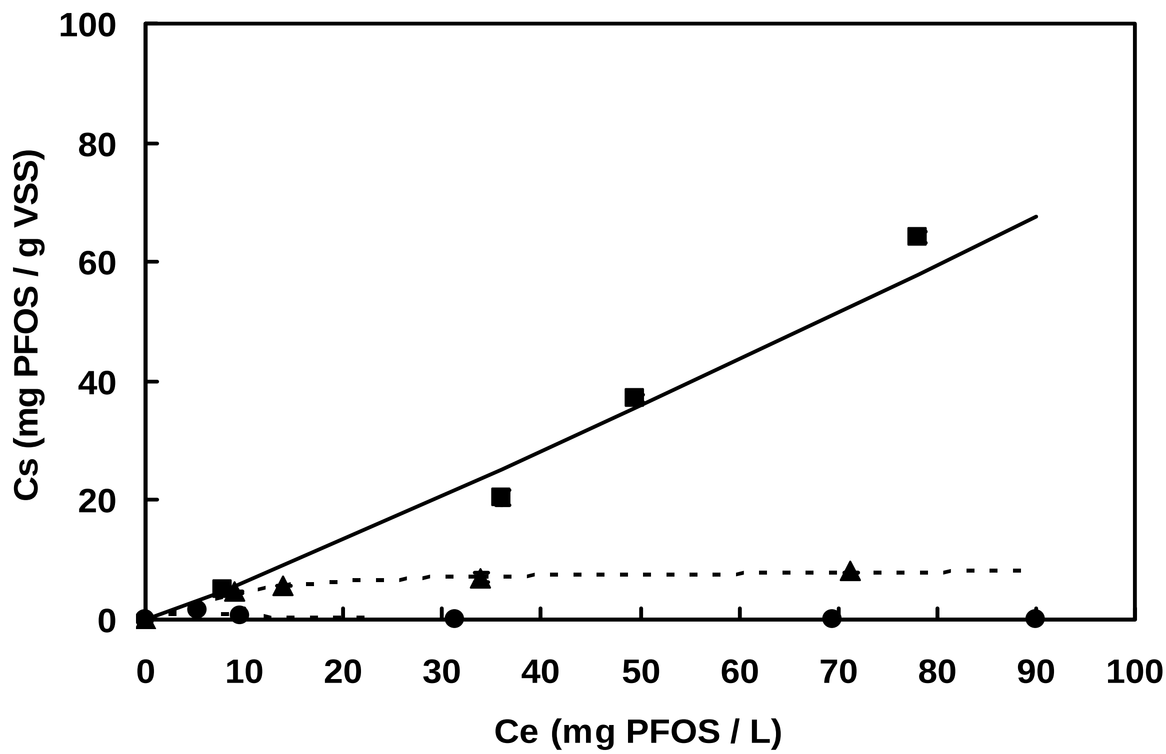

Fig. 8. Adsorption isotherms of PFOS onto wastewater treatment sludge. Legend: (■) anaerobic granular sludge, (▲) anaerobic digested sludge (●) activated sludge; (dashed line) experimental data fit to Langmuir model; (solid line) experimental data fit to Freundlich model.

The ADS data fit best to a Langmuir isotherm, whereas the granular anaerobic sludge data fit a linear Freundlich isotherm.

The removal of PFOS by ADS is poor compared to removal by anaerobic granular sludge. Although, at treated effluent concentrations lower than 9 mg PFOS/l, the affinities of ADS sludge and anaerobic granular sludge for PFOS are comparable. The former sludge is estimated to become saturated when the equilibrium concentration of PFOS in the aqueous phase is higher than 14 mg/l, whereas anaerobic granular sludge shows a linear correlation between the sorbed PFOS concentration and all studied equilibrium concentrations in solution

PFOS adsorbed significantly to anaerobic granular sludge, poorly to ADS sludge and it did not adsorb to RAS. Similar adsorptive behavior should be expected for ADS and anaerobic granular sludge, which showed comparable VSS content, if partitioning of PFOS onto the biomass was only governed by the amount of organic matter in the sludge. The very different adsorptive capacities determined suggest that characteristics other than organic matter content must contribute to controlling sorption of the perfluoroalkyl sulfonate to wastewater treatment sludge. Given the dual lipophilic-hydrophobic nature of PFOS, it is unlikely that they obey simple hydrophobic partitioning paradigms. In humans, PFOS and related PFCs appear to associate with proteins rather than lipid moieties (Jones *et al*., 2003).

Table 1. Langmuir isotherm constants a (mg PFOS/g sludge-VSS) and b (l/mg PFOS) and Freundlich isotherm constants K_F [(mg PFOS/g sludge-VSS)(mg PFOS/l)$^{-n}$] and n for the adsorption of PFOS from aqueous solutions onto wastewater treatment sludge.

	Langmuir isotherm				Freundlich isotherm		
Sludge	*a*	*b*	**r2**		*Kf*	*n*	**r2**
Anaerobic granular sludge	-181.7	-0.003	0.430		0.5	1.080	0.983
ADS sludge	9.0	0.115	1.000		2.7	0.262	0.930

ACKNOWLEDGEMENTS

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An Investigation in the Upper Santa Cruz River 2005 Riparian Vegetation Die-off

Basic Information

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Focus Category:	Wetlands, Surface Water, Drought
Descriptors:	
Principal Investigators:	Barron J. Orr

Publication

A. Problem and Research Objectives

The overall objective of this research project was to conduct a preliminary investigation into the potential causes, observed consequences, and management implications of a sudden and widespread mortality of woody riparian and bosque vegetation along a 16-km stretch of the Upper Santa Cruz River in southeastern Arizona. Our proposed objectives were to document the spatial and temporal context within which the die-off occurred and assess strong candidate causes associated with water quality and tree pathology. Given the nature and significance of this problem, we anticipated that this preliminary investigation will provide the foundation for a larger, interdisciplinary research initiative addressing the dynamics of coupled natural and human systems within the context of riparian ecosystems and riparian ecohydrology.

Key Findings

Our research suggests that the Upper Santa Cruz River tree mortality occurred in response to a combination of individual stressors, primarily decreased levels of groundwater, reduced infiltration from streamflow and flood events due to a five year drought, and the formation of an impervious streambed clogging layer from increasingly high nutrient levels in effluent discharged from the Nogales International Wastewater Treatment Plan (NIWTP). Each of these individual impacts converged in the Rio Rico sub-basin of the Santa Cruz Active Management Area due to the unique hydrogeology and streambed dynamics along that stretch of the river.

High transmissivity within the Rio Rico sub-basin normally allows for tightly coupled interactions between streamflow and groundwater levels that support both gaining and losing reaches, depending upon the frequency of flood events and groundwater levels. However, drought conditions have greatly impacted precipitation patterns in the region and there were no significant flood events from 2001 through 2005. During this time, groundwater levels dropped precipitously as pumping rates were maintained and mountain front and streambed recharge rates decreased. High nutrient levels in the effluent simultaneously supported the formation and growth of a clogging layer in the stream channel of the Santa Cruz River. Under favorable climate conditions, this clogging layer is routinely scoured by high intensity flood events. However, due to the drought conditions, the clogging layer continued to grow and expand in the absence of floods from 2001-2005 and increasingly prevented infiltration from the stream channel into the groundwater tables and floodplain that supports the riparian forest. Cumulative impacts from the drought and the clogging layer likely combined to cause a threshold event in the riparian forest along the Rio Rico sub-basin of the Upper Santa Cruz River. Within approximately six months, the health of the riparian forest crashed and there was widespread mortality along the length of the Rio Rico sub-basin.

This event highlights a number of future research needs. There are numerous unresolved ecohydrological issues regarding the release of effluent, a third source of water, into ground-water dependent riparian systems. Studies to date have not addressed the role of flooding as a natural disturbance process in these partially unnatural systems. While natural systems are adapted to disturbance and highly resilient during and after floods and droughts, it is not known whether effluent-dominated stream ecosystems exhibit a comparable recovery capacity, or even if disturbance events are important to the functional integrity to the ecohydrological processes of an effluent-dominated riparian ecosystem (Patten et al. 1998). Few if any studies have studied how native riparian vegetation responds to continued inflows of nutrient-rich effluent and the possible associated changes in riparian community composition and structure. No studies have examined this from the perspective of climate variability and the potential for prolonged droughts and rising temperatures to increase freshwater demands, further degrade riparian systems, and potentially increase the number of streams reliant upon effluent to maintain surface flows and associated riparian habitats. Ultimately, a lack of understanding about the dynamics of effluent-dominated streams has created a void in ecological methods and policy responses suitable for evaluating and protecting the ecological integrity of these systems (Brooks et al. 2006).

B. Methodology

Much of the die-off occurred on 35,000 acres of private land within the floodplain of the Upper Santa Cruz River. The majority of that private land is owned by one landowner. We met on at least six occasions with the landowner to discuss this research project and took two field trips with the landowner and associated colleagues into the most severe areas of the die-off prior to June 2006. However, in June 2006 the landowner officially denied us access to the land by sending a letter to the University of Arizona. We initially proposed to conduct water quality and tree pathology tests directly on the riparian floodplain land impacted by the die-off, however since much of our proposed testing sites were on the private land that we could not access, we had to adjust our means of analysis to comply with these restrictions. As a result, we were unable to take water quality and tree pathology samples from the affected areas and we were unable to ground-truth our estimations of the extent and patterns of the die-off. We will discuss our alternate methods of analysis in the narrative that follows.

Landscape Analysis

To delineate the spatial extent and pattern mosaic of the die-off, we developed a map of the affected region showing the degree of mortality throughout the floodplain. Initially we compared a Quickbird satellite image taken on September 1, 2006 with 2004 DOQQ imagery and aerial photographs from the past decade to identify areas of tree mortality that occurred in 2005. However, we found that the resolution of the imagery was not fine enough to delineate the boundaries and varying degrees of mortality along the river. We therefore created a base map of the river and conducted a hilltop visual assessment of the die-off region from the Tumacácori Mountains west of the river and from the San Cayetano Mountains east of the river. To augment this visual assessment, we took an overflight of the river on October 11, 2006 with EcoFlight to conduct an aerial assessment of the die-off region. From these land and air-based vantage points, we were able to visually determine the areas of mortality with some degree of accuracy, despite our inability to groundtruth the maps due to landowner access restrictions (Figure 1).

Plant Pathogens and Insect Infestations

The role of plant pathogens and insect pests in a sudden and widespread mortality of woody plants may indicate cause or consequence, but very little information is available to determine their contribution. We were furthermore limited in our analysis of the potential role of plant pathogens or insect infestations in the die-off due to the land access restrictions. To accommodate this limitation, we were able to make one field visit to the site before June 2006 with three professional plant pathologists from the University of Arizona and the U.S. Forest Service. We conducted on-site investigations of affected cottonwoods (*Populus freemontii*), Goodding willow (*Salix gooddingii*), and Netleaf hackberry (*Celtis reticulata)* trees to determine the presence or absence of insects and/or diseases.

Water Quality

Our water quality analysis was greatly limited by the restrictions on land access and we were unable to take water quality samples from wells in the die-off area as we proposed. To accommodate this restriction, we analyzed readily available water quality monitoring data from the RiverWatch program of Friends of the Santa Cruz River (FOSCR) and from Arizona Department of Environmental Quality (ADEQ). We analyzed the data for water quality trends that may have a bearing on the health, vitality, and composition of the riparian forest.

C. Principal Findings and Significance

Landscape Analysis

The *Upper Santa Cruz River riparian Mortality and Severity Index* map (Figure 1) depicts three levels of mortality:
Low = less than 30% mortality
Medium = 30% - 80% mortality
High = more than 80% mortality

These levels represent not only the degree of mortality within a gradient along the river, but also depict the variable pattern of mortality. From the map, it is apparent that the mortality is highest in the south at Rio Rico Road and tapers off as it extends north to the boundary of Tumacácori National Historical Park. The mortality appears to be distinctly bound on the south and on the north thus suggesting a difference in hydrological and/or ecological conditions in the areas adjacent to the die-off. In addition, the pre-2005 imagery did not indicate that the riparian vegetation was exhibiting usual physical responses to drought or groundwater decline, such as canopy die-back or leaf senescence (Stromberg et al. 1996, Scott et al. 1999, Rood et al. 2000, Shafroth et al. 2000, Amlin and Rood 2002, Shafroth et al. 2002, Rood et al. 2003). This apparent lack of well-documented drought responses exhibited by the Upper Santa Cruz River riparian corridor is both notable and surprising and may indicate a threshold change between alternative riparian conditions, or states, that has yet to be described in published research.

We considered this gradient of mortality in the context of the hydrogeology of the river basin. The Santa Cruz River is a tightly coupled groundwater and surface water system. Small and geologically constrained micro-basins within the younger alluvium form a series of cascading water tables along the Santa Cruz River. These microbasins can be rapidly depleted by groundwater pumping as well as rapidly re-filled during significant storm events. Their dynamic nature can provide some buffer against prolonged drought if at least one yearly storm event continues through a prolonged drought period. However, the dynamic nature of the microbasins can also leave the region vulnerable to depleted water supplies if groundwater pumping and prolonged drought combine to lower groundwater levels.

Observational studies have shown that the Rio Rico Sub-area represents a subsurface reservoir that stores water from storm recharge events, effluent inflows, and subsurface flow (Nelson 2007). High transmissivity within the younger alluvial aquifer along this stretch of the river allows for rapid and highly efficient recharge (Nelson 2007). This can be seen in Figure 2 where there is a tight correlation between flood events and spikes in aquifer recharge. These shallow water tables depend, in part, on regular storm events during the monsoon and winter precipitation seasons for adequate recharge. However, the current drought conditions throughout the Sonoran Desert region have significantly reduced the number and intensity of storm and flood events.

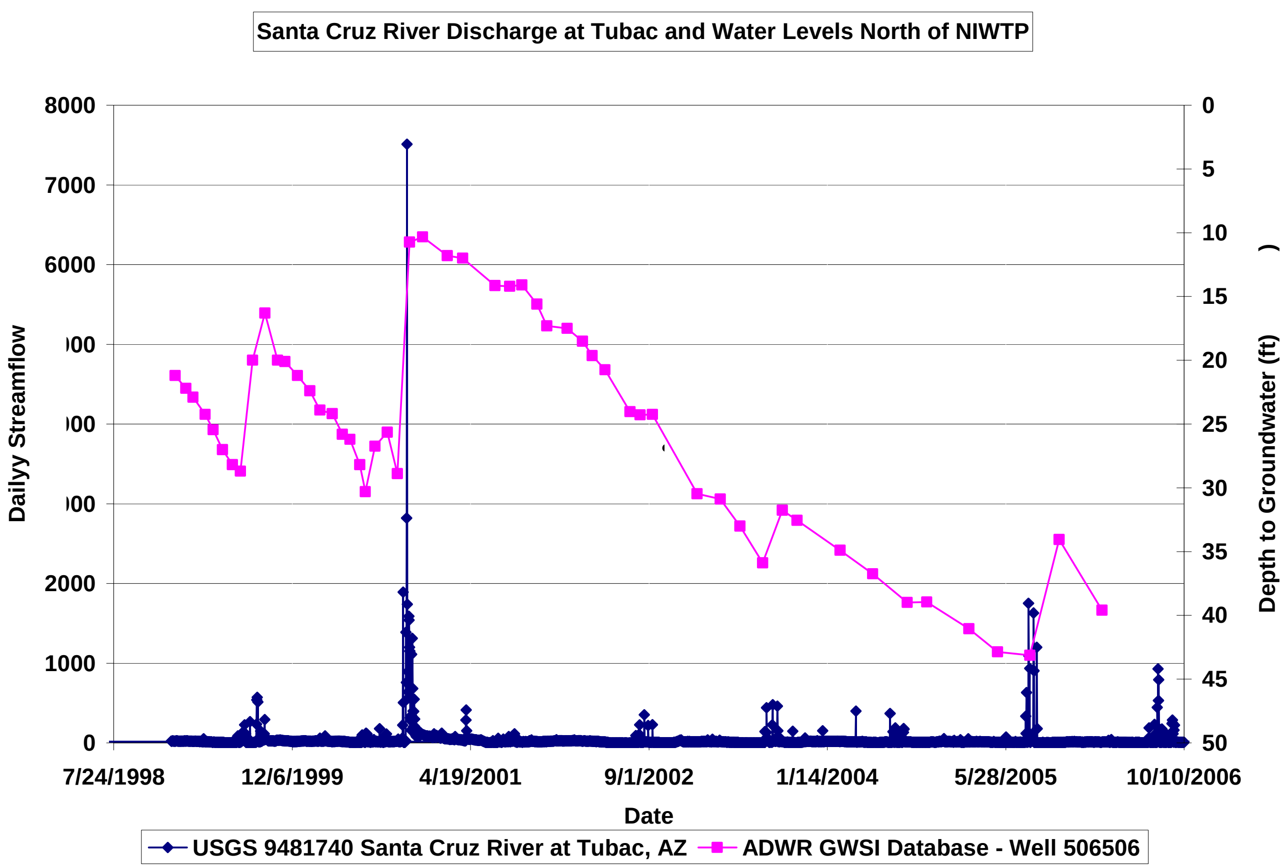

Figure 2. Correlation between streamflow and groundwater levels (Colleen Filippone, unpublished data)

An analysis of recent precipitation trends shows that the drought in this region has been severe. Precipitation at Tumacácori NHP has fallen to approximately 50%-60% below average (Figure 3). In addition, there were no significant flood events between 2001 and 2005 at the Tubac USGS streamflow gauge, as seen in Figure 4. The relationship between the riparian vegetation and the natural flow regime of the river is integral to healthy and functional riparian ecosystems. The Santa Cruz River native riparian forest is dominated by pioneer species (primarily *Populus* and *Salix* spp.) that rely upon physical disturbances such as floods to re-set successional stages (Stromberg 1993). Alterations to the natural hydrologic flow regime result in significant changes to the vegetation composition of the riparian system. Native riparian species that depend upon pulsed and seasonal flooding for seed germination have been shown to have decreased recruitment when flood pulses are eliminated from the system, and as a result are replaced by more opportunistic, and often non-native, species (Nagler et al. 2005). The Santa Cruz River die-off could have been partially triggered by the severity and length of this current drought event.

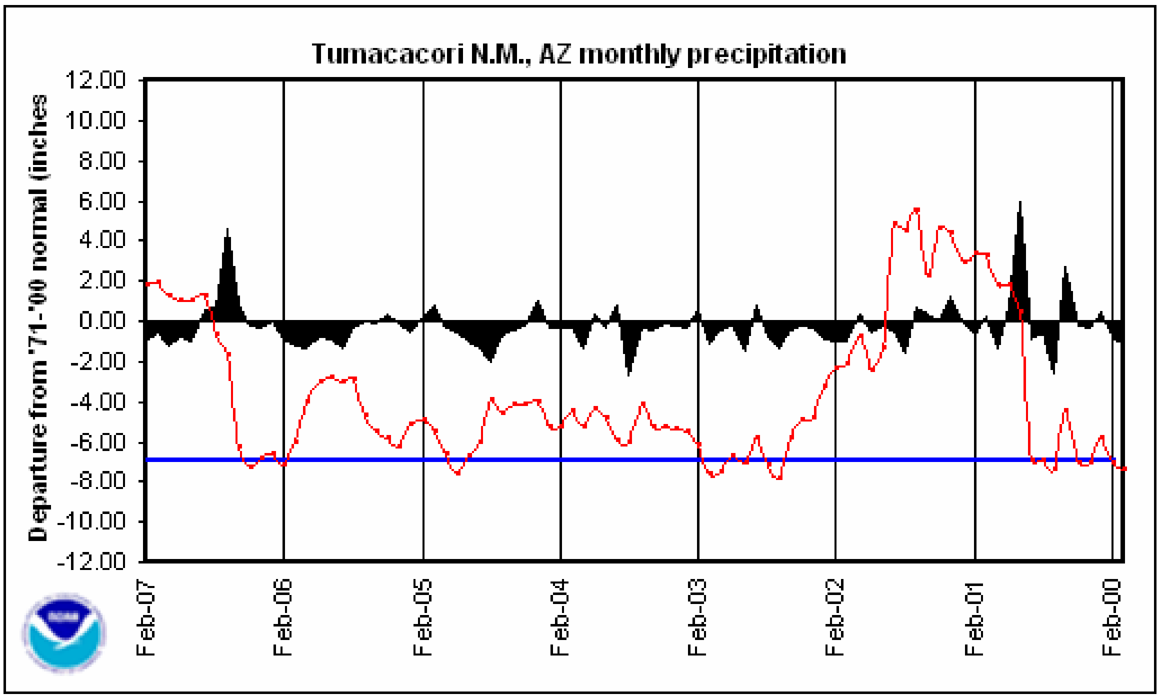

Figure 3. Tumacácori NHP monthly precipitation trends

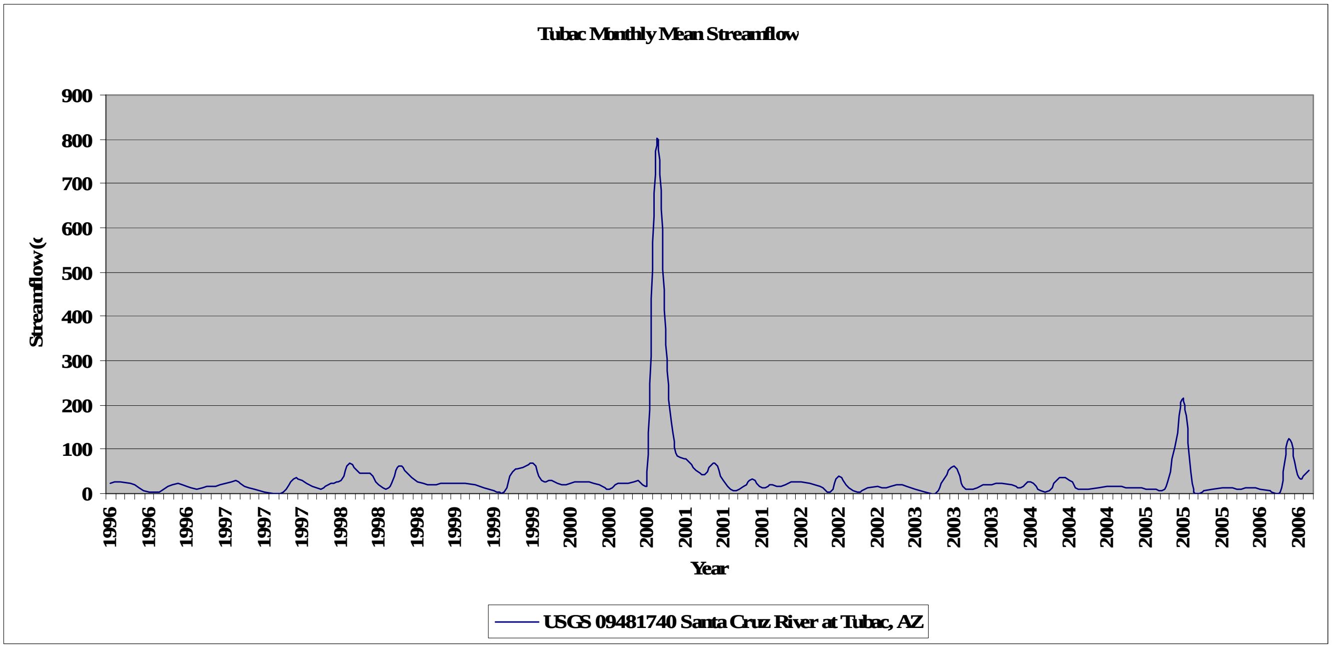

Figure 4. Streamflow at the Tubac USGS gauge

Plant Pathogens and Insect Infestations

Frequently, the activity of pathogens and insects may be an indication of plant health that in turn may be an important part of any equation for dynamic management strategies in riparian ecosystems. Pathogens of plant species common to the Santa Cruz River basin have been described in other habitats (University of Arizona 2006, Streets 1969), and records of wood rotting fungi that cause heart rots of living trees are housed in The University of Arizona's Robert L. Gilberstson Mycological Herbarium. Several pathogens are problematic on cottonwood trees that have been planted in landscapes or reforestation sites (University of Arizona 2006), but none has ever been the single cause of large scale mortality. In our investigation, *Inonotus munzii* was found to be very common in mature living and dead cottonwood trees in the affected area. It is not known if this is a distribution common to unusually stressed areas or whether it is common to healthy areas as well, however it is frequently found in dead or mostly dead trees. As a result, the plant pathologists did not feel that the presence of *Inonotus munzii* was a significant contributing factor to the die-off.

Known insect infestations have historically occurred in the Santa Cruz River riparian corridor and are mostly known through observations by long-time residents. It is possible that an insect infestation has not yet been detected and that such an impact is affecting the area presently, though this is unlikely. We did notice that several dead Netleaf Hackberry's in Calabasas County Park (located about one-mile south of the southern die-off boundary) displayed woodboring insect patterns under the bark. It is currently unknown whether or not these patterns are normal or are an indication of a potentially deadly infestation, however since only 5 hackberries appeared affected in this region we again felt that this was not a major contributing cause of the die-off. The following beetles could be the species found in the hackberries.

- A longhorn beetle *(Anelaphus villosus)* (Figure 5, left photo) occurs westward into Arizona. Longhorn beetle larvae typically leave rounded holes in the wood due to the shape of their heads. However, not all longhorn beetle larvae bore into the wood. They may feed only in the cambium-phloem region lightly scoring the sapwood.
- Hackberry bark beetle (Figure 5, right photo) has been reported as far east as N.M. They feed under the bark producing distinctive horizontal adult galleries & vertical larval galleries best described as a two-sided comb.
- Redheaded ash borer *(Neoclytus acuminatus)* (Figure 5, lower photo) has been reported in Colorado & N.M. on hackberry. Larvae feed almost entirely in the sapwood. More than one generation may occur in warmer climates. Parasitic wasps & predatory beetles are commonly associated with this borer.

Figure 5. Potential wood-boring insects affecting Netleaf Hackberry trees

Water Quality

In the Upper Santa Cruz River, discharges of effluent, or treated wastewater, can augment surface flow in ephemeral or intermittent streams and enhance riparian habitat (Tellman 1992, Marler et al. 2001, Bouwer 2002, Brooks et al. 2006). In addition to providing additional water to riparian systems, effluent is also high in nutrients and supplies additional nitrogen to the river system (Stromberg et al. 1993). In our analysis of the water monitoring data from FOSCR, we found that ammonia levels have been increasing at Rio Rico and Chavez Crossing from 1993-2004, with substantially higher ammonia levels detected at Rio Rico (Figure 6). As a corollary to that increasing trend, nitrogen levels have been increased from 1993-2004, with substantially higher nitrogen levels detected at Chavez Siding reflecting the breakdown process of the ammonia as it moves downstream through the riparian corridor (Figure 7).

In a review of riparian nutrient literature, we found that Marler *et al.* (2001) demonstrated in a controlled environment along several Arizona streams, including the Upper Santa Cruz River, that Fremont cottonwood (*Populus fremontii*), Goodding willow (*Salix gooddingii*), and exotic saltcedar (*Tamarix ramosissima*) increased their shoot:root biomass ratio as nitrogen increased from effluent inflows. In a field experiment, Adair and Binkley (2002) demonstrated that cottonwood germinants were co-limited by both water and nitrogen, indicating that nitrogen may play an important role in riparian vegetation productivity and composition. Therefore, additional inflows of N into the

Upper Santa Cruz River may impact the rate of nutrient cycling as well as contribute to increased phreatophytic growth and abundance.

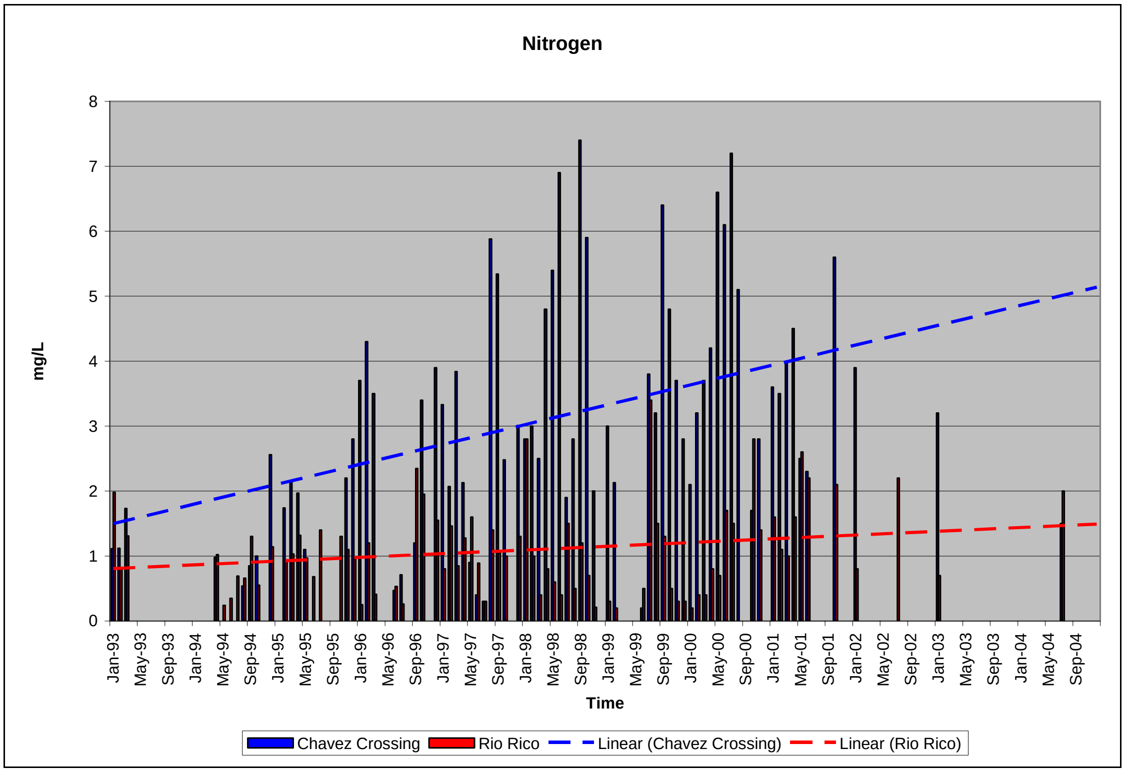

Figure 6. Nitrogen levels at Chavez Crossing and Rio Rico from 1993-2004

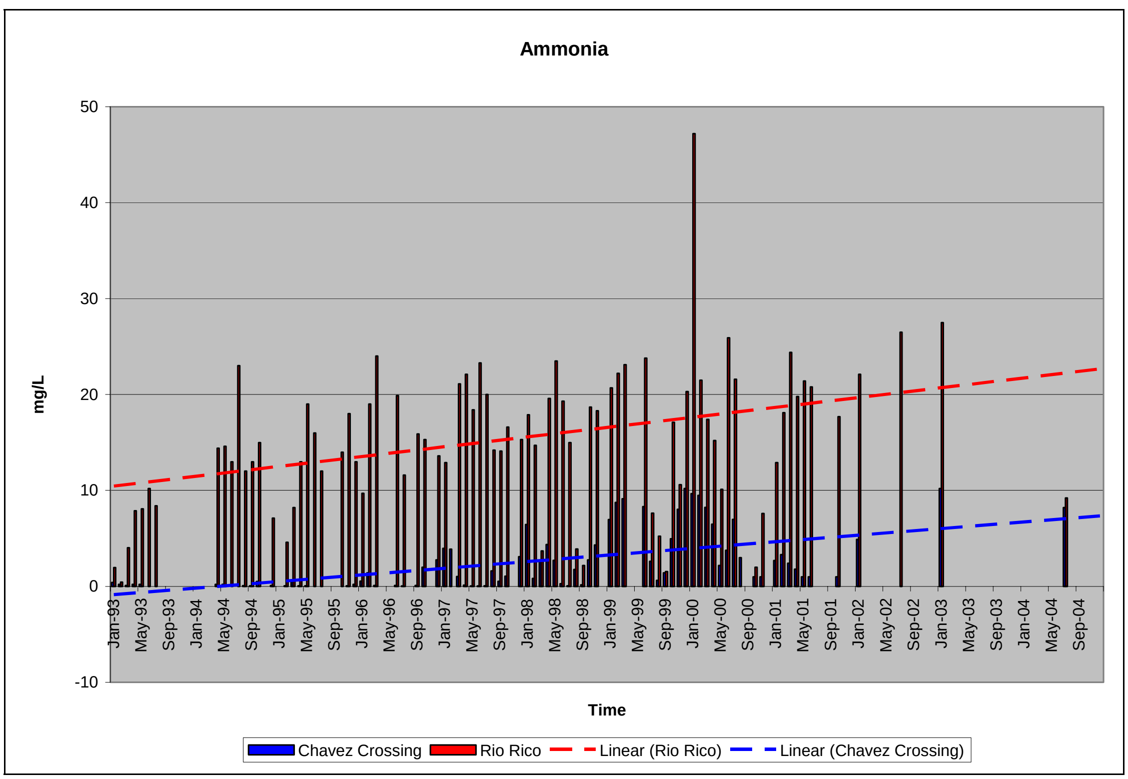

Figure 7. Ammonia levels at Chavez Crossing and Rio Rico from 1993-2004

Early research on nutrient cycling in stream systems predicted that the rate of uptake of essential nutrients is proportional to the rate of organic matter accretion in the system (Vitousek and Reiners 1975). This prediction was made in light of successional vegetation stages that occur after a flood event. During this successional time, early stages will show little uptake, middle stages of high biomass accretion will demonstrate high uptake rates, and later steady-state systems will once again exhibit low uptake as the inputs and outputs of nutrients equilibrate (Figure X) (Vitousek and Reiners 1975, Fisher et al. 1982). While this analysis applies to stream systems that sustain a natural flow regime, it is not known how an effluent-dominated stream system will accommodate consistent nutrient availability or how a constant nutrient supply will impact the successional stages of vegetation or if there are nutrient loading rates above which biotic structure and function are degraded (Stromberg et al. 1993). It is possible that increased amounts of N could "overload" the system by temporarily providing a water and nutrient buffer against drought and supporting an increasingly robust riparian vegetation community until the energy requirements of the system exceed available resources. In this scenario, the system would not have adapted to the drought conditions through the linear and progressive mechanisms usually exhibited, but could instead experience a threshold crash under the weight of its own energy requirements.

This possibility is support by E.P. Odum's theory that explains how systems are impacted by "subsidies", or supplemental additions such as effluent to a certain ecosystem (Odum et al. 1979). While many subsidies may have beneficial results, such as additional nitrogen in a nitrogen-limited system, at some point those additions may allow the system to increase its energy demands beyond what can be sustained by the functions and processes in place, particularly simultaneous with a disturbance or perturbation, such as drought (Figure 8).

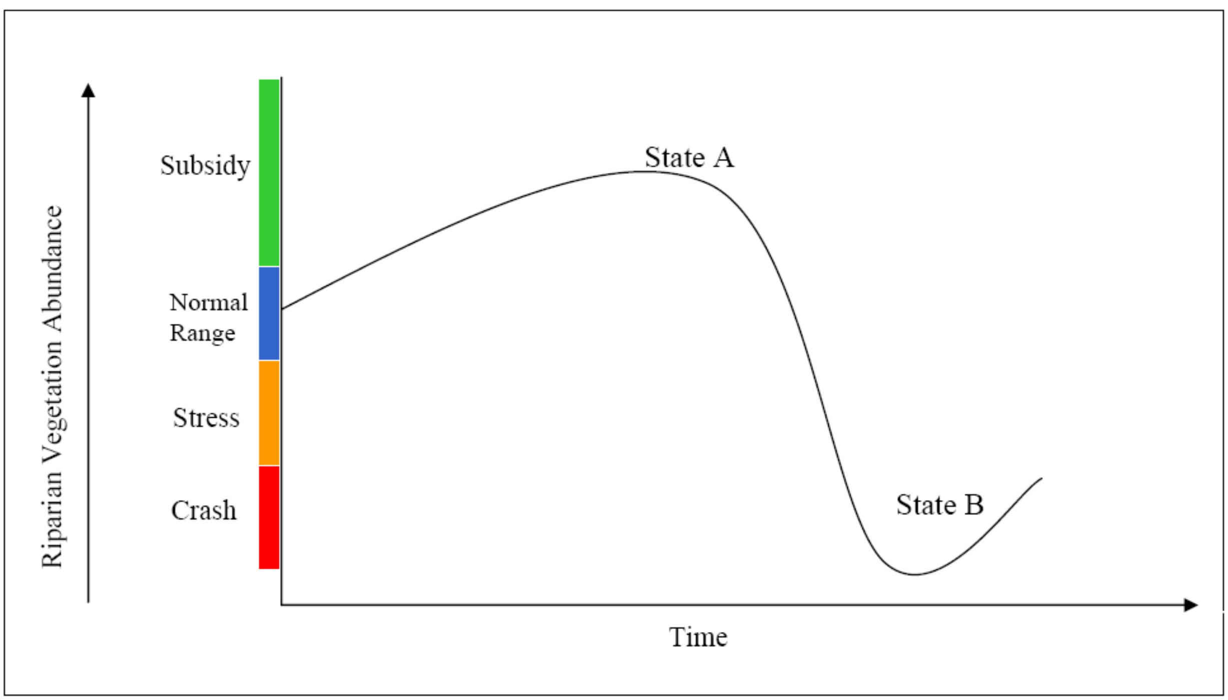

Figure 8. Subsidy-stress curve for an effluent-dominated system. Modified from Odum (1979)

In the case of the Upper Santa Cruz River, the effluent flows provided additional water and nitrogen to a system co-limited by both. The vegetation was bolstered and streamflow was augmented concurrent with a drought and declining groundwater tables. Under normal conditions, the riparian vegetation would adjust its energy demands to accommodate a balance between water conductance and evapotranspiration demands. According to past research, all riparian cottonwoods display leaf senescence that visibly precedes branch and crown die-back following drought stress (Rood et al. 2003), however current satellite imagery data does not indicate such a conspicuous drought response in the Upper Santa Cruz River.

Furthermore, natural hydrologic regimes in riparian forests tend to create heterogeneity in riparian ecosystems that enables the system to adapt and recover from perturbations like floods and water stress. Effluent, on the other hand, due to its consistent delivery of nutrients and water, homogenizes the system and potentially diminishes its resilience to perturbations and stress. This is likely the case in the Upper Santa Cruz River where supplemental nutrients and water provided by the effluent masked the impacts of the drought and muted the normal physiological response to water stress. Nutrients from the effluent bolstered vegetation production and ultimately shifted the energy requirements beyond that which the ecohydrological system could support. The riparian system was therefore less resilient and crossed a threshold into a new alternative state.

Advanced Biotechnology for Recycling Dairy Wastewater

Basic Information

Title:	Advanced Biotechnology for Recycling Dairy Wastewater
Project Number:	2006AZ160B
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Research Category:	Biological Sciences
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Descriptors:	None
Principal Investigators:	Qiang Hu, Milton Sommerfeld

Publication

1. Hanson, Karyn, 2006, Dairy Wastewater Nutrient Remediation Using Microalgae, MS Thesis, the Department of Applied Biological Sciences, College of Science and technology, Arizona State University at Polytechnic campus, Mesa, AZ 85212 (pp: 104)
2. Zhang,C., K. Hanson, M. Sommerfeld, and Q. Hu, Dairy wastewater-fed algae feedstock production for biofuel. (in preparation)

A. Problem and Research Objectives

Concentrated dairy feeding operations, a billion-dollar industry in Arizona, not only provide a healthy and high-quality food supply, but also are essential to the state's economic stability and the viability of many rural communities. However, the growing scale and concentration of dairy feeding operations in the state has contributed to concerns about environmental and human health impacts. It is particularly relevant to the 12,250 square-mile Middle Gila Watershed surrounding the metro Phoenix area that has a fragile landscape and biodiversity. Over 100,000 dairy cows, or more than 70% of the total dairy cows in Arizona, are confined on this watershed. These dairy cows produce a total of more than 3 billion kilograms of manure waste per year, including some 12 million kilograms of nitrogen and 4 million kilograms of phosphorous (based on data from Van Horn et al. 1994). The vast amounts of waste nutrients produced by dairy cows overwhelm the ability of local soils and crops to absorb the nutrients, and result in degradation of water quality, threaten drinking water sources, and may influence air quality in the region. For instance, manure containing high concentrations of ammonia is highly toxic to fish and other aquatic organisms at low levels. On the other hand, increased amounts of nitrogen and phosphorus from dairy wastewater that could enter rivers and streams can cause algal blooms, and deplete the oxygen as the algae decompose, which in turn can devastate the aquatic food chain. Unpleasant algal blooms can also affect water recreational activities.

When nutrients from dairy wastewater seep into underground sources of drinking water, the amount of nitrate (converted from ammonia through nitrification) in the ground water supply can reach unhealthy levels. The Middle Gila River watershed with its highly permeable soil facilitates pollutant transport and increases the risk of ground water contamination. High concentrations of nitrate in groundwater can pose a serious health risk to the State's residents, particularly in places where residents rely on groundwater supplies for drinking water. It has been shown that high levels of nitrate can be fatal to infants when nitrate is reduced to nitrite in the stomach, and the latter combines with hemoglobin in the blood to form methemoglobinanemia, leading to a condition known as "blue baby syndrome" (Gangolli et al. 1994). Reduction of nitrate to nitrite can also represent a risk to adults deficient in glucose-phosphate dehydrogenase (Pontius 1993). Moreover, nitrite can react with secondary amines or amides in water or food to form *N*-nitroso compounds that are potential animal carcinogens (Gangolli et al. 1994). Long-term consumption of drinking water containing nitrate concentrations of ≥ 18 mg L^{-1} has also been reported to contribute to the risk of non-Hodgkin's lymphoma (Ward et al. 1996). In addition, dairy farms may also cause air quality problems due to gases emitted from the decomposition of animal wastes and by the dust generated by animal activity and farming practices. These air pollutants can cause respiratory illness, lung inflammation, and increase vulnerability to respiratory diseases, such as asthma (U.S. EPA Animal waste home, www.epa.gov).

Concentrated dairy feeding operations are under increasing pressure to develop best management practices (BMPs) that address water conservation along with water quality. Currently, facultative lagoons and land application are standard nutrient management methods used in the Gila River Watershed. However, a multi-year monitoring of 6 dairy feedlots revealed that significant contamination of nitrate, ammonia, chloride, and total dissolved solids occurred in groundwater due to leakage and seepage from lagoons (Arnold and Meister 1999). Some waste lagoons, even with clay liners, allow contaminants to leach into the groundwater below the lagoon. For instance, it was estimated that a 3-acre lagoon could legally leak more than a million gallon of wastewater a year at the maximum allowable rate (Weida 2000). Applying too much dairy wastewater to fields too rapidly or by inadequate methods can also cause the contaminants in dairy waste to pollute streams or ground water before they can be completely absorbed by the land and crops. Although aeration, anaerobic digestion, and constructed wetlands have been suggested to mitigate wastewater pollution, these techniques alone cannot remove sufficient nutrients to make treated wastewater reusable. Therefore, environmentally friendly and cost-affordable sustainable technologies for dairy wastewater remediation is needed.

The goal of this research project was to demonstrate the technical feasibility of removing waste nutrients (mainly ammonia) from dairy wastewater and recycling the treated water on the farm using an advanced microalgal biotechnology. To achieve this goal, two specific technical objectives were identified below:

1) Construct and evaluate a novel vertical column photobioreactor. The system was designed to reduce high concentrations of ammonia-N in dairy wastewater to <10 mg N L^{-1}, and return treated, reclaimed water back to the dairy operation.

2) Evaluate performance and nutrient uptake efficiency of isolated and native wastewater-born algal strains. The superior algal strain was used in the vertical column photobioreactor to demonstrate effectiveness and efficiency of the system for sustainable water conservation.

B. Methodology

Photobioreactor: A vertical photobioreactor was fabricated and operated for nutrient removal from dairy wastewater.

Organisms: *Scenedesmus* sp. and *Chlorella* sp. are two green algal strains used in this study. The *Scenedesmus* strain was isolated from a lake near Phoenix, while the Chlorella strain was obtained from native dairy wastewater. Our previous USGS/WRRC project on screening of high-performance microalgae for remediation of nitrate-contaminated groundwater already identified the *Scenedesmus* sp. to be a suitable candidate for rapid growth and nitrate uptake potential. The newly isolated *Chlorella* strain from a dairy waste lagoon also exhibited growth in full strength dairy wastewater, although its nutrient uptake rate has yet to be determined.

Indoor algal culture: Laboratory study of algal nutrient uptake rate was conducted in mini-glass column bioreactors each containing 300 ml of culture volume. Algal cultures that contained either full-strength or diluted (by 25 and 50%) dairy wastewater were maintained at 25 ^{0}C and with a light intensity of ~ 200 mol m^{-2} s^{-1}. Growth rate and concentrations of ammonia, nitrate and phosphate were measured in each column daily.

Outdoor algal culture: Algal performance in the outdoor column photobioreactor was assessed in a batch culture mode. The column photobioreactor was filled with diluted dairy wastewater (e.g., 5 to 15% wastewater) and inoculated with pre-cultured algal cells. When ammonia concentrations in the column are reduced to below 10 mg L^{-1} N, the whole culture was removed from the column and subjected to downstream processing to remove algal cells from treated water. The growth rate, as indicated by changes in biomass (e.g., cell dry weight), was monitored using a UV-VIS spectrophotometer. Aliquots of culture were taken from individual columns at certain time intervals for nutrient analysis, using an automated nutrient analyzer (Lachat QuickChem 8000 Flow Injection Nutrient Analyzer).

C. Principal Findings and Significance

Fabrication of the vertical column photobioreactor:

The vertical column photobioreactor consisted of 32 clear acrylic columns arranged in four rows, each consisting of eight columns. All columns were 6-inch in diameter and 6-foot in height, and each with a capacity of 32 liters. The total culture volume of the system is over 1,000 liters. Eight columns in a row were interconnected through the base caps, which were designed such that wastewater and algal suspension in individual columns can be filled or drained simultaneously or separately. All rows of columns were also interconnected using manifold connectors (Fig. 1).

Fig. 1. Overview of a vertical column photobioreactor for dairy wastewater bioremediation. The bioreactor design student team members: from left to right: Chad Jackson, Brian Blum, Shaun Whitney, Andrew Miles, and Andres Dale.

Aeration mixing system:

Algal culture mixing was was provided by a compressed air stream containing 0.5-1.0% CO_2 through tubing inserted into the base cap of the column.

Temperature control system:

An evaporative cooling system was installed on the columns and cooling water was collected and reused.

Algae harvesting and wastewater refilling system:

Dairy wastewater was supplied to individual columns using a water pump. The same system was also used to harvest algal culture suspension and refill the columns with growth medium or wastewater.

Growth kinetics of *Scenedesmus* sp. and *Chlorella* sp. in dairy wastewater

The green algae, *Scenedesmus* sp. and *Chlorella* sp., were able to grow in the dairy wastewater with or without dilution with tap water. However, the concentration of dairy wastewater did affect growth. The higher the dairy wastewater, the slower the growth and longer the leg phase before growth resumed to grow. Compared with *Chlorella* sp., *Scenedesmus* cells exhibited a faster growth rate and a higher final cell density at every dilution rate tested (**Fig. 5**). Based upon these findings, the *Scenedesmus* strain was selected for further investigation in the vertical column photobioreactor outdoors.

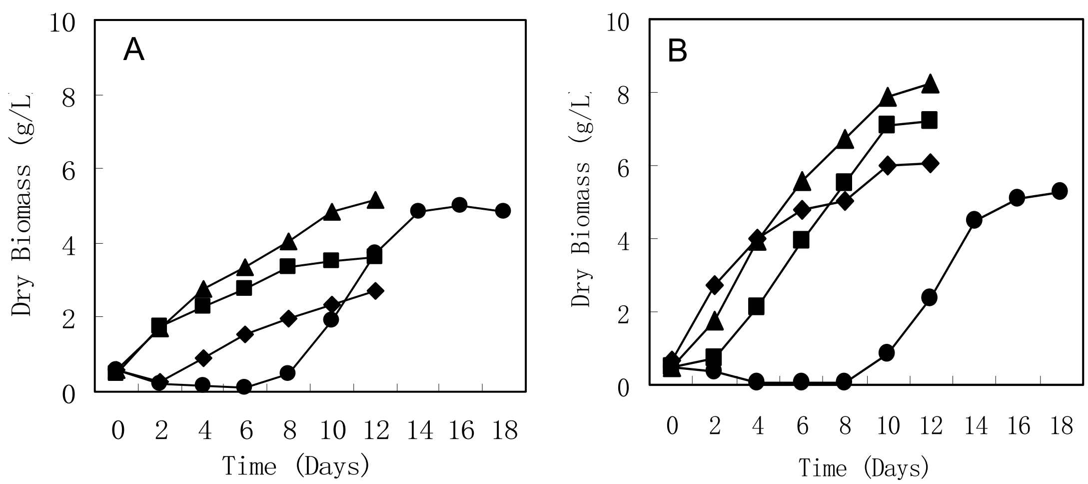

Fig. 5. Growth of *Chlorella* sp. (A) and *Scenedesmus* sp. (B) maintained in 25% (▲), 50% (■), 75% (◆), and 100% (●) of dairy wastewater.
Each data point represents an average of three independent cultures. Culture temperature: 25 °C, light intensity: 170 μmol m^{-2} s^{-1}, and CO_2 concentration: 1%

Nutrient removal from dairy wastewater by *Scenedesmus* sp.

The ammonia concentration was measured in *Scenedesmus* cultures maintained in dairy wastewater with different initial dilution rates. Rapid uptake of ammonia by *Scenedesmus* cells occurred in all the treatment cultures, yet the higher the initial wastewater concentration the longer it took for algal cells to remove ammonia from the culture medium (**Fig. 6**). On average, the uptake rate of ammonia by *Scenedesmus* cells was ca. 3.8 mg L^{-1} h^{-1}.

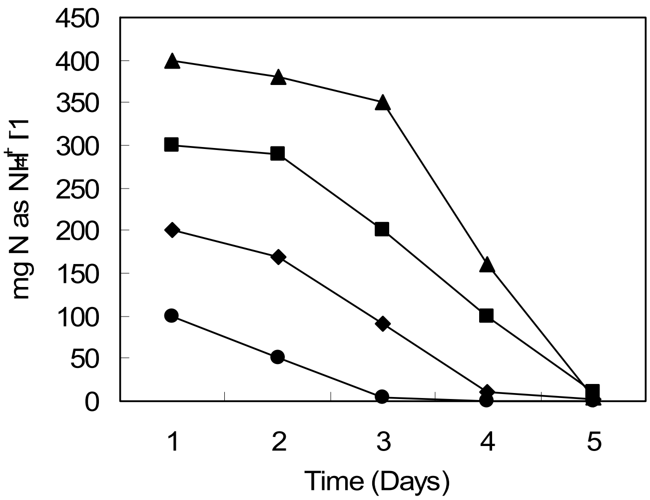

Fig. 6. Reduction in ammonium concentration in wastewater as a function of wastewater dilution rate. *Scenedesmus* cells grew in 25% (●), 50% (■), 75% (◆), 100% of wastewater (▲). Error bars represent confidence intervals α=0.05 (n=3).

Fig. 7 demonstrates the technical feasibility of ammonia removal from dairy wastewater using the vertical column photobioreactor outdoors. Quantitative assessment of the vertical column reactor for dairy wastewater bioremediation is underway.

Fig. 7. Sustainable dairy wastewater treatment by a vertical column photobioreactor.

Significance of the project:

The major accomplishments of the research project were the identification and evaluation of isolated algal strains that can thrive in dairy wastewater and rapidly remove ammonia, and the development and exhibition of an innovative column photobioreactor for cost-effective recycling dairy wastewater. Based upon the results obtained from this study, a commercial full-scale photobioreactor system should be able to treat and recycle 50,000 to 100,000 gallons/day of wastewater to meet the U.S. EPA standard, a capacity that can satisfy the needs of dairy operations of various sizes. While treating large quantities of wastewater, the innovative photobioreactor system would only need a small portion of the land (about 10%) otherwise required by dairy operators for land application.

Project beneficiaries included dairy producers throughout the Gila River Watershed and across the southwest and western regions of the US, regional water districts, local and state water quality regulators, and all stakeholders in regional water conservation efforts. If the ultimate goal of the project could be achieved through our continuous R&D efforts along this line, it is believed that this technology will not only benefit dairy producers by assisting them in meeting National Pollutant Discharge Elimination System (NPDES) requirements and exposing producers to a new innovative method for conserving water, but also enable dairy producers to incorporate the developed technology in their CNMPs to: a) reduce amounts of water, b) reduce amounts of nitrogen and phosphorous being discharged (corresponds with reduction in acres needed to land apply wastewater), and c) develop an improved odor control BMP for the dairy operation.

The technology developed through this project can benefit agricultural water districts and local water quality regulators by demonstrating a workable method for efficiently controlling waste nutrients from other agricultural and industrial sources.

Information Transfer Program

Information Transfer

Basic Information

Title:	Information Transfer
Project Number:	2006AZ167B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	5
Research Category:	Not Applicable
Focus Category:	Education, Water Use, Law, Institutions, and Policy
Descriptors:	EDU, WS, M&I, LIP
Principal Investigators:	Sharon Megdal, Carl Bauer, Susanna Eden, Joe Gelt, Jackie Moxley, Kerry Schwartz, Terry Wayne Sprouse

Publication

1. Browning-Aiken, A., R. G. Varady, D. Goodrich, H. Richter, T. Sprouse, and W. J. Shuttleworth, Integrating science and policy for water management: a case study of the Upper San Pedro River Basin, in Hydrology and Water Law Bridging the Gap: A Case Study of HELP Basins, ed. by J. S. Wallace and P. Wouters, IWA Publishing, 2006.
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4. Eden, Susanna, AZ has much to offer, learn by taking part in global water affairs, Guest View, Arizona Water Resource, Vol. 14, No. 3, Jan-Feb 2006.
5. Megdal, Sharon, Front-Row View of Federal Water Lawmaking Shows Process Works, Arizona Water Resource, January-February 2007.
6. Megdal, Sharon,Featured Interview in, To Quench a Thirst, The University of Arizona Alumnus, Winter 2007.
7. Megdal, Sharon, Arizona's Recharge and Recovery Policies and Programs, in Bonnie G. Colby and Katharine L. Jacobs, ed., Arizona Water Policy: Management Innovations in an Urbanizing, Arid Region, RFF Press, 2007.
8. Megdal, Sharon, Good Intentions, Unintended Consequences: The Central Arizona Groundwater Replenishment District, with Christopher Avery, Carla Consoli and Robert Glennon, Arizona Law Review, forthcoming, 2007.
9. Megdal, Sharon, Municipal Water Reuse in Tucson, Arizona, in Mohammed K. Zaidi, ed., Wastewater Reuse Risk Assessment, Decision-Making and Environmental Security, Springer, AK/Nato Publishing Unit, forthcoming, 2007.
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15. Megdal, Sharon, Arizona Officials Grapple with Growth Water Supply Dilemma, Arizona Water Resource, May-June 2006.
16. Megdal, Sharon, Water Budget Can Be Monstrously Complicated, Arizona Water Resource, March-April 2006.
17. Schwarz, Kerry, Arizona Conserve Water Conservation Guide (steering committee member and contributing author), Project WET International Foundation, 2007.
18. Schwarz, Kerry, Waters of Arizona (steering committee and co-author), Project WET International Foundation, 2007.

19. Schwarz, Kerry, Drought, (steering committee and a contributing author), Project WET International Foundation, 2007.
20. Schwarz, Kerry, Discover a Watershed: the Colorado Educators Guide(steering committee and a contributing author), Project WET International Foundation, 2007.
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INTRODUCTION

The University of Arizona's Water Resources Research Center (WRRC) promotes understanding of critical state and regional water management and policy issues through research, community outreach and public education.

A research and extension unit of the College of Agriculture and Life Sciences, the UA's WRRC is the designated state water resources research institute established under the 1964 Federal Water Resources Research Act. The WRRC conducts water policy research and analysis, and its information transfer activities include publications, conferences, lectures, seminars and workshops. Water news and information are provided to the academic community, water professionals, elected and appointed officials, students and the public. The WRRC is one of four UA water centers responsible for implementing the Water Sustainability Program, which receives funding from the UA's Technology and Research Initiative Fund.

STAFF OUTREACH AND EDUCATION

The WRRC has established itself as a primary link among water-related personnel in the academic community, local, state and federal government, and the private sector. The WRRC, with 40 years of experience addressing water resource problems and issues, places great importance on utilizing its experience and expertise to address statewide water issues. WRRC staff reaches out to the community through presentations and lectures, service on boards, committees and panels, written articles and research activities.

The WRRC professional staff is comprised of Sharon Megdal, Director, Carl Bauer, Associate Director, Kerry Schwartz, Water Education Program Director, Kristine Uhlman, Senior Program Coordinator, Susanna Eden, Coordinator, Applied Research, Joe Gelt, WRRC editor, Jackie Moxley, TRIF Program Coordinator, and Terry Sprouse, Senior Research Specialist.

In addition to serving as WRRC Director, Dr. Sharon Megdal, is also a professor/specialist in the UA Department of Agricultural and Resource Economics, a professor in the UA Department of Public Administration and Policy, a member of the Arid Lands Resource Sciences Graduate Interdisciplinary Program, joint faculty in the Department of Soil, Water and Environmental Science, and has courtesy status with Department of Geography and Regional Development. Dr. Megdal was also appointed interim Water Sustainability Program Director, while Eugene Sander, Dean, College of Agriculture and Life Sciences, is serving as interim UA Provost.

Dr. Megdal, as usual, gave numerous presentations on the topic of water management and planning, around the state. She also conducted scientific research, and she frequently published articles, reports and commentary. In particular, her research and report on *Water Resource Availability for the Tucson Metropolitan Area* generated much interest and commentary. Since the release of the report last summer, she presented its findings numerous times. The report promoted public understanding of the many factors related to the sufficiency of water supplies, and how assumptions regarding these factors affect the conclusions.

Dr. Megdal co-authored the article, “Artificial Recharge,” for the WRRC’s Arroyo Newsletter, she was the featured interview in “To Quench a Thirst” for the *University of Arizona Alumnus*, and she gave a presentation to the Israel Water Commission on Arizona Water Management, Tel Aviv, Israel, June 28, 2006 . Dr. Megdal also continues to teach her popular graduate-level water policy course.

Since joining the UA and WRRC in August 2006, Associate Director, Carl Bauer, has been settling into the many dimensions of his new position. He was part of the core group of PIs (including Sharon Megdal) who wrote a large proposal to the NSF to establish a new Ph.D. program in Water Reallocation and Reuse. In spring 2007, he became the faculty coordinator of the UA’s new Graduate Certificate in Water Policy, which will begin operation in fall 2007. Dr. Bauer is teaching a graduate seminar in Comparative and International Water Policy in the Geography Department, and he will teach Water and Sustainability to undergrads in the fall. Dr. Bauer has also continued his international outreach. He gave invited talks at water policy conferences in Denmark and Portugal, and he has helped organize an international conference on environmental flows that will take place in Australia in September 2007. He brought three experts to UA as visiting speakers on water policy, from South America, Spain, and Oregon. Dr. Bauer is building collaborations for comparative research on water banks and policy reforms in the Western US and Spain. In addition, he is continuing his studies of hydropower and water management in Patagonia.

Kerry Schwartz directed activities of Arizona Project WET (Water Education for Teachers). As the State Coordinator for Project WET International, a nationally recognized, teacher-tested program, she coordinates a network of Project WET facilitators, conducts educator and facilitator workshops, and promotes water education statewide. She also was on the steering committee and a contributing author of three educational water guides: *Waters of Arizona*, *Drought*, and *Discover a Watershed: the Colorado Educators Guide*.

Susanna Eden, Coordinator, Applied Research, has led the WRRC’s collaborative effort with the Water Education Foundation to develop a *Layperson’s Guide to Arizona Water*. She was lead author on the well-received *Arroyo* issue “Artificial Recharge: A Multi-Purpose Management Tool.” Her chapter in the Arizona Town Hall 2006 Background Report has been adopted for use as a concise introduction to Arizona water resource issues in the Water Harvesting course, Department of Soil, Water and Environmental Science. She is participating in WSP funded research on the impact of exempt wells on groundwater sustainability in southeastern Arizona, and on an Arizona Water Institute funded grant to synthesize the state of knowledge on environmental flows for the Verde River. She also continues her evaluation of decision support activities for SAHRA (Sustainability of semi-Arid Hydrology and Riparian Areas).

Jackie Moxley, Program Coordinator for the Water Sustainability Program (WSP), runs the competitive grants program and student fellowship program, and conducts the annual research forum and poster competition. She organized a timely and well attended workshop on emerging contaminants. Ms. Moxley obtained an Arizona Water Institute Internship of $5,000 in January 2007, to hire a graduate student to start-up coordination of campus sustainability efforts and serve as liaison among campus student groups, faculty, staff and community organizations. As part of campus sustainability, Jackie is on the core planning team for a collaborative "Sustainability Week" in October. A previous publication, "Arizona Know Your Water" received additional WSP funds in 2006/07 to reprint and for translation and printing of a Spanish version. A downloadable web-based version is available on the WSP web site www.uawater.arizona.edu.

As an Area Assistant Agent with Extension, Kristine Uhlman is working with several Arizona Counties on projects addressing water resources. She continues her role as the Arizona NEMO (Non-point Education for Municipal Officials) Program Coordinator and is responsible for the development of watershed-based planning documents and educational outreach to land-use decision makers on non-point source pollution issues. Other projects include developing volunteer watershed monitoring programs for watershed partnerships across the state; development of a predictive model to assess ground water vulnerability to nitrate contamination; and, a series of county-based water resource fact sheets for the domestic well owner.

In addition, Ms. Uhlman is Principal Investigator on a series of Rapid Watershed Assessments with the Natural Resources Conservation Service (NRCS). NEMO and the Water Resources Research Center (WRRC) have contracted with the Natural Resources Conservation Service (NRCS) to develop a series of Rapid Watershed Assessments for seven of Arizona's seventeen watersheds.

Joe Gelt writes and edits the *Arizona Water Resource* and edits *Arroyo,* the two WRRC newsletters. An ongoing project is working with Susanna Eden to produce *The Layperson's Guide to Arizona Water*, a project undertaken with the Water Education Foundation located in California.

Terry Sprouse, senior research specialist, continues his U.S.-Mexico border research with a WSP grant to study the economic value to southern Arizona of Mexican effluent. He is working on local rainwater harvesting projects in southern Arizona, and helped organize a rainwater harvesting conference in Tucson. Dr. Sprouse works with Project NEMO, coordinating grant activities in the Benson watershed, and helping to produce Rapid Watershed Assessment Reports for seven watersheds in Arizona. He is also coordinating an update of the popular Arizona Water Map Poster.

NEWSLETTERS

The highly acclaimed *Arizona Water Resource* Newsletter, edited by Joe Gelt, is a 12-page newsletter that focuses on state and regional water issues. It is published six times per year and is sent free of charge to over 2600 people. The newsletter has wide distribution; the majority of its readers are from Arizona, but the newsletter also is mailed to 42 states and 14 foreign nations. The publication regularly includes a feature article, a guest view, news briefs, sections on special projects and on legislation and law, and public policy column written by the WRRC Director, as well as announcement and publication notices.

Most issues of the newsletter include a four-page special supplement inserted in the center fold. By sponsoring a supplement and having it "piggy-back" on the newsletter, an agency or organization distributes information about its activities and also assists in covering newsletter costs. The organizations sponsoring a supplement this year were U.S. Geological Survey, Bureau of Reclamation and the UA Water Sustainability Program.

AWR Feature Articles - 2006-2007

Need Grows for CAP Tucson Reliability
Long Delayed, Nogales Wastewater Treatment Plant Now On Track
Interconnected Energy/Water Savings and Uses Worked Into Conservation Planning
Geothermal Using Water to Generate Energy and Provide Heat
Urban Heat Island Higher Temperatures & Increased Water Use
Bioremediation — Water Treatment Tool to Fix Pollution Problems
Study Says Northern Arizona's Water Supplies Unsustainable
U.S. Supreme Court to Hear Arizona Case Challenging ESA Primacy
Arizona to Nevada Water Export Plan Proposed, Contested

An edition of the *Arroyo* was published this year, titled Artificial Recharge: A Multi-Purpose Water Management Tool. Joe Gelt had a significant role in the group effort of writing and editing the text of this edition of *Arroyo*. This represented a relaunching of *Arroyo*, a WRRC publication that had not been published since May 2002.

WRRC WEB PAGE

Another effective outreach vehicle is the Internet, and we at the WRRC endeavor to make effective and extensive use of our web site, now being redesigned, as part of our outreach effort. The new webpage will be more user-friendly, and easier to manage. In addition to the 104B and WSP reports, we post papers and presentations and link to many other water sites.

ANNOUNCEMENT DISTRIBUTION

Another component of WRRC information transfer is to keep researchers of the three Arizona universities apprized of upcoming conferences and other special events. The WRRC maintains several email lists that are used to distribute announcements and notices we receive from a wide range of other institutions and organizations to appropriate recipients.

WRRC SEMINAR PROGRAM

Our brown bag seminar series offers additional opportunity for two-way dialogue and for community-university interaction. We focus on topics of broad interest to academics from multiple disciplines and members of the water community. We showcase basic research as well as "real-world" happenings.

Brown Bag Seminars 2006 - 2007

- Brad Lancaster, author, permaculturalist and water harvester, "Turning Water Scarcity into Water Abundance with Water Harvesting: Guiding Principles to Welcome Rain Into Your Life and Landscape"
- Margot Garcia, Professor Emeritus, and member of the Natural Resources Council Panel to restore Louisiana Wetlands, "Oops! There goes New Orleans."
- Val Little, Director, Water Conservation Alliance of Southern Arizona (WaterCASA), "The ECoBA Program: an evaluation and cost-benefit analysis of municipal water conservation programs."
- Joe Abraham, PhD student, UA Department. of Geography and Regional Development, "Assessing Drought Vulnerability."
- Eric Betterton, Professor, UA Atmospheric Sciences, "Cloud Seeding in Arizona – Theory and Practice."
- Bradley Udall, Director, Western Water Assessment Center, "The Colorado River Compact: A Perspective from the State of Colorado."
- Mike Leuthold, UA Atmospheric Sciences/Institute of Atmospheric Physics, "The Southwest Regional Weather Modeling Consortium."
- Dennis Dickerson and Claire Zucker, Pima Association of Governments (PAG), "PAG's Watershed Planning Program."
- Rededication of the updated Sol Resnick Conference Room, and introduction of the new WRRC Associate Director, Carl Bauer.
- Sharon Megdal, Director, UA Water Resources Research Center, "Water Resource Availability for the Tucson Metro Region."
- Kathy Jacobs, Arizona Water Institute, Dave Meko, UA Tree Ring Lab, Bonnie Colby, UA Agricultural and Resource Economics, and Peter Troch, UA Hydrology and Water Resources, "Enhancing Colo. River Water Supply Reliability through Climate Information."
- Patrick Jones, Director, UA Office of Technology Transfer, "Technology Transfer: Variations on a Theme."
- Trevor T. Hill, President, Global Water Resources, LLC, "Changing the Arizona Water Paradigm - A Private Utility's Perspective on Reclamation & Reuse."
- Mark Apel, Planning Manager, Cochise County Planning & Zoning Commission, "Water Policy - Planning and Implementation at the County Level."
- Cliff Neal, Director of the Central Arizona Groundwater Replenishment District, "Question and Answer Session for Cliff Neal about CAGRD."
- Kristin Mayes, Commissioner, Arizona Corporation Commission, "Mandating Conservation by Arizona's Private Water Companies."

- Jim Crosswhite, Ranchowner near Nutrioso Creek in the White Mountains, “Ecosystem Restoration on Nutrioso Creek: Landowner Experience from the Field.”
- Federico Aguilera, Professor, University of La Laguna Tenerife, Canary Islands, Spain, “Water Markets in the Canary Islands: An Evaluation.”
- Andrew Purkey, Program Director, Columbia Water Transactions Program, Portland, Oregon, “Cooperative, Market-Based Flow Restoration: Experience from the Pacific Northwest.”
- Catherine Cay, Oil Shale Organizer for Western Colorado Congress, “Oil Shale – The Elusive Addiction.”
- Andy Laurenzi, Program Director, Land and Water Policy, The Sonoran Institute, “Sustainable Water Management: Guidelines for Meeting the Needs of People and Nature in the Arid West.”

THE TRIF WATER SUSTAINABILITY PROGRAM

WRRC is one of four founding UA water centers comprising the Water Sustainability Program (WSP). Now in its sixth year, this campus-wide collaboration of scientists and educators has made significant contributions to the body of research, education and outreach applied to Arizona water resources issues. Funded through the state Technology and Research Initiative Fund (TRIF) the WSP will allocate $3.2 million/year over the next four years, as approved by the Arizona Board of Regents.

WRRC continues to play a pivotal role in implementing, developing, and managing program components that include a competitive grants program, student fellowships, a recruitment and research initiative, center activities and directed initiatives and an education and outreach program.

A key component of the WSP is the competitive grants program. Each year $1million is allocated to UA faculty and staff to fund projects relevant to critical Arizona water issues. In 2007, 15 new projects were selected through a panel review process and nine projects were granted continuation of funding for the next cycle beginning July 1, 2007. The total number of grant-funded projects was 74. Each project funded through the TRIF WSP competitive grant process is associated with one of the four UA water centers. More information on the grants can be found at www.uawater.arizona.edu.

New projects awarded WSP funds that involve WRRC staff and/or hosted by the WRRC for 2007/08 include the following:

1. Estimating Water Use: Monitoring Rural Domestic Wells with Low-cost, Near-real Time Water Metering. $58,970- 2 years. Susan Pater, Kim McReynolds, Cado Daily, Cochise County Cooperative Extension, Sharon Megdal and Susanna Eden, Water Resources Research Center, David Quanrud, Arid Lands Studies, Gary Woodard and Ramon Vazquez, SAHRA, Dept of Hydrology & Water Resources.

2. San Pedro River Volunteer Monitoring, Community Watershed Alliance, Cochise County, AZ. $4,895 – 1 year. Kristine Uhlman, Water Resources Research Center and Phil Guertin, School of Natural Resources.

3. 'Paper Water' Demystified: An Economic Evaluation of CAGRD Spatial Dynamics. $26,434 - 1 year. Paul Wilson, Dept of Agricultural & Resource Economics, D. Phillip Guertin, School of Natural Resources, Sharon Megdal, Water Resources Research Center/Dept of Agricultural & Resource Economics.

4. Arizona Project WET Evaluation: Examining Impact and Developing a Computer-based Tutorial and Assessment System $49,979 – 1 year. Jerome D'Agostino, Dept of Educational Psychology and Kerry Schwartz, Water Resources Research Center.

5. Brine Minimization/Salt Management Using VSEP® Technology to Maximize Water Recovery. $49,945 – 1 year. Eric Betterton, Dept of Atmospheric Sciences/Chemical & Environmental Engineering, Robert Arnold and Wendell Ela, Dept of Chemical & Environmental Engineering.

6. Compound Specific Isotope Analysis of Natural Attenuation Activity in Chlorinated-Solvent Contaminated Aquifers in Arizona. $23,834 – 1 year. Mark Brusseau, Dept of Soil, Water & Environmental Science.

One additional multi-year irrigation project hosted by the WRRC, **Promoting the Adoption of Subsurface Drip Irrigation by Arizona's Farmers** James Walworth, Department of Soil, Water and Environmental Sciences, Edward Martin, Department of Agricultural and Biosystems Engineering, Patrick Clay, Maricopa County Cooperative Extension, Mary Olsen, Department of Plant Pathology, and Russell Tronstad, Department of Agricultural and Resource Economics has received $20,000 awards for the last two years and will have one more year of funding through 2007/08.

The following projects were hosted by WRRC through the 2006/07 grants cycle that ends June 30, 2007:

1. Spanish Translation and Reprints of the Booklet, *Arizona: Know your Water* (2004). **$23,100 – 1 year.** Janick Artiola, Department of Soil & Water Science, Katherine Farrell-Poe, Department of Agricultural and Biosystems Engineering, Jacqueline Moxley, Water Resources Research Center.

2. On-line Access to Distance-Learning Tools for Watershed Stewardship in Rural Arizona. $41,469 - 1 year. Robert Emanuel, Arizona Cooperative Extension, Garry Forger, Learning Technologies Center, George Zaimes, School of Natural Resources, Michael Crimmins, Department of Soil, Water, & Environmental Science.

3. Valuation of Binational Effluent in the Upper Santa Cruz Basin: Estimating Willingness to Pay. **$39,552- 1 year.** George Frisvold, Department of Agricultural & Resource Economics, Terry Sprouse, Water Resources Research Center.

4. Watershed Rainfall, Ground Water Usage, Riparian Stream Flow and Vegetation Monitoring, Middle San Pedro River Basin, Cochise County, AZ. $2,500 - 1 year. Phil Guertin, School of Natural Resources, Kristine Uhlman, Water Resources Research Center.

5. Predicting Groundwater Vulnerability to Nitrate in Arizona. $69,992 - 1 year. Tauhidur Rahman, Department of Agricultural and Resource Economics, Kristine Uhlman, Water Resources Research Center.

6. Mapping Accumulation of Soil Salinity in Landscapes Irrigated with Reclaimed Water. $31,154 - 1 year. Ursula Schuch, Department of Plant Sciences, James Walworth, Department of Soil, Water and Environmental Sciences.

7. Implementation of Efficient Surface Irrigation Practices in the Lower Colorado River Region. $40,000 - 1 year. Dawit Zerihun, Charles A. Sanchez, Yuma Agricultural Center.

WRRC – WSP COLLABORATIVE ACTIVITIES AND DIRECTED INITIATIVES

In addition to the TRIF grants projects conducted in-house or hosted by the WRRC, the WSP funding for center activities and directed initiatives has provided opportunities for the WRRC to strengthen educational programs, support new and continuing projects and expand ties to other departments and colleges in the area of water policy and management. In 2006/07 WRRC provided start-up funds to recruit Carl Bauer to UA. Dr. Bauer is the WRRC Associate Director, and Professor, Department of Geography and Regional Development, specializing in water policy. WRRC also helped fund a number of projects that includes rainwater harvesting; a drought reporting system; water recharge and recovery publication; continued support of enhanced drought preparedness planning and the Colorado River; and continued support of Project WET education programs. A new publication on Arizona water in collaboration with the Water Education Foundation is in process.

WRRC WSP money will fund half of two Translational Science Fellows awards sponsored by the Institute for the Study of Planet Earth (ISPE). The Water Center is also funding a part of a video project Kristine Uhlman of Project NEMO, and part of the cost of hosting a lecture by Peter Gleick, of the Pacific Institute.

ARIZONA PROJECT WET

The Arizona Project WET (APW) Program's mission is to promote responsible water stewardship through excellent and effective water education. The goal of the WRRC's Arizona Project WET program is to educate people about Arizona's water resources in an engaging and understandable way. To accomplish this goal the Center is utilizing the nationally recognized Project WET (Water Education for Teachers) program, in which solid pedagogy has been used in developing curriculum guides. The lessons are interactive, multidisciplinary, research-based, constructivist (learners construct knowledge for themselves) and promote critical thinking.

The Director of Arizona Project WET is supported by a full time and part time staff position and five UA students working together keep this program effective and thriving. In Maricopa County an extension agent provides support to the Arizona Project WET program. A five-year million dollar grant through the City of Phoenix funds a program coordinator and a student position supporting the cities APW water education program. Facilitators are trained in water content, facilitation, and teaching methods in intensive workshops. At present the Program has 144 volunteer facilitators in three areas of the state available to conduct workshops for K-12 teachers and other educators. Coordinators and facilitators trained 581 teacher/educators in 45 workshops, educating a reported 39,507 students during the reporting period.

Arizona Makes a Splash with Project WET Water Festivals Program

The comprehensive Arizona Project WET program is the foundation for the *Arizona Make a Splash with Project WET Water Festivals*. Water Festivals are intensive and interactive learning experiences for 4th grade students and their teachers. Content is in accordance with the state mandated learning objectives for the students and includes the water cycle, watersheds and water supply, riparian systems, groundwater and water conservation. At the festival, structured hands-on lessons are used to engage students in understanding natural systems and water resources while having fun.

Arizona water festivals were held at eight locations reaching 6,289 students, 262 teachers, 77 schools and 575 volunteers in 2006. The addition of a Program Coordinator in 2004 has enabled the water Festival program to expand while maintaining effective education standards.

These Arizona Water Festivals were supported by sponsors, school administrators, teachers, students and communities. The ongoing commitment of the U.S. Bureau of Reclamation, Arizona Department of Water Resources, Arizona Department of Environmental Quality, Salt River Project and Central Arizona Project as well as other local sponsors resulted in a budget of $83,500 for 2006 Water Festivals. In-kind donations for 2006 from over 40 organizations totaled over $80,000.

WATER EXPO 2007 AT THE ARIZONA STATE CAPITOL

In what has become an annual event, this year's expo was held on February 27. Co-sponsored by UA's Water Sustainability Program, Central Arizona Project (CAP), Salt River Project (SRP) and the U.S. Bureau of Reclamation, this was an opportunity to bring water information and education to Arizona lawmakers about ongoing projects across the state. Eighteen senators and 37 legislators attended the event featuring 40 exhibits and a luncheon program. Other guests included 19 legislative committee members, and board members from the Arizona Water Institute, SRP, and CAP. Conducted on the Senate lawn of the Arizona State Capitol, exhibitors represented state agencies and associations, state universities and colleges, small and large municipalities, rural county and watershed partnerships, and federal organizations working locally.

RECEPTION AND REDEDICATION OF RESNICK CONFERENCE ROOM

A reception to re-dedicate the Sol Resnick Conference Room, October 30, 2006, was an opportunity to thank Salt River Project and the Central Arizona Project for their generous contributions to lobby and conference room refurbishing and renovation. This event was combined with the introduction of the new WRRC Associate Director, Carl Bauer.

BOOK SIGNING EVENT

In February 2007, WRRC hosted a well attended book signing and reception for the newly released *Arizona Water Policy: Management Innovation in an Urbanizing Arid Region*, edited by Bonnie Colby and Katharine Jacobs. WRRC Director, Sharon Megdal, contributed a chapter to the book entitled, “Arizona’s Recharge and Recovery Programs.” Production of this book was supported by WRRC – WSP funds in 2005/06.

ANNUAL WRRC CONFERENCES

2006 Conference

Over 400 people attended the he 2006 WRRC Conference, held in Phoenix on June 20-21. The conference, titled “Providing Water to Arizona's Growing Population: How Will We Meet the Obligation?” provided a timely dialogue on water and growth. Day one of the conference featured a session on the different ways city, town and rural area managers addressed the issue “water planning for growth,” followed by a panel of diverse water professionals who considered “where is the water coming from?” Afternoon sessions included perspectives from developers, home builders, and realtors; the role of the Central Arizona Groundwater Replenishment District; and views from public officials.

The second day of the conference was an optional half-day workshop hosted by Arizona State University’s Global Institute of Sustainability. It focused on in-depth discussion of ideas for meeting the long-term water needs of Central Arizona and implications for the rest of the state. Presentation of a background paper and a panel discussion on the political decisions, infrastructure investments and water management programs necessary were followed by a facilitated open discussion on key policy questions and issues that need to be addressed. Conference presentations are posted at www.cals.arizona.edu/AZWATER.

2007 Conference

Titled "The 20th anniversary of the Environmental Quality Act and ADEQ: Assessing and Protecting the State's Water Quality," the June 5 event was cosponsored by the Arizona Department of Environmental Quality and the Arizona Water Institute. It was conducted at the Hyatt Regency, Phoenix at Civic Plaza.

The one-day conference featured panels on the genesis and history of the Environmental Quality Act and ADEQ, the water quality assurance revolving fund (WQARF), emerged and emerging contaminants, emerging policy challenges, and the future of ADEQ. Also included was a luncheon presentation on the state of ADEQ by Director Steve Owens and insights from former directors.

OUTSTANDING 104B PROJECT WINS AWARDS AND CREATES NEW COURSE

University of Arizona senior, Emilie Brill-Duisberg, received the highly competitive Student Sustainability Leadership Award from the Association for the Advancement of Sustainability in Higher Education in the amount of $750. She was a student project leader for a USGS 104B grant in which students completed two rainwater harvesting projects on the UA campus.

Project PI, Jim Riley, was awarded the Community Xeriscape Leader Award for 2007 by the Arizona Department of Water Resources and Tohono Chul Park for work related to the project. The award came with a special recognition by the Arizona Governor, Janet Napolitano.

In addition to the completion of these physical projects, the 104B funds have helped to create an official course in rainwater harvesting, in Spring 2006.

WRRC RESEARCH & INFORMATION TRANSFER PROJECTS 2006-2007

Listed below are the 2006-2007 project grants and funding sources.

- Evaluation of the Arizona Department of Water Resources Management Plans for the Active Management Areas
  Funding: Arizona Department of Water Resources (ADWR)
- Evaluation of the Arizona Department of Water Resources Management Plans for the Active Management Areas
  Funding: Arizona Water Institute
- Arizona Water Resource
  Funding: Bureau of Reclamation
- Rapid Watershed Assessments for Seven Priority Watersheds in Arizona
  Funding: Natural Resources Conservation Service
- Projects to Enhance Arizona's Environment: An Examination of their Function, Water Requirements and Public Benefits
  Funding: US Bureau of Reclamation
- AZ Make a Splash with Project WET Water Festival
  Funding: Arizona Department of Environmental Quality
- Arizona WET Water Festival
  Funding: ADWR (2 grants)

- 2006 Arizona Children's Water
  Funding: ADWR
- Arizona WET Water Festival-Prescott AMA
  Funding: City of Prescott
- Water Festival
  Funding: Project WET
- Phoenix AMA Wet Facilitators Training
  Funding: ADWR
- AZ Project WET Evaluation
  Funding: City of Phoenix
- Water Education for Teachers Project WET
  Funding: City of Tucson

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	42	5	0	0	47
Masters	4	0	0	0	4
Ph.D.	4	4	0	0	8
Post-Doc.	1	0	0	0	1
Total	51	9	0	0	60

Notable Awards and Achievements

Sharon Megdal discussed Water Issues related to Tucson, Growth, and the Environment, on KUAT Television, Tucson, Arizona, August 7, 2006.

Sharon Megdal gave a presentation to the Israel Water Commission on Arizona Water Management, Tel Aviv, Israel, June 28, 2006.

Sharon Megdal provided a press briefing on her research, entitled, Water Resource Availability for the Tucson Metropolitan Area, WRRC, July 17, 2006.

Sharon Megdal made a presentation on Water Management in Arizona with a Focus on the Border, to the Border Issues Committee of the Arizona-Mexico Commission, Sierra Vista, Arizona, May 19, 2006.

Sharon Megdal provided testimony to the Subcommittee on Water and Power of the United States House of Representatives Resources Committee relating to the United States-Mexico Transboundary Aquifer Assessment Act, Washington, DC, May 10, 2006.

Carl Bauer was plenary speaker at 5th Iberian Conference on Water Management and Planning, Faro, Portugal, December 2006 ("The range of water banks in the Americas").

Carl Bauer was appointed full professor in the Department of Geography and Regional Development .

Kristine Uhlman produced the video, "Stormwater Management from a Watershed Perspective: Extreme Western Climates" which won an Award of Distinction for the Communicator Awards group, an international competition that recognizes excellence in communication.

Kristine Uhlman was reappointed by the Governor for another 3-year term on the Water Protection Fund Commission.

Jackie Moxley received an Arizona Water Institute Internship Grant in January 2007, to hire a graduate student to start-up coordination of campus sustainability efforts and serve as liaison among campus student groups, faculty, staff and community organizations.

Terry Sprouse was interviewed about Rainwater Harvesting on KUAT Television, Tucson, Arizona, October 15, 2006.

Ms. Emily Brill Duisberg, Project 2006AZ131B, the President of the student group, PARASOL, which implemented the project, was awarded the Student Sustainability Award at the national conference of the Association for the Advancement of Sustainability in Higher Education, AASHE.

Jim Riley, Project 2006AZ131B, was awarded the Community Xeriscape Leader Award for 2007 by the Arizona Department of Water Resources and Tohono Chul Park for work on this project. The award came with a special recognition by the Governor of Arizona, Janet Napolitano.

The students working on Project 2006AZ131B won a Sustainable Solutions Award from Cummings Publishing.

Publications from Prior Projects

None