

**Texas Water Resources Institute
Annual Technical Report
FY 2009**

Introduction

The Texas Water Resources Institute (TWRI), a unit of Texas AgriLife Research, Texas AgriLife Extension Service and the College of Agriculture and Life Sciences at Texas A&M University, and a member of the National Institutes for Water Resources, provides leadership in working to stimulate priority research and Extension educational programs in water resources. Texas AgriLife Research and the Texas AgriLife Extension Service provide administrative support for TWRI and the Institute is housed on the campus of Texas A&M University.

TWRI thrives on collaborations and partnerships and currently manages over 80 projects, involving 125 faculty members from across the state. The Institute maintains joint projects with 14 Texas universities and three out-of-state universities; more than 30 federal, state and local governmental organizations; more than 20 consulting engineering firms, commodity groups and environmental organizations; and numerous others. In fiscal year 2009, TWRI obtained more than \$4.5 million in funding and managed more than \$22 million in active projects.

TWRI works closely with agencies and stakeholders to provide research-derived, science-based information to help answer diverse water questions and also to produce communications to convey critical information and to gain visibility for its cooperative programs. Looking to the future, TWRI awards scholarships to graduate students at Texas A&M University through funding provided by the W.G. Mills Endowment and awards grants to graduate students from Texas universities with funds provided by the U.S. Geological Survey.

Research Program Introduction

Through the funds provided by the U.S. Geological Survey, TWRI funded 10 research projects in 2009-10 conducted by graduate students at Texas A&M University (6 projects), Texas Tech University (2 projects), Rice University (1 project), and the University of Texas at El Paso (1 project). Additionally, through funds provided by the U.S. Geological Survey, TWRI facilitated the continuation of three competitive research programs at Texas A&M University.

Thomas Abia, of Texas A&M University's department of biological and agricultural engineering, studied in situ groundwater arsenic removal using iron oxide coated sand.

Joy Archuleta-Truesdale, of the environmental science and engineering department at the University of Texas at El Paso, examined sources and risks of waterborne pathogens in the El Paso del Norte region.

Deborah Carr, from the environmental toxicology department at Texas Tech University, researched the biotransformation of pharmaceuticals and personal care products (PPCPs) at an effluent land application site.

Dex Dean, in the ecosystem science and management department at Texas A&M University, studied the ecohydrology of forested wetlands on the Texas Gulf Coast.

Takele Dinka , of Texas A&M University's soil and crop sciences department, determined the influence of land use and terrain on surface hydrology in shrink-swell soils.

Adcharee Karnjanapiboonwong , of the department of environmental toxicology at Texas Tech University, studied the occurrence of pharmaceuticals and personal care products (PPCPs) at an effluent-dominated wastewater application site.

Andrew Leidner, of the department of agricultural economics at Texas A&M University, completed an economic analysis of proposed seawater desalination facility in Brownsville, Texas.

Israel Parker , from Texas A&M University's department of Wildlife and Fisheries Sciences, studied the role of free-ranging wildlife in the deposition of escherichia coli into a Texas river floodplain.

Aarin Teague , of Rice University's department of civil and environmental engineering, examined the Lake Houston Watershed water quality prediction system.

Yujin Wen , of the soil and crop sciences department at Texas A&M University, examined regulated deficit irrigation application and cotton production in southwest Texas.

Dr. Vijay P. Singh, of the department of biological and agricultural engineering at Texas A&M University, continued researching hydrological drought characterization for Texas under climate change, with implications for water resources planning.

Dr. Benjamin F Schwartz, of the department of biology at Texas State University, continued examining the role of epikarst in controlling recharge, water quality and biodiversity in karst aquifers – comparing Virginia and Texas.

Finally, the third competitive research grant is a multi-state, international effort that involves the collection and evaluation of new and existing data to develop groundwater quantity and quality information for binational aquifers between Arizona, New Mexico, Texas and Mexico. The United States-Mexico

Research Program Introduction

Transboundary Aquifer Assessment Program is in the first year of the five-year program.

USGS Grant No. 07HQAG0077 - Enhancing the Livestock Early Warning System (LEWS) with NASA Earth-Sun Science Data, GPS and RANET Technologies

Basic Information

Title:	USGS Grant No. 07HQAG0077 - Enhancing the Livestock Early Warning System (LEWS) with NASA Earth-Sun Science Data, GPS and RANET Technologies
Project Number:	2007TX318S
Start Date:	6/1/2007
End Date:	5/31/2010
Funding Source:	Supplemental
Congressional District:	08
Research Category:	Climate and Hydrologic Processes
Focus Category:	Drought, Agriculture, Climatological Processes
Descriptors:	
Principal Investigators:	Steve Whisenant

Publications

There are no publications.

**Enhancing the Livestock Early Warning System (LEWS) with
NASA Earth-Sun Science data, GPS and RANET Technologies:
A Collaboration with USGS/EROS**

**Annual Report
June 2009 to May 2010**

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**Enhancing the Livestock Early Warning System (LEWS) with NASA
Earth-Sun Science data, GPS and RANET Technologies:
A Collaboration with USGS/EROS**

Project Description

A study was initiated in 2007 to enhance the Livestock Early Warning Systems (LEWS) decision support system (DSS) by using NASA Earth-Sun Science data by adding water resources monitoring and herd migration tools that are disseminated to pastoral communities using RANET technologies. The existing LEWS project had recognized a need to improve the existing DSS to better identify situations where water becomes a limitation to pastoral use of forage supplies in a given region. The region identified for study provides a rich environment where the technology would greatly enhance water resource monitoring and provide high impact on the national livestock sector. Monitoring the status of waterholes and rivers is important not only to the pastoralists but also for better management of the environment in terms of land degradation brought about by excessive concentration of livestock during droughts.

The project was located in a transboundary site in East Africa where pastoralism is a significant component of the economy (Abule et al., 2005). The study area traverses an ecologically, ethnically and institutionally heterogeneous transect of approximately 750 kilometers, from Yabello in southern Ethiopia south through Baringo, Marsabit, Isiolo, Wajir, Mandera and Samburu districts in northern Kenya. The spatial extent of the study area is approximately 150,000 km². This study area was chosen not only because of the international nature of its extent (i.e., Ethiopia and Kenya) but also to capture variation in ecological potential, market access, livestock mobility and ethnic diversity across the region. It is also an area characterized by a growing number of conflicts between pastoralist communities over land, water and pasture.

The study area is inhabited by several main pastoral ethnic groups: the Boran, Gabbra, Somali, Rendille, Samburu and others. Climatically, southern Ethiopia is semi-arid to arid. The main pastoral group in this zone is the Boran people who are pure pastoralists. Somali clans are also found in this zone. Northern Kenya can also be characterized as semi-arid to arid with the major pastoral groups in this region being the Samburu, Turkana, Borana and Somali. All these groups are pure pastoralists and practice transhumance (i.e. the practice of moving between seasonal base camps throughout the year to optimize use of forage resources). Their livelihoods depend on herds of cattle, sheep, goats and camels for food security. They move their livestock seasonally in order to exploit grazing in areas away from their permanent settlement sites. The animals owned are used for milking, slaughtered for meat, sold for cash or bartered for other commodities.

Pastoralism by definition is an extensive system of livestock production in which a degree of mobility is incorporated as a strategy to manage production over a heterogeneous landscape characterized by a precarious climate. Because of the need to take full advantage of the landscape, pastoralism is poorly fitted to the rigid structure of national and international boundaries. The pastoral strategy of mobility therefore underscores the need for a regional perspective, especially since other impacts such as resource access conflict, spread of disease and livestock rustling are side effects of pastoral mobility. For this study, we are conducting four

integrated activities that will provide a prototype application for arid regions in East Africa that will greatly improve the scope and effectiveness of the LEWS DSS. These four activities/objectives are as follows:

- 1) Characterization and verification of water resources identified with NASA Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER), Shuttle Radar Topography Mission (SRTM) data to add a water resource mapping component to the LEWS DSS;
- 2) Improvement of the forage mapping component of the LEWS DSS using Moderate Resolution Imaging Spectroradiometer (MODIS) Vegetation Continuous Fields (VCF) data to extend field collected data to other unsampled areas;
- 3) Mapping of seasonal migration patterns and resource utilization of pastoral lands using GPS technology;
- 4) Operational monitoring of water resources with NASA Tropical Rainfall Measuring Mission (TRMM) data.

For each of these activities, the current status and results of each of these activities will be provided.

Activity 1: Characterizing water resources with ASTER and SRTM data

The main objective of this activities is to create a regional water resources inventory through the construction of a geo-database of waterholes, land cover and their drainage areas using spectral analysis of Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) and Moderate Resolution Imaging Spectroradiometer (MODIS) satellite imagery and applying watershed delineation tools on the 90m Shuttle Radar Topography Mission (SRTM) data. In May 2007, the USGS/EROS Data Center conducted the spectral analysis of the study area using ASTER imagery acquired during the period from 2000 to 2006. A total of 70 scenes were acquired that covered almost 85% of the study area. The analysis by USGS EROS identified 88 possible waterholes in the study area. For these, 52 were in Ethiopia, 34 in Kenya and 2 in Sudan. Only cloud free areas of the images were used to identify these waterholes, which could imply the possible existence of more waterholes that were not visible in the image due to clouds and cloud shadows.

Starting in August 2007, field surveys were conducted to verify the satellite-based classifications of water holes delineated by USGS-EROS and to acquire further ancillary data for incorporation into the geodatabase on water resources in the study area. This data will include characterization of the general hydrology of the water hole (rain-fed or subsurface), flow regimes as well as technical details and locations of other water schemes such as boreholes, ponds, dry river beds, shallow wells, *birkas*, earth dams and other watering points, including those that were not identified during the ASTER imagery/SRTM analysis. The field inventory emphasized temporal characteristics on prevailing patterns of seasonal water availability as used by pastoralists and was particularly focused on those regions where water becomes limiting during dry periods of the year.

Field Verification – Kenya

Field Verification continued during Kenya during the reporting period. However during the months of April to November, no data were collected at the majority of waterholes in Kenya due to an extreme drought in the region that caused the monitors to have to move out of the region to be able to access water for their livestock. KEN-15 and KEN-16 waterholes were the exception with monitoring occurring at these sites during this period. Data collection continued at all of the selected waterholes during the period from December (Figure 1) to present. Data have been transferred to USGS and South Dakota State University for processing and validation studies.



KEN-22 as it appeared in August 2007 and December 2009. The inlet seen on the left photo had now been covered by water to a height of about 1 meter. The pan is very well taken care of and the water is very clear.

Photos: Gatarwa Kariuki

Figure 1. KEN-22 waterhole differences during 2007 vs. 2009 data collection.

Field Verification – Ethiopia

Field verification of waterholes continued in Ethiopia throughout the reporting period. Due to large rain volumes during late 2009, many of the waterholes were filled and exceeded the gauges that had been established for monitoring depths in the waterholes (Table 1). Data have been transferred to USGS and South Dakota State University for processing and validation studies.

Benchmarking Surveys

A baseline benchmarking survey was developed for use by the field teams in both Ethiopia and Kenya to gather information from local users of the water resources. The field teams conducted community interviews to gather information on community use of the water resources and to gather baseline data on the use of LEWS DSS products. Community interviews in Kenya have been completed. The community interviews covered the major ethnic groups while ensuring good geographical distribution. A total of 144 community members, most of whom were male (95.8%) participated in the focal group discussions.

Table 1. Results of water gauge reading comparing August and October 2009 water level and previous year's water level (2008).

No	Name of pond (Haro)	October 2008 reading (cm)	August 29 th reading(cm)	October 28 th reading(cm)	Changes from the previous	Remark
1	Wirwita (ET-3)	25	50	150	+100	Found in a good condition. Irrigation started near the dam
2	Dembi Korba (ET-5)	75	0	0	0	The water shrink about 21 feet toward the center from the gauge
3	Bake (ET-13)	130	50	106	+56	Characterized by shallow depth and large surface area
4	Orbate (ET-15)		-	-	-	Its embankment collapse by gully
5	Dimtu (ET-26)	0	40	>200	>160	The water overtop the gauge
6	Jilo Dokicha (ET-29)	18	0	110	+110	Gully erosion started at the inlet of dam
7	Muyate	25	160	150	-10	Sand water treatment started near the dam by AFD

A survey conducted for government and aid institutions in the region. This survey was conducted using online tools so that it could be easily disseminated and not require teams to conduct the survey. The survey was sent out to government and aid institutions in August 2008. Since that time, 27 individuals/organizations have taken the survey. As with the communities, the government and aid organizations were asked to rank problems related to livestock within their region according to the severity of the problem. Shortage of forage and shortage of water were ranked by most respondents as the most important factor when making decisions to migrate (Table 2).

Table 2: Government and aid organization’s ranking of reasons in order of their importance for a family decision to migrate from one area to another.

Question	Major Consideration	Minor Consideration	Not a Factor	Rating Average	Response Count
Shortage of forage	14	0	1	2.87	15
Poor forage quality	2	11	1	2.07	14
Shortage of water	14	0	1	2.87	15
Poor water quality	3	7	2	2.08	12
Disease outbreak (specify)	8	4	1	2.54	13
Conflict/insecurity emerging	10	3	1	2.64	14
Need to market livestock	2	5	6	1.69	13
Traditional time to move	4	7	2	2.15	13
Wildlife menace	0	8	5	1.62	13
Access to social amenities e.g. school, dispensary, shops, etc.	0	8	5	1.62	13
Other (please specify)					0

Benchmarking Workshops

Two workshops were held in east Africa in an effort to introduce a new NASA/LEWS Decision Support System (DSS) product to key stakeholders and decision makers on 24th and 25th March in Nairobi, and on 29th and 30th March in Addis Ababa, Ethiopia. The primary purpose of the workshops was to engage stakeholders in discussion about (i) incorporation of key components from the forage monitoring component of the livestock early warning system (LEWS) (<http://glews.tamu.edu/africa>) (ii) the livestock market information system (LMIS) associated with the Livestock Information Network and Knowledge System (LINKS) project (<http://www.lmiske.net> and <http://www.lmiset.net> for Kenya and Ethiopia, respectively) (iii) the new water-monitoring tool developed by USGS (<http://watermon.tamu.edu>) to enhance the existing LEWS DSS. Ultimately, the intent was to create a new enhanced early warning system DSS called the Livestock Vulnerability Index (LVI). The NASA/LEWS team was composed of: Gabriel Senay (USGS), Jay Angerer (Texas AgriLife Research), Manohar Velpuri (SDSU/USGS), Gatarwa Kariuki (ILRI-Kenya), Sintayehu Alemayehu (ILRI-Ethiopia), and Steven Hockett (Texas AgriLife Research).

The objectives for the workshop were to: 1) discuss existing early warning products and gather stakeholder feedback; 2) evaluate this feedback and discuss how we might develop final products; 3) identify who the target audience should be and how best to disseminate information to them, and; 4) to explore options for combining data/tools to assist other development efforts in arid and semi-arid lands. The proposed LVI was envisioned to provide producers, marketers, pastoral communities and decision makers’ access to early warning information regarding water and forage in an easy to use one-stop shopping format. This format would provide near real-time data regarding forage and water conditions by combining data from existing information systems to enhance the ability to pinpoint areas of vulnerability, and thus, to better protect livelihoods. Ultimately, the LVI would be a valuable tool for addressing food security issues related to livestock, conflict management, and provide important information for livelihood improvement efforts throughout East Africa.

The first workshop, held in Nairobi Kenya at the Jacaranda Hotel, had 19 participants in attendance. The second workshop was held in Addis Ababa, Ethiopia on the International Livestock Research Institute campus where 31 individuals participated. These participants represented a range of institutions (attendee lists for both workshops are attached). Topics of discussion included an introduction to NASA technologies available to identify waterholes (surface water resources) in semi-arid east Africa using remotely sensed data and imagery, and an introduction and demonstration of a simulation model designed for processing this information into a user friendly format.

The hands-on demonstration of the Water Monitoring website (<http://watermon.tamu.edu>) online demonstration was enthusiastically received by all participants in both workshops and generated many discussions about how it could be adapted to fill specific needs for various projects. The consensus was that this was a very good product with many applications ranging from livestock movement and livelihood improvement to conflict zone mitigation efforts.

After the online demonstration, a survey was conducted using four questionnaires that focused on 1) the usefulness of the waterhole monitoring data for livestock early warning, 2) the waterhole monitoring product, 3) on the performance of the waterhole monitoring website, and 4) on evaluating the improved-performance of the project compared to existing methods.

After demonstration of the water monitoring product, an overview of the existing LEWS and LMIS systems was presented on the second day of the workshop. These deliberations then turned to the introduction of the Livestock Vulnerability Index (LVI) concept. The primary focus of the second day of the workshop was to engage stakeholders in a discussion about the LVI concept to elicit ideas for how best to develop the LVI to maximize its utility as a DSS. The audience proved to be quite interested in such a product and joined in animated discussion and debate about how best to develop the product, who would be the primary audience and users of this information, and how best to disseminate the product to stakeholders. Feedback from participants included their observations of major strengths and weaknesses of the proposed LVI systems and suggestions for improving the concept. These major points were:

Strengths

- The LVI would provide a “one-stop” shopping portal for early warning information related to livestock and livelihoods that rely on livestock
- Combined several key data sources to provide better and integrated early warning information
- Near-real time information for decision makers
- Presentation is simple and easy to use/understand
- Ability to model trends in waterholes and range vegetation through time
- Provides a tool to monitor effects of with climate change, land use and degradation
- Relevancy for the pastoralists, real users
- Important to involve users in consultations and collective decision-making
- potential to inform trans-boundary issues on trade and animal health

Weaknesses

- The need to include borehole and well monitoring
- Need to increase coverage area to include more waterholes; expansion to other pastoral areas
- Concern that small waterholes are not captured
- Need to assess or account for water volume at waterholes
- Need to improve the vegetative cover to maintain livestock and link to status of the water points
- Need to work on dissemination so as to maximize the utility of the DSS
- The need develop capacity to forecast water conditions at least one month into future
- Literacy among pastoralists and lack of access will reduce its use
- Need to get input of private sector or other stakeholders

An important consideration discussed was how to disseminate the information produced with the LVI and the water monitoring products. Several mediums such as radio, ministry bulletins, news outlets, traditional communications (word of mouth) were discussed. A second important discussion point was the issue of institutionalization. Because of past challenges of maintaining project-based activities beyond termination of the project, it is our intent to develop the system and institutionalize it as soon as possible so that “ownership” of the LVI system becomes embedded in the host countries. Adoption of the system is envisioned to be by a willing national government agency, regional non-government organization, or other appropriate institution, and be technically supported by Texas A&M/Texas AgriLife Research or USGS. This of course will depend primarily on how rapidly local capacity to operate and maintain the LVI is developed.

The LVI concept was enthusiastically received by stakeholders at both workshops, as a way to amalgamate several existing early warning products into an efficient and useful DSS for improving management of livestock resources throughout the East Africa region. This model is intended to serve as an affordable clearinghouse of key information for governments, NGOs and pastoral communities to enhance their decision making ability for livelihood improvement and policy development more holistically than has been the case in the past. Information derived from LVI can be easily integrated with existing programs within regional governments, USGS-Famine Early Warning Systems Network (FEWS NET), Intergovernmental Authority on Development's (IGAD) Conflict Early Warning and Response Mechanism (CEWARN), and livestock market information systems (LMIS), to name a few.

Due to its near real-time GIS-based platform, pastoral communities will have an effective tool for planning livestock movement based on availability of water and forage. Other tangible uses of this product include early warning information for alleviating effects of drought (water and forage conditions), policy development, conflict mitigation between different groups over issues pertaining to access to water and grazing resources, early warning to assist with marketing decisions, and future research and feasibility studies for new waterhole locations. It was felt that existing ministries of livestock or water resources would have a comparative advantage with its extensive structure of extension and network of field monitors at local levels. It is the intent of the U.S. partners to continue providing technical back-stopping of the product. Potential consumers and partners of the LVI identified in the workshop include the following:

- Pastoral Communities
- Regional Governments, Ministries of Water Resources / Livestock
- Ministries of Northern Kenya, Southern Ethiopia, and other Arid Areas
- Disaster Risk Management and Food Security Sector (DRMFSS) – Early Warning and Response Directorate
- NGOs: CARE International, VSF Consortium, JICA, GAA, CordAID, GTZ, Acted, OCHA, Save the Children, CARE Pastoralists Coordination Program, UNICEF – Emergency Water Cluster, OXFAM (GB, USA, Spain), ACF, Global Water Initiative (GWI) - Regional Program
- World Bank, African Development Bank, DFID, ASERACA, UN-WFP Vulnerability Analysis and Mapping (VAM) and FAO - Emergency and Recovery Unit
- Regional Universities
- Famine Early Warning Systems Network (FEWSNET)
- Pastoral Community Development Program, Arid Lands Resource Management Program,
- Consultants and other private livestock groups

A central, under-lying theme of these workshops was to facilitate more collaboration among research and development institutions which takes steps toward more effective livelihood improvement efforts throughout East Africa and beyond.

NASA-LEWS PARTICIPANTS – Kenya (top) and Ethiopia (bottom)

Activity 2: Mapping forage baseline with MODIS Vegetation Continuous Fields

Livestock Early Warning System (LEWS) Methodology

As part of the implementation of the forage monitoring simulation model for the LEWS DSS, baseline plant community information is determined by a ground sampling approach in which selected sites are visited by the LEWS teams to characterize vegetation community parameters. Simulation model runs are then parameterized for each of the sampling sites using the field information and near real-time climate data as driving variables. Modeling results for the sampling sites are then geostatistically interpolated to unsampled areas using NDVI data to produce regional maps of forage conditions. For this activity, we began the assessment on whether we could use MODIS Vegetation Continuous Fields (VCF) data to identify new monitoring sites and assist in forage model parameterization at these new sites to alleviate the need for additional field sampling.

During the current reporting period, data were prepared for developing simulation model runs using the PHYGROW model with generic tree and herbaceous components parameterized for forage production using the VCF values. This analysis is ongoing and the data will be presented in the final report.

Activity 3: Mapping seasonal migration patterns with GPS technology

Under this activity, the movement patterns of pastoralists and their livestock herds in response to changing forage and water supply will be tracked using GPS tracking technology. This will allow comparisons of the various communities' mobility and grazing management behaviors to the prevailing forage and water resource conditions and provide insights that will allow improvement in the LEWS information flow in the target region. The outcome of this activity will be to develop practical recommendations that pastoral communities and land managers can use to optimally exploit the forage and water resources and improve the productivity in these arid and semi-arid rangelands.

During the reporting period, the initial efforts of providing GPS units to pastoralists to use for the herd migration study proved to be inadequate because of logistical issues with batteries and for collecting the instruments for download. It was decided that a more useful method of collecting this data would be to meet with personnel and NGO's that were collecting this data as part of ministry work and relief efforts in the area and to conduct interviews with village leaders. In May 2010, field surveys were conducted in Northern Kenya and Southern Ethiopia. Data from NGOs and ministry officials was gathered and maps of migration routes during the last 10 years were provided in some cases. The data and maps will be used to develop a herd migration route geodatabase that can be used to inform decision making in response to drought and lack of water. This, when combined with the water monitoring and forage products, will be useful in developing appropriate migration strategies in the event of future droughts. Analyses of the results of this study are ongoing and will be provided in the final report for the project.

Activity 4: Operational monitoring of water resources with TRMM

In this activity, it is planned that new water resources monitoring products will be added into the LEWS DSS. These new products will be essential for monitoring the conditions of water resources that are vital in decision making by the user community of herders. In particular, daily water availability monitoring products will be developed for individual waterholes, and daily river flow hydrographs of major streams along the migration routes will be produced.

The majority of tasks for this activity are being conducted by the USGS/EROS team in association with the ASTER imagery analysis under Activity 1. USGS-EROS has developed daily rainfall estimates subsetted from the NASA TRMM dataset for Africa. A modeling framework for modeling daily catchment runoff for the contributing areas around waterholes using the TRMM dataset has been developed and is fully operational. Daily water level changes (whether positive or negative) are being estimated for sixteen (16) major waterholes identified under Activity 1 of this study using similar techniques by Senay and Verdin (2004).

The Texas AgriLife Research team has worked with USGS and their subcontractor South Dakota State University to develop a web portal for displaying the water monitoring activities. The website can be viewed at <http://watermon.tamu.edu>. This website offers users the ability to monitor and download waterhole depth information from 1998 to present. The sixteen representative waterholes in the region are being operationally monitored (with a day lag) for

variations in waterhole depths. The site provides the current status of depths for each waterhole (daily depth variation information) which would enable pastoral communities to make appropriate decisions on their migratory movements in search of water and forage. It also allows users to examine the median water levels along with past years data.

During this reporting period, the site has been enhanced to provide a low-bandwidth version to allow easier access of information in rural areas of Ethiopia and Kenya with slow internet connections. The site was also enhanced to provide near real-time tracking of the status of the waterhole conditions by color coding the indicators on the Google map interface (Figure 2). The help and information components were also improved to make the site more user-friendly.

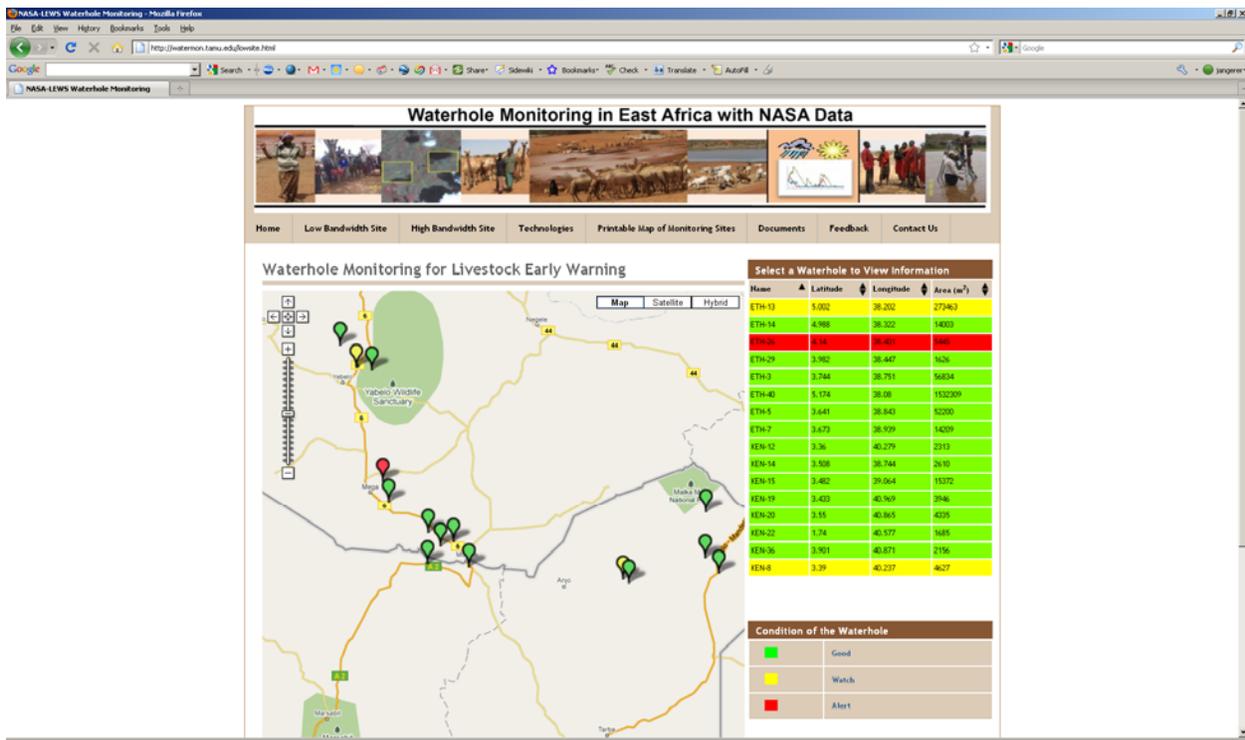


Figure 2. Water monitoring website depicting the color coding of the waterhole condition on the Google map interface.

References

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Award No. 08HQAG0118 Transboundary Aquifer Assessment Program

Basic Information

Title:	Award No. 08HQAG0118 Transboundary Aquifer Assessment Program
Project Number:	2008TX353S
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End Date:	3/30/2013
Funding Source:	Supplemental
Congressional District:	
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Models, Hydrology
Descriptors:	
Principal Investigators:	Ari Michelson

Publications

There are no publications.

**UNITED STATES – MEXICO TRANSBOUNDARY AQUIFER
ASSESSMENT PROGRAM
ANNUAL REPORT FOR FISCAL YEAR 2009 – April 2009 to March 2010
New Mexico and Texas Water Resources Research Institutes
in Collaboration with USGS NM and TX State Offices
Prepared by TWRI and Texas AgriLife Research Center at El Paso**

Objectives of the Transboundary Aquifer Assessment Program are to collect and evaluate new and existing data to develop high-quality, comprehensive groundwater quantity and quality information and groundwater flow models for selected priority binational aquifers in Arizona, New Mexico and Texas and Mexico. The Mesilla Basin aquifer was selected as the primary initial focus of the New Mexico and Texas assessment program because of the importance and immediate need for information regarding this aquifer. In the first year (FY 08), the project team of the New Mexico and Texas WRI's and USGS State Offices focused efforts on coordination with stakeholders, development of a scope of work and a review of existing literature and hydrologic models regarding the Mesilla Basin aquifer. Achievements for FY 2009 include:

- ❖ Updated the joint New Mexico and Texas WRI and USGS coordinated Work Plan based on research findings and analysis conducted in the initial phase of the Mesilla Basin aquifer assessment.
- ❖ Accomplishments of the Work Plan tasks in FY2009 include:
 - Expanded review and evaluation of approximately 800 publications and previous studies on the Mesilla Basin and development of a database for bibliography search and sharing; All the publications have been incorporated into the EndNotes.
 - Continued to review and assessment of existing geological, hydrogeologic monitoring data, ancillary databases, and GISs for the Mesilla Basin from different sources, such as U.S. Geological Survey, New Mexico Office of State Engineer, Texas Water Development Board, Paso del Norte Watershed Council as well as available Mexico data and information;
 - Continued review and evaluation of existing hydrogeologic framework models with expanded scope into Mexico portion of Mesilla Basin;
 - Finished review of seven existing groundwater models for the Mesilla Basin aquifer;
 - Continued to identify data gaps and additional information needed for hydrogeologic model development;
 - Prepared a preliminary technical report on “Previous Studies on Characterization of Transboundary Aquifer at Fillmore Pass between the Mesilla Bolson, New Mexico and the Hueco Bolson, Texas” and additional field work planned pending approval of Fort Bliss.
- ❖ More than six bi-national meetings were held with the Commissioners and Principal Engineers of the U.S. and Mexican Sections of the International Boundary and Water Commission, Mexican National Water Commission, USGS National and State Offices and the three Water Resources Research Institutes to negotiate and finalize an agreement for scientific exchange, coordination and collaboration between U.S. and Mexican agencies, organizations and scientists regarding this transboundary aquifer assessment program. The agreement was signed by IBWC and CILA August 19, 2009 in a ceremony on the International Bridge.
- ❖ In collaboration with the New Mexico Water Resources Institute an RFP and proposal template were prepared and provided to Mexico researchers in preparation for MX proposal submission to the TAA program. Proposal development for the next FY was initiated through IBWC/CILA.
- ❖ A presentation on The US-MX Transboundary Aquifer Assessment program was made in a special session on world-wide transboundary water resource programs at the American Water Resources Association Annual Conference in Seattle, WA, November 2009.

- ❖ Frequent conference calls and e-mail correspondence continue to be used to collaborate and coordinate TWRI, El Paso Research Center, NMWRRI, AZWRRI, and USGS national, and the three USGS State Offices scientists in this program.

Occurrence of Pharmaceuticals and Personal Care Products (PPCPs) at an effluent-dominated wastewater application site: Estrogens, Triclosan, and Caffeine

Basic Information

Title:	Occurrence of Pharmaceuticals and Personal Care Products (PPCPs) at an effluent-dominated wastewater application site: Estrogens, Triclosan, and Caffeine
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FINAL REPORT

Occurrence of Pharmaceuticals and Personal Care Products (PPCPs) at an effluent-dominated wastewater application site: Estrogens, Triclosan, and Caffeine

Project Number 2009TX319B

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Abstract

Pharmaceuticals and personal care products (PPCPs) have recently been identified in the environment; their potential effects on ecosystems are of increasing concern. These contaminants can reach the soil and aquatic environment through land application of wastewater effluent and agricultural runoff. The objective of this work was to assess the fate of PPCPs at field scale. PPCPs were measured systematically in a wastewater treatment plant (WWTP), and in soil and groundwater receiving the treated effluent from the WWTP. The occurrence of target PPCPs was evaluated to determine PPCP transfer from the WWTP to soil and groundwater. The Lubbock Land Application Site (LLAS) was used as the study site, which has received treated wastewater effluent for more than 70 years in order to remove additional nutrients and irrigate non-edible crops. The site was ideal for investigating the long-term fate of PPCPs in the environment above drinking water sources. Target compounds (e.g., estrone, 17 β -estradiol, estriol, 17 α -ethynylestradiol, triclosan, and caffeine) in wastewater, sewage sludge, soil, and groundwater were determined using HPLC/UV as the primary mode of analysis with qualitative confirmatory analyses using GC-MS on a portion (10%) of the samples. Samples were collected quarterly over twelve months for wastewater and sludge samples and over nine months for soil and groundwater samples. The results indicated that concentrations of PPCPs in the influent, effluent, sludge solid phase, and sludge liquid phase were in the range of not detected (ND)-127 $\mu\text{g/L}$, ND-83 $\mu\text{g/L}$, ND-19 $\mu\text{g/g}$, and ND-50 $\mu\text{g/L}$, respectively. Concentrations in soil and groundwater samples from the LLAS were in the range of ND-136 ng/g and ND-1,745 ng/L . Overall, data suggested that PPCPs in the effluent from the wastewater treatment plant could be transported both

vertically and horizontally in the soil, and eventually transported to groundwater via land application of the effluent.

Problem and Research Objectives

Pharmaceuticals and personal care products (PPCPs), which are identified in the environment, have prompted an important concern on their ecotoxicity and persistence in the environment (Daughton and Ternes 1999). Some natural estrogens such as estriol, estradiol and estrone are considered to be potent endocrine disruptors (Gross et al. 2004; Ying et al. 2004). However, the fate and persistence of these compounds in the environment are still unclear (Daughton and Ternes 1999; Gross et al. 2004; Kolpin et al. 2002; Ankley et al. 2007). Other antimicrobial compounds (for example, triclosan is used in many personal care products) are believed to lead to the development of antibiotic resistance and are considered as persistent chemicals in the environment (Ying and Kookana 2007). These PPCPs transport to municipal wastewater treatment plants (WWTPs) and eventually are discharged into aquatic environments or continued to exist in surface water, groundwater, and soil (Chu and Metcalfe 2007; Allaire et al. 2006).

Hundreds of tons of PPCPs are estimated to be produced and consumed annually in the developed countries (Scheytt et al. 2006; Polar 2007). The effluent from WWTPs is the primary route of these PPCPs being introduced into the environment. Since wastewater treatment processes are designed to remove pathogens and nutrients from sewage, PPCPs can only be incidentally removed and the elimination is variable (Daughton and Ternes 1999; Heberer 2002a). Most PPCPs consumed by humans enter the wastewater system; they can be excreted completely unmetabolized, rinsed off of the body, or disposed as unused medications. Some PPCPs are conjugated in the body prior to excretion. These conjugated forms are often broken during the wastewater treatment process and transformed back to the parent compound. The PPCPs are not typically persistent, but are constantly released into the environments and hence, PPCPs have the potential for continual environmental entry (Heberer 2002a; Kümmerer 2004; Gielen et al. 2009). Several studies have determined that PPCPs exist in effluents in the range of high ng/L to low µg/L concentrations, and can be detected in stream surveys in the United States (Gross et al. 2004; Haggard et al. 2006; Waltman et al. 2006; Glassmeyer et al. 2008). Although PPCPs occur at relatively low concentrations, their continual long-term release may result in significant environmental concentrations.

Effluents from WWTPs are increasingly applied to irrigate crops and public areas in arid regions in the United States, as well as other countries to reduce the demand on water supplies (Pedersen et al. 2005; Kinney et al. 2006). The effluent is also applied to lands for the natural treatment of wastewater as the effluent moves through the natural filter provided by soil and plants (Davis and Cornwell 1998; Overcash et al. 2005). Such application to lands is considered as the oldest method for the treatment and disposal of wastes. There are around 600 communities in the United States reusing the effluent from municipal wastewater treatment plants for surface irrigation (Davis and Cornwell 1998). However, the application of wastewater to lands is also a route of PPCPs transfer to soil (Oppel et al. 2004). Various PPCPs in the effluent, such as estrogens, can sorb to soil once the soil is exposed to these compounds (Casey et al. 2005; Drillia et al. 2005; Hildebrand et al. 2006). These compounds can be transported from the soil to other

aquatic systems such as surface water and groundwater, the extent of which is dependent on various factors including the solubility, sorption behavior, and persistence of the contaminant as well as climatic conditions and physicochemical properties of the soil (Boxall 2008). Since PPCPs remaining in treated wastewater can leach or percolate through the soil to groundwater supplies during runoff events or subsurface flow, concerns about these compounds in the effluent entering potential drinking water resources and the environment are increasing. There are several reports indicating that PPCPs such as estrone, ibuprofen, diclofenac, and chlorthalidone can be detected in groundwater and drinking water (Ternes et al. 2001; Heberer 2002b, Rodriguez-Mozaz et al. 2004).

The objective of this work was to study the fate of PPCPs at field scale. The PPCPs were measured systematically in a WWTP, and in soil and groundwater receiving effluent from the WWTP. The occurrence of target PPCPs were evaluated to obtain the overall view of PPCPs transfer from the WWTP to soil and groundwater. The unique study site “the Lubbock Land Application Site (LLAS)” selected for the project is a wastewater land application site used for nutrient removal and non-edible crop production. The LLAS has received wastewater effluent for over 70 years, and is the ideal site to determine the long-term fate of PPCPs in the environment above drinking water sources. Target PPCPs included estrone (E1), 17 β -estradiol (E2), estriol (E3), 17 α -ethynyl estradiol (EE2), caffeine, and triclosan. Target PPCPs were determined using HPLC/UV as the primary mode of analysis; qualitative confirmatory analyses utilized GC-MS on a portion (10%) of the samples. The GC-MS technique was applied for the confirmatory analyses because of its ease of convenience over the LC-MS.

Materials and Methods

Study Area

The Lubbock Water Reclamation Plant (LWRP) located in Lubbock, Texas, served as the test facility for the fate of PPCPs in a full-scale WWTP. Wastewater is delivered to the plant through 900 miles of collection lines and 21 lift stations. Lubbock’s water consumers can be characterized as residential (85%), small commercial (10%), municipal (4%); other user classes (1%) include industrial, schools, wholesale, and irrigation. The LWRP treats approximately 21 million gallons of wastewater per day and has an average daily flow design capacity of 31.5 million gallons. There are three process streams for the plant including one bio tower process and two activated sludge processes (Fig.1). The primary treatment of the influent to the plant consists of screening and grit removal. After primary treatment, the flow streams are split before secondary treatment. The plant applies activated sludge in Plants 3 and 4 for secondary biological treatment. Plant 2 uses biotowers for secondary treatment. Without tertiary removal, treated effluent is reused; nearly two-thirds of wastewater produced each day are reused by agricultural irrigation at land application sites and as industrial cooling water. Some effluents are also disposed by discharge to streams. Sludge from secondary treatment is thickened, digested in anaerobic digesters, dewatered, and landfilled.

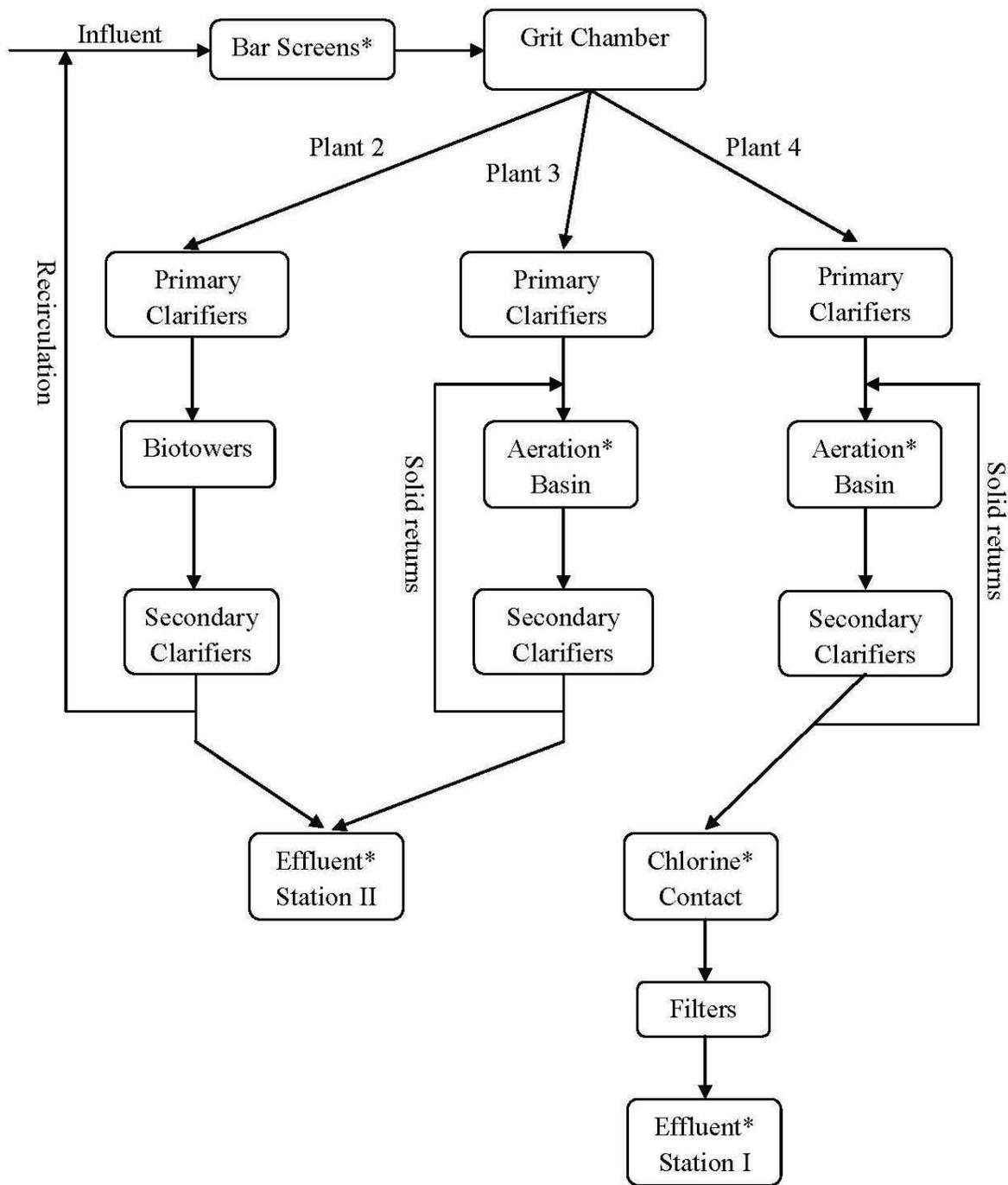


Fig. 1 Process schematic of the Lubbock Water Reclamation Plant (LWRP). The asterisk (*) indicates sampling locations.

The Lubbock Land Application Site (LLAS) is the 6,000-acre irrigated farmland used by the city of Lubbock as a site of secondarily-treated wastewater effluent application. The LLAS is seeded with grasses, cotton and legume plant species that absorb and utilize the high amount of nitrogen compounds present in the effluent. The site has been in use for this purpose since 1937, starting with 200 acres with additional land purchased over time. Since then, monitoring wells have been constructed and used to determine the amount of pollutants, especially nitrate concentrations in the groundwater at various locations. Pivot irrigation systems are employed to apply the effluent to 31 treatment plots comprising a total land area of 2,538 acre. A storage reservoir of 412 million gallon enables the farm to store and distribute treated effluent to the treatment plots as needed. On a daily basis, approximately 13 million gallons of effluent from the LWRP are applied to treatment plots. Prairie dogs occupy approximately 700 acres of the 6,000-acre site; however, only about 30% of the occupied area is under the center pivot points.



Sampling points inside pivot irrigation at the LLAS

Sample Collection

Wastewater and sludge. Grab samples of wastewater and sludge were collected from various sampling points at the LWRP (Fig. 1) quarterly from December, 2008 through September, 2009 to determine the fate of target compounds in the plant. As the LWRP contains three independent process trains referred to as Plant 2, 3, and 4, samples were collected from Plants 3 and 4 in order to compare water quality between these plants that attain different effluent water quality. Approximately 50 percent of the plant flow was sent to Plant 4. Since the removal of PPCPs from the wastewater stream may indicate the chemicals present in the sludge, it was important to obtain the data of PPCPs concentration in both wastewater and sludge for determining the phase in which the chemical persists, if it was not degraded. Wastewater samples were collected at bar rack, aeration basin, chlorine contact chamber, and effluent station. Sludge samples were collected from feed sludge, which was the wasted sludge from the secondary treatment, and anaerobic digester. All samples were collected in 1-L amber jars stored on ice during transport to the laboratory and refrigerated at 4°C until extraction.

Groundwater and soil. Groundwater and soil samples were collected at the LLAS to determine whether PPCPs accumulate in the soil and/or transport into the groundwater. There were four sampling points named after the code of monitoring wells: CL-11, CL-29, CL-43 and CL-48. The CL-29 and CL-48 were the wells located outside the area of pivot irrigation, while the CL-11 and CL-43 were under the center pivot points. At all sampling points, both groundwater and soil samples were collected quarterly in the same days from March, 2009 through September, 2009. Groundwater samples were collected from a tap above the wells, stored in 1-L amber glass bottles on ice during transport to the laboratory, and refrigerated at 4°C until processed prior to analysis. Soil cores were collected from each sampling point at a depth of 0-30 inch to cover target soil depths of 0-6 inch, 12-18 inch, and 24-30 inch. A soil core sampler with diameter of 4.5 cm was used for soil sampling. Soil cores were stored at 4°C until further use for PPCPs analysis.

Chemical and Reagent

Anhydrous caffeine (purity > 99%) and estrogenic compounds, including E1 (purity > 99%), E2 (purity > 98%), E3 (purity > 99%), EE2 (purity > 98%), β -estradiol-17acetate (purity > 99%), and triethylamine (purity > 99%) were obtained from Sigma-Aldrich (St. Louis, MO). Triclosan (purity > 97) was purchased from Fluka Chemie GmbH (Buchs, Switzerland). Relevant chemical properties of the test compounds are shown in Table 1. HPLC-grade acetonitrile was obtained from Fisher Scientific (Fair Lawn, NJ). Ultra-pure water (> 18M Ω) was prepared by a Barnstead NANOpure infinity ultrapure water system (Dubuque, IA). Standard solutions of test compounds were prepared in 1:1 (v/v) acetonitrile:water for estrogens and 100% acetonitrile for caffeine and triclosan.

Table 1 Chemical properties of the test compounds

Compound	Water solubility (mg/L at 20 °C)	log K _{ow}	K _d (mL/g)	Vapor pressure (mm Hg)
Estrone (E1)	13 ^b	2.95 ^a	67.7 ^d	1.41 x 10 ^{-7 c}
17β-estradiol (E2)	13 ^b	3.86 ^a	115.8 ^d	1.26 x 10 ^{-8 c}
Estriol (E3)	13 ^b	2.45 ^a	8.6 ^d	1.97 x 10 ^{-10 c}
17α-ethynylestradiol (EE2)	4.8 ^b	3.67 ^a	176.2 ^d	2.64 x 10 ^{-9 c}
Triclosan	10 ^c	4.76 ^c	256.8 ^d	6.45 x 10 ^{-7 c}
Caffeine	2.16 x 10 ^{4 c,*}	-0.07 ^c	18.5 ^d	15 ^c

* at 25 °C

^a Machatha and Yalkowsky (2005)

^b Ying and Kookana (2005)

^c National Library of Medicine Toxnet (<http://toxnet.nlm.nih.gov>)

^d Karnjanapiboonwong et al. (2010)

Sample Preparation

Wastewater. Wastewater samples were first filtered through a 10-cm P5 filter paper (Fisher Scientific, PA, USA) to remove suspended solids. Solid phase extraction (SPE) was applied for target PPCP analysis. The extraction procedure of target compounds (E1, E2, E3, EE2, triclosan, and caffeine) was modified partially based on methods reported in the literature (Kvanli et al, 2008) using C18 SPE cartridge. β-estradiol-17acetate (EA) was also used as an internal standard for QA/QC purpose. The 200 mL of sample was passed through an SPE cartridge (Honeywell Burdick & Jackson, MI, USA, Product No.9008), which was first conditioned with 3 mL of acetonitrile followed by 3 mL of Milli-Q water. Then, samples were extracted through SPE cartridges at a flow rate < 5 mL min⁻¹ and were subsequently eluted with 3×1 mL of acetonitrile. The eluate was then analyzed using HPLC/UV or derivatized for GC-MS analysis on a portion (10%) of samples. The recovery of this extraction method in both clean (Milli-Q) water and wastewater matrices were shown in Table 2. The method applied also provided adequate detection limits (Table 3) using the U.S. EPA guidelines (U.S. EPA, 2000).

Sludge. Sludge samples (200 mL) were filtered by using 10-cm P5 filter papers to separate the solid phase from the liquid phase. Filtrate was extracted with the same procedure as described in wastewater samples extraction. The solid phase of sludge samples was air-dried and the dry weight was noted. In 250-mL FEP centrifuge bottles, the air-dried sludge samples were extracted for the determination of estrogens, caffeine, and triclosan by 30 mL of acetonitrile. The EA was also used as an internal standard for QA/QC purpose. The samples were then agitated on an orbital shaker for 2 hours and

centrifuged for 10 min (4,000 rpm). The supernatant was collected, evaporated to about 500 μ L under nitrogen stream, and made up to 3 mL with acetonitrile.

Sludge supernatants collected were analyzed to determine target PPCPs by using HPLC/UV. A portion of samples (10%) were derivatized for the qualitative confirmatory analyses using GC-MS. The recovery and detection limit of sludge extraction methods are shown in Tables 2 and 3, respectively.

Groundwater. Groundwater samples were first filtered through a 10-cm P5 filter paper to remove suspended solids. The extraction of PPCPs was performed by the same procedures as described in wastewater samples extraction. The 500 mL of groundwater sample was passed through C18 SPE cartridge which was conditioned with 3 mL of acetonitrile followed by 3 mL of water. Samples were then eluted with 3 \times 1 mL of acetonitrile, evaporated to about 100 μ L under nitrogen stream, made up to 1 mL by acetonitrile, and analyzed by using HPLC/UV. Detection limits of these methods based on the U.S. EPA guidelines are presented in Table 3.

Soil. Each soil core sample was subdivided into five 6-inch segments. Only soil samples at the depths of 0-6 inch, 12-18 inch, and 24-30 inch were applied to determine the concentration of target PPCPs. Each sample was air dried and mixed well for homogeneity. The extraction of PPCPs was done by the same procedures as those for sludge samples. 30 g of soil was extracted in a 250-mL FEP centrifuge bottle with 30 mL of acetonitrile for the extraction of E1, E2, EE2, and triclosan, and with 30 mL of 3:1 acetonitrile:water (v/v) for the extraction of E3 and caffeine. EA was also used as an internal standard for QA/QC purpose. Then, samples were agitated on an orbital shaker for 2 hours and centrifuged for 10 min (4,000 rpm). The supernatant was collected, evaporated to about 500 μ L under nitrogen stream, and made up to 3 mL with acetonitrile.

Soil supernatants collected were analyzed to determine target PPCPs by using HPLC/UV. A portion of samples (10%) were derivatized for the qualitative confirmatory analyses using GC-MS. The recovery and detection limit of sludge extraction methods are shown in Tables 2 and 3, respectively.

Derivatization.

Prior to GC-MS determination, samples were derivatized using N-methyl-N-(trimethylsilyl)-trifluoroacetamide (MSTFA) following methods of Ternes et al. (2002) and the U.S. EPA Method 1698. Derivatized samples were analyzed by GC-MS in the selected ion monitoring (SIM) mode using the respective parent and 1-2 daughter ions for each compound.

Table 2 The recovery obtained from extraction methods and HPLC/UV analysis applied for PPCPs in different types of matrices (n=3).

Compound	Recovery (%)			
	Milli-Q water ^a	Wastewater ^a	Sludge ^b	Soil ^b
E1	105.9 ± 1.1	102.5 ± 5.7	51.1 ± 3.2	98.5 ± 0.2
E2	109.8 ± 7.9	106.0 ± 0.5	38.9 ± 4.2	94.7 ± 1.7
E3	104.9 ± 3.9	105.7 ± 2.7	38.0 ± 0.4	103.7 ± 1.4
EE2	114.4 ± 5.1	106.3 ± 5.4	45.5 ± 6.6	99.8 ± 0.9
EA	90.7 ± 11.9	105.8 ± 3.3	28.3 ± 3.8	98.7 ± 1.6
Caffeine	84.0 ± 5.1	101.8 ± 4.1	72.1 ± 2.5	90.6 ± 0.7
Triclosan	82.9 ± 1.0	79.1 ± 0.4	79.6 ± 4.7	93.0 ± 1.0

^a Prepared from spiking each compound at 100 µg/L into sample.

^b Prepared from spiking each compound at 0.1 µg/g dry weight into sample.

Table 3 Calculated detection limits for target PPCPs obtained from HPLC/UV analysis of spiked samples.

Compound	Method detection limit*			
	Wastewater (µg/L)	Groundwater (ng/L)	Sludge (ng/g dry weight)	Soil (ng/g dry weight)
E1	0.12	8.08	6.42	0.96
E2	0.12	3.19	6.42	0.96
E3	0.12	17.73	6.42	0.40
EE2	0.12	4.78	6.42	0.96
EA	0.12	17.34	6.42	0.96
Caffeine	0.10	9.95	6.39	0.30
Triclosan	0.12	14.09	5.87	1.04

*Determined using U.S.EPA guideline (2000) where MDL = SD × t (99%; n-1) and assuming 1L of water and 1g of sludge/soil were extracted.

Instrumental Analysis

HPLC. The HPLC with UV detection was used for the determination of target PPCPs. An Alltech Prevail C18 column (25 cm × 4.6 mm i.d., 5 µm) was used for PPCPs separation. Mobile phase characteristics varied depending on the analyte of interest. For estrogens, the mobile phase was acetonitrile:water (gradient, flow rate = 0.8 mL/min) which was set at 60:40 (v/v) initially. The mobile phase was changed to 65:35 at 1.0 min, and to 100% acetonitrile at 11.5 min. Then, the mobile phase was maintained at 100% acetonitrile until 15.0 min, changed to 60:40 at 15.5 min, and maintained at 60:40 until 21.0 min. For caffeine separation, the mobile phase was 50:50 acetonitrile:water (isocratic; flow rate = 0.8 mL/min). Triclosan was chromatographed using a mobile phase containing acetonitrile:water (isocratic; 80:20 v/v; flow rate = 0.8 mL min⁻¹). Detection wavelengths were at 200 nm for estrogens and triclosan, and 254 nm for caffeine.

Principal Findings

PPCPs in Wastewater

The concentrations of target PPCPs in wastewater samples collected from the LWRP are presented in Table 4. All target PPCPs were detected in the process at a range of not detected (ND) -126.53 µg/L with the observed concentrations fluctuated among quarters. This fluctuation in PPCPs concentrations may be attributed to the use of PPCPs that likely varied daily, let alone quarterly. In general, concentrations of PPCPs in effluents at both stations were less than those in influents from bar rack or aeration basin in the same quarter except for EE2 in the first and the third quarters. This indicated that target PPCPs can be removed during the treatment process. Among PPCPs studied, E3 had the highest concentrations in the effluent from both chlorine contact chamber and effluent stations at a range of ND-86.71 µg/L. In some quarters, E1, E2, E3, and EE2 appeared to have lower concentrations in samples collected from bar rack than those collected from aeration basins, chlorine contact chamber, or effluent stations. This indicated that these compounds may not be easily degraded, or the inactive conjugates of estrogens may be deconjugated during the wastewater treatment process resulting in the release of the active parent compounds that produce higher effluent concentrations. Another possible reason of the higher concentrations of PPCPs in effluents than those of their input may be the daily variations of these compounds in the inlet since influent samples at bar rack were collected between 2 pm and 4 pm, which might not be during the peak load. Although wastewater samples at bar rack were collected at the same period as other wastewater sampling points, samples at other points were proportional samples in 24 hours, in which their concentrations may be affected by the previous load.

There was the difference of PPCPs concentrations between plant 3 and plant 4, specifically both between aeration basins and between effluent stations of each plant. In addition, in some quarters, concentrations of PPCPs in effluents from effluent station were higher than those collected from chlorine contact chamber of the same plant. The reason may be explained by the fact that samples collected were proportional samples in 24-hour flow and conditions between these two basins or effluent stations were not exactly the same. At detectable concentrations, E2, triclosan, and caffeine were detected in effluents at lower concentrations than in the influent during the entire study period, suggesting that these compounds can be removed efficiently from wastewater by the LWRP.

In general, there is no wastewater treatment process particularly responsible for the removal of PPCPs. However, several studies indicated that these compounds can be reduced or eliminated in biological wastewater treatment systems using the activated sludge (aeration basin) process where sorption to particles and biotransformation are potential mechanisms of PPCPs removal (Sedlak and Pinkston 2001; Giger et al. 2003; Andersen et al. 2005; Bester 2005; Thomas and Foster 2005; Thompson et al. 2005; Nakada et al. 2006; Kim et al. 2008). Some of the PPCPs in this study were probably also removed from wastewater via chlorination. Snyder et al. (2008) suggested that a majority of PPCPs in wastewaters such as estrogens and triclosan can be effectively oxidized using chlorination. In our study, data obtained can be supported by Snyder et al. (2008) since concentrations of PPCPs in the wastewater collected from bar rack were generally higher than in the samples collected from aeration basins, chlorine contact chamber, and

effluent stations. However, because the conjugated form of estrogens may be deconjugated by microbial processes without further degradation effluent, concentrations of estrogens can be higher than those in the corresponding influent samples (Kirk et al. 2002; Andersen et al. 2003; D'Ascenzo et al. 2003).

PPCPs in Sludge

The concentrations of target PPCPs in sludge samples collected from the LWRP are presented in Table 5. All target PPCPs were detected in solid phase of sludge at a range of ND-18.62 $\mu\text{g/g}$. In sludge liquid phase, target PPCPs were detected at a range of ND-50.14 $\mu\text{g/L}$ except for EE2, which was not detected during the entire study period. Concentrations of estrogens in sludge solid phase might be underestimated due to the low recovery of these compounds ($<51.1 \pm 3.2\%$). In sludge solid phase, target PPCPs in samples from anaerobic digester generally had less concentration than those from feed sludge chamber, except for E1 in the second quarter, E2 in the second and the third quarters, E3 in the fourth quarter, and triclosan in the third quarter. The less PPCPs concentration in the solid phase of digested sludge may be due to the desorption of PPCPs from the solid phase into the liquid phase. In sludge liquid phase, EE2 was the only compound that was not detected from both feed sludge chamber and anaerobic digester during the entire study period, while caffeine was not detected in any samples from anaerobic digester. For other compounds in sludge liquid phase, compared to those in anaerobic digested sludge, the tendency of PPCPs concentrations in feed sludge was hard to predict. In some quarters, PPCPs had less concentration in sludge liquid phase from feed sludge than those from anaerobic digester, but this fashion did not occur in other quarters. E1, E2, E3, and triclosan were detected in sludge liquid phase from either feed sludge or anaerobic digester, except for some quarters in which they were not detectable in both sampling points. From the result explained earlier, the unpredictable concentrations in sludge liquid phase along the treatment train (from feed sludge chamber to anaerobic digester) together with the fluctuated amount of sorbed PPCPs in sludge solid phase of same samples indicated the slow sorption kinetics. No equilibrium may occur between the sorbed and dissolved PPCPs in sludge during the treatment system at the LWRP.

Sorption to sludge is considered to be an important mechanism for the removal of hydrophobic organic chemicals from wastewater (Harrison et al. 2006). Therefore, it is necessary to know the phase of sludge at which PPCPs may present, including their concentrations at the phase. Among estrogens studied, E3 had the lowest octanol-water partition coefficient ($\log K_{ow}$) with high water solubility (Table 1); therefore, it had less tendency to sorb into sludge particles. This explained our findings that compared to other estrogens E3 had generally higher concentrations in the effluent from wastewater treatment plant (Table 4) and sludge liquid phase (Table 5). EE2 had a high $\log K_{ow}$ with the lowest water solubility among the studied estrogens and could have a high tendency to sorb into sludge. However, it was rarely detected in both solid and liquid phase of sludge in this study. This may be due to the consequences of non-detectable or very low concentrations of EE2 presented during the wastewater treatment, which was the input of sludge treatment. E1 and E2 were detected in both phases of sludge more frequently than other estrogens. This indicated that these compounds readily sorbed or desorbed in sludge, probably due to a high value of $\log K_{ow}$ with high water solubility of E1, and a

moderate value of Log K_{ow} with high water solubility of E2 compared to other estrogens. The lower concentrations of estrogens in the anaerobic digester may also be the result of biodegradation during sludge treatment process. Studies also reported that estrogens can be biodegraded during anaerobic sludge digestion (Holbrook et al. 2002; Kreuzinger et al. 2004a).

Among all PPCPs, triclosan had the highest log K_{ow} at 4.76 with the low water solubility at 10 mg/L. Although triclosan was detected at moderate concentrations in wastewater samples compared to other compounds, it was the only compound detected in all sludge samples both in solid and liquid phases. This finding indicated that triclosan may readily sorb into sludge solid phase, but may not be easily biodegraded in anaerobic digester. Our results can be also supported by other studies reporting that only little or no biodegradation of triclosan occurred under anaerobic sludge digestion (McAvoy et al. 2002; Chenxi et al. 2008). Compared to other PPCPs, caffeine had a very high water solubility at 2.16×10^4 mg/L with the lowest log K_{ow} at -0.07. Therefore, caffeine was not likely to sorb to sludge and it was rarely detected in sludge solid phase. Studies also reported that caffeine may be readily biodegraded during wastewater treatment system (Ternes et al. 2001; Buerge et al. 2003; Thomas and Foster 2005). The biodegradation of caffeine may result in the lower or non-detectable concentrations in both solid phase and liquid phases of sludge along the treatment process.

PPCPs in Soil

The concentrations of target PPCPs in soil samples collected from the LWRP are presented in Table 6. PPCPs can be detected at the range of ND- 34.52 ng/g in the soil inside pivot irrigation (CL-11 and CL-43) and ND-135.92 ng/g in the soil outside pivot irrigation (CL-29 and CL-48). Except for caffeine, target PPCPs were detected in both inside and outside pivot areas indicating that PPCPs may transport via runoff. Among PPCPs studied, caffeine was the only compound which was not detected in all soil samples. The observed concentrations of other target PPCPs in soil fluctuated among quarters, but were unpredictable among soil depths. EE2 was the only compound which was not detected in any samples at the depth of 24-30 inch although it was detected at the upper soil depths at the same sampling point. This indicated that EE2 may not be easily leached through the soil and hence, the vertical transport of EE2 might be low.

The fluctuated concentrations of PPCPs in soil among quarters were more likely due to the application of various concentrations of PPCPs in the effluent on the site. The PPCPs to the land through the application of irrigation were subject to volatilization at soil surfaces and vegetation, chemical and biological degradation, sorption by soil organic matter, and plant uptake (Cordy et al. 2004; Cardoza et al. 2005; Boxall 2008; Xu et al. 2009). These factors also affected the concentrations of PPCPs in the soil. In the soil environment, while the sorption is considered as an important process governing the mobility of organic compounds including PPCPs (Drillia et al. 2005, Boxall 2008), the volatilization and degradation processes govern the elimination of these compounds from the soil. In this study, E1, E2, E3, and triclosan were detected in the soil sampled at the depth of 24-30 inch indicating that these compounds were mobile and persistent enough to undergo percolation through the soil. However, the extent of concentrations of each compound was variable among soil depths. In this study, the tendency of PPCPs concentrations along soil depth was hard to be predicted or generalized. This is because

of the consequences of various biodegradation rates of PPCPs along soil depth as degradation of PPCPs can be affected by environmental complexities and conditions such as soil temperature, pH, moisture content, soil organic carbon, presence of specific microorganisms, and presence/absence of oxygen (Colucci et al. 2001; Boxall 2008; Monteiro and Boxall 2009). For instance, Ying and Kookana (2005) found that the degradation of E2 and EE2 were different in non-sterile aerobic soil with half-lives at 3 and 4.5 days, respectively, but no degradation of both compounds occurred in the sterile soil within 70 days. In anaerobic soil, E2 was degraded slowly with a half-life of 24 days, while no significant degradation of EE2 was observed within 70 days. Hence, studies suggested that the degradation, which affects the concentration of PPCPs in soil, was influenced by the presence of microorganisms and oxygen that could vary along soil depths. In this study, the volatilization was not likely to be a pathway of PPCPs elimination in soil since all target PPCPs had very low vapor pressures ($\leq 1.41 \times 10^{-7}$ mm Hg) except for caffeine. Caffeine had the highest vapor pressure (15 mm Hg) among target PPCPs and the biodegradation of caffeine in soil could occur rapidly both in aerobic and anaerobic conditions (Topp et al. 2006), which might explain the reasons why caffeine was not detectable in all soil depths in the study.

Among estrogens studied, E1 was detected in soil at the LLAS more frequently compared to other estrogens, and was detected at the highest concentrations although it presented at the same level as E2 and at less concentration than E3 in the effluent applied from the LWRP. Several studies reported that E2 was biotransformed to E1 rapidly under both aerobic and anaerobic soil conditions (Colucci et al. 2001; Jacobsen et al. 2005; Ying and Kookana 2005; Xuan et al. 2008). The high concentrations of E1 in all soil depths in our study might be caused by biotransformation of E2 into E1. For E3, it was detected in the soil at concentrations lower than E1 although it presented at higher concentrations than E1 in the effluent from the LWRP which was applied to the land. This might be attributed to a higher mobility of E3 compared to that of E1 in the soil as E3 had lower $\log K_{ow}$ and K_d than those of E1, resulting in less concentration of E3 sorbed into the soil.

PPCPs in Groundwater

The concentrations of target PPCPs in groundwater samples collected from the LLAS are presented in Table 7. Concentrations of PPCPs in groundwater were in the range of ND-1,744.62 ng/L. All target PPCPs can be detected in groundwater samples in both inside and outside pivot areas indicating that these compounds can move via runoff, which eventually leach or percolate through the soil to groundwater. Compared to other compounds, E3 was detected in groundwater at the highest concentrations except for the last quarter in which E3 was not detectable. This suggested that E3 had a higher mobility in the soil than other compounds since it was the most compound detected in groundwater but not much detected in soil. In the third quarter (late summer), most PPCPs studied were non-detectable except for EE2 and caffeine that were detected at low concentrations, i.e., 10.87 and 16.03 ng/L, respectively. This can be a result of high degradation rates of PPCPs in soil and groundwater that may occur during summer. Although caffeine was not detected in any soil samples, it was detected in some effluent and groundwater samples. This suggested that caffeine did not readily sorb to the soil or had a higher degradation rate than other target PPCPs in the subsurface environment.

PPCPs contaminated in groundwater may be originated from these compounds persisted in the soil. Since the field runoff and subsurface transport are the important processes for the movement of PPCPs and other organic compounds from soil to groundwater (Mansell and Drewes 2004; Overcash et al. 2005; Sangsupan et al. 2006). PPCPs in the soil at the site applied with the effluent may transport to groundwater through these processes. The extent of PPCPs in groundwater can be affected by sorption and biodegradation of these compounds during the soil-aquifer treatment (Kreuzinger et al. 2004b; Mansell et al. 2004; Snyder et al. 2004; Osenbrück et al. 2007). Sorption is considered as an important process governing mobility and transport of hydrophobic organic compounds in the soil-water environment (Lai et al. 2000; Cardoza et al. 2004; Casey et al. 2005; Mansell et al. 2004; Oppel et al., 2004; Scheytt et al. 2005; Sangsupan et al. 2006). Therefore, the tendency of PPCPs to persist in soil or remobilize to groundwater may be indicated by $\log K_{ow}$ and sorption coefficient (K_d) of these compounds. The less the coefficient, the more the tendency of PPCPs to move from soil into groundwater. Among PPCPs studied, E3 was detected at the highest concentrations in groundwater. This may be due to a low K_d of E3 at 8.6 mL/g compared to other target PPCPs. Caffeine was detected in groundwater samples, whereas it was not detected in any soil samples. This may be caused by a very low $\log K_{ow}$ at -0.07 and a high water solubility of caffeine.

Significance

PPCPs can be detected in wastewater, sludge, soil, and groundwater at the LWRP and LLAS. PPCPs can be removed from wastewater during the treatment process with aeration basin (activated sludge); however, E3 and EE2 can be occasionally detected in the effluent at higher concentrations than in the influent. All PPCPs studied can be detected in both sludge solid phase and sludge liquid phases except for EE2 which was not detected in sludge liquid phase. Regardless of season, concentrations of PPCPs in wastewater, sludge, and at each soil depth (0-6 inch, 12-18 inch, and 24-30 inch) varied with an unpredictable extent. Only groundwater tended to have less occurrence of PPCPs during summer. PPCPs had both vertical and horizontal (via runoff) transports at the study sites, which were detected along soil depth, and in soil and groundwater both inside and outside pivot irrigation, respectively. Caffeine was detected in effluent and groundwater, but not detected in soil, suggesting that caffeine may not readily sorb to the soil or degradation rate of caffeine was high in the soil during the study period. E3 was the most compound detected in groundwater, but not the most detected in soil, indicating that E3 may have a higher mobility in the soil than other target PPCPs. Overall, findings of this study indicated that PPCPs in the effluent from the wastewater treatment plant was eventually transported to groundwater via the land application of effluent, which is essentially an important concern for the possible long-term effects due to the contamination of PPCPs in the groundwater if it is used for drinking-water purposes. The result presented in this study may provide useful information for the wastewater treatment system to be upgraded or for other effective measures to be adopted to reduce these PPCP concentrations in soil at the LLAS.

Table 4 Concentrations ($\mu\text{g/L}$) of PPCPs in wastewater

Compound	Date	Bar rack	Aeration basin		Chlorine Contact Chamber	Effluent	
			Plant 3	Plant 4		Station I	Station II
E1	12/16/08	3.25	3.18	3.67	*	1.43	1.82
	3/11/09	1.47	0.74	1.63	0.42	0.49	0.59
	6/3/09	ND	0.22	2.82	1.54	0.33	0.48
	9/9/09	1.29	ND	ND	ND	ND	ND
E2	12/16/08	4.62	1.30	1.38	*	ND	1.37
	3/11/09	2.29	ND	1.12	0.36	0.50	ND
	6/3/09	0.90	1.66	1.58	0.80	0.26	0.75
	9/9/09	1.58	0.73	0.50	ND	ND	0.67
E3	12/16/08	0.68	7.45	13.97	*	0.25	7.60
	3/11/09	110.71	126.53	29.19	86.71	83.43	59.23
	6/3/09	ND	37.51	7.29	7.66	13.08	2.76
	9/9/09	25.71	ND	ND	ND	ND	ND
EE2	12/16/08	ND	ND	ND	*	0.08	0.39
	3/11/09	7.89	ND	ND	0.16	ND	ND
	6/3/09	ND	ND	0.12	0.81	0.26	ND
	9/9/09	ND	ND	ND	ND	ND	ND
Triclosan	12/16/08	5.10	0.12	ND	*	0.26	0.13
	3/11/09	8.12	ND	0.77	ND	ND	ND
	6/3/09	1.90	0.44	ND	0.14	0.15	0.17
	9/9/09	0.70	ND	ND	1.41	0.18	0.35
Caffeine	12/16/08	23.60	ND	ND	*	N	ND
	3/11/09	41.04	0.35	ND	0.12	0.17	0.34
	6/3/09	45.48	5.35	ND	ND	ND	ND
	9/9/09	53.43	ND	ND	ND	ND	ND

*No sample

ND = Not detectable

Table 5 Concentrations of PPCPs in sludge

Compound	Date	Feed sludge chamber		Anaerobic digester	
		Solid phase ($\mu\text{g/g}$)	Liquid phase ($\mu\text{g/L}$)	Solid phase ($\mu\text{g/g}$)	Liquid phase ($\mu\text{g/L}$)
E1	12/16/08	3.27	39.87	1.60	28.17
	3/11/09	2.40	0.42	2.52	2.60
	6/3/09	0.70	3.22	ND	50.14
	9/9/09	6.59	14.12	1.16	11.20
E2	12/16/08	0.70	1.54	0.04	0.48
	3/11/09	2.23	2.84	1.50	3.47
	6/3/09	0.13	ND	0.22	ND
	9/9/09	ND	18.33	0.12	9.44
E3	12/16/08	ND	3.55	ND	3.49
	3/11/09	ND	46.50	ND	16.38
	6/3/09	0.01	2.76	0.01	0.61
	9/9/09	ND	ND	0.01	ND
EE2	12/16/08	0.34	ND	0.19	ND
	3/11/09	ND	ND	ND	ND
	6/3/09	ND	ND	ND	ND
	9/9/09	ND	ND	ND	ND
Triclosan	12/16/08	7.79	6.98	3.35	12.11
	3/11/09	3.52	2.84	3.39	3.73
	6/3/09	4.70	1.00	5.67	3.47
	9/9/09	18.62	11.59	2.48	4.22
Caffeine	12/16/08	ND	0.53	ND	ND
	3/11/09	0.02	ND	0.01	ND
	6/3/09	ND	ND	ND	ND
	9/9/09	ND	24.85	ND	ND

 ND = Not detectable

Table 6 Concentrations (ng/g) of PPCPs in soil

Compound	Sampling Date	CL-11 ^a			CL-29 ^b			CL-43 ^a			CL-48 ^b		
		0-6"	12-18"	24-30"	0-6"	12-18"	24-30"	0-6"	12-18"	24-30"	0-6"	12-18"	24-30"
E1	3/9/09	*	*	*	7.55	10.04	8.52	7.82	34.52	20.61	5.30	8.68	6.73
	6/30/09	9.62	3.45	ND	9.53	7.33	4.96	3.28	9.59	20.83	4.60	7.63	6.71
	9/16/09	ND	ND	ND	ND	44.06	135.92	ND	ND	ND	2.03	ND	ND
E2	3/9/09	*	*	*	ND	ND	1.20	0.19	ND	3.33	0.17	0.58	0.65
	6/30/09	2.09	2.41	ND	ND	ND	ND	1.71	ND	ND	1.86	ND	ND
	9/16/09	2.84	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
E3	3/9/09	*	*	*	4.07	ND	ND	7.73	ND	ND	ND	ND	ND
	6/30/09	ND	1.01	ND	2.22	1.18	ND	1.63	3.14	1.20	2.98	1.00	1.08
	9/16/09	ND	ND	0.53	0.46	3.60	5.98	2.10	0.85	0.76	0.98	ND	ND
EE2	3/9/09	*	*	*	ND	ND	ND	ND	ND	ND	ND	ND	ND
	6/30/09	1.21	1.26	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/16/09	ND	2.62	ND	2.03	2.70	ND	ND	ND	ND	ND	ND	ND
Triclosan	3/9/09	*	*	*	5.24	3.20	ND	ND	ND	ND	ND	ND	ND
	6/30/09	ND	2.91	ND	8.16	1.24	1.09	1.94	1.33	7.81	ND	ND	ND
	9/16/09	ND	ND	ND	ND	ND	ND	19.15	ND	ND	ND	ND	ND
Caffeine	3/9/09	*	*	*	ND	ND	ND	ND	ND	ND	ND	ND	ND
	6/30/09	ND	ND	ND									
	9/16/09	ND	ND	ND									

* No sample, ND = Not detectable, ^a inside pivot irrigation, ^b outside pivot irrigation

Table 7 Concentrations (ng/L) of PPCPs in groundwater

Compound	Sampling Date	CL-11 ^a	CL-29 ^b	CL-43 ^a	CL-48 ^b
E1	3/9/09	*	79.15	75.15	61.74
	6/30/09	ND	ND	ND	ND
	9/16/09	ND	ND	ND	ND
E2	3/9/09	*	12.16	146.54	34.30
	6/30/09	39.40	ND	ND	77.51
	9/16/09	ND	ND	ND	ND
E3	3/9/09	*	1744.62	874.16	538.32
	6/30/09	685.68	321.83	1660.75	675.96
	9/16/09	ND	ND	ND	ND
EE2	3/9/09	*	ND	230.32	101.66
	6/30/09	14.51	ND	ND	ND
	9/16/09	ND	ND	ND	10.87
Triclosan	3/9/09	*	16.69	15.74	11.57
	6/30/09	ND	44.73	53.27	ND
	9/16/09	ND	ND	ND	ND
Caffeine	3/9/09	*	118.57	166.17	163.52
	6/30/09	ND	ND	ND	ND
	9/16/09	16.03	ND	ND	ND
	9/16/09	ND	ND	ND	ND

* No sample

ND = Not detectable

^a inside pivot irrigation

^b outside pivot irrigation

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Role of Free-ranging Wildlife in the Deposition of Escherichia coli into a Texas River Floodplain

Basic Information

Title:	Role of Free-ranging Wildlife in the Deposition of Escherichia coli into a Texas River Floodplain
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Focus Category:	Non Point Pollution, Management and Planning, Water Quality
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Principal Investigators:	Israel David Parker, Roel R Lopez

Publication

1. Parker, Israel, 2010, The Role of Free-Ranging Wildlife in the Deposition of Escherichia coli into a Texas Floodplain, "Ph.D. Dissertation," Wildlife and Fisheries Sciences, College of Agriculture, Texas A&M University, College Station, TX.

REPORT

Title

The Role of Free-Ranging Wildlife in the Deposition of *Escherichia coli* into a Texas Floodplain

Project Number 2009TX321B

Primary PI

Israel David Parker

Other PIs

Roel R. Lopez, Ph.D.

Abstract

The role of wildlife in the deposition of *Escherichia coli* (*E. coli*) is not well understood. Although water quality studies incorporate wildlife data, the data often lacks a clear connection between wildlife density and *E. coli* deposition. One tool for wildlife management is the adjustment of animal populations. Minimal understanding of species-specific fecal pollution and the role of species density on water quality complicates attempts by natural resource managers to adjust wildlife populations to improve water quality. My goal for this research was to determine the impact of free-ranging mammals (in general and species-specific) on *E. coli* loads in the floodplain. The objectives of this research were to determine the density of important free-ranging wildlife in the study area, research fecal deposition rates, and determine fecal *E. coli* loads for each species. I conducted a comprehensive literature review to determine fecal deposition rates for important mammals. I conducted mark-recapture and mark-resight populations density estimates (2008–2009) for meso- and large mammals in the study areas. I collected fecal samples from study species for *E. coli* analysis at university labs. Finally, I walked transects to determine spatial distribution of fecal material. I found that raccoons (*Procyon lotor*) provided the most *E. coli* into the floodplain followed by feral hogs (*Sus scrofa*), Virginia opossum (*Didelphis virginiana*), and white-tailed deer (*Odocoileus virginianus*) as the next biggest contributors.

Problem and Research Objectives

Although previous *E. coli* research has investigated the role of traditional sources of fecal pollution, little research has investigated the role that free-ranging wildlife plays in water contamination. Further studies are needed to understand the role of free-ranging wildlife populations in the deposition of *E. coli* in order to accurately describe the sources of fecal contamination. Land managers and natural resource decision-makers need to understand the role of wildlife in the deposition of *E. coli* into Texas watersheds in order to successfully manage water supplies in the state and to implement effective pollution control strategies. Furthermore, information concerning the contribution of *E. coli* from free-ranging wildlife populations is needed to improve watershed-level contamination models and reliability of model results.

Our study objectives were to identify, characterize, and quantify *E. coli* deposition from free-ranging wildlife populations into a floodplain of an impaired water body. This project sought to

clarify the spatial distribution of fecal sources, subsequent fecal deposition, and *E. coli* locations. Target species were exclusively mammalian (medium to large; e.g., white-tailed deer [*Odocoileus virginianus*], feral hogs [*Sus scrofa*], raccoons [*Procyon lotor*], etc.). Specific objectives were as follows:

1. Identify and population densities of major wildlife contributors of fecal material in the study floodplain. Focal species were limited to those in direct contact to water course.
2. Evaluate the presence and persistence of *E. coli* levels in fecal samples from identified major wildlife contributors.
3. Estimate the approximate amount of fecal material deposited by major contributors into the watershed on a daily basis.

Materials/Methodology

I used infrared triggered cameras to aid in determining population densities of mid-size to large mammals present within the floodplain. I determined medium-sized mammal population densities by analyzing trapping numbers in live-trap grids. I conducted a literature review to determine the mammal species likely to be found in the study areas and tailor the trap efforts accordingly. I collected fecal material of major contributing species during transects and during medium-sized mammal trapping. In order to identify potential seasonal *E. coli* fluctuations, I collected fecal samples of relevant and dominant identified sources during the winter and summer seasons for 2 consecutive years. I also live-trapped medium-sized mammals in order to collect fresh fecal material. I conducted feral hog and white-tailed deer trapping on one of the cooperating properties to collect fecal samples. I conducted a comprehensive literature review to determine fecal shedding rate for species. Floodplain-scale estimates of the amount of species-specific fecal material were then extrapolated.

Principal Findings

I combined the highest and lowest seasonal density estimates with conservative estimates of fecal deposition rates and found that white-tailed deer, raccoons, and feral hogs deposited the most fecal material into the watershed. Using the fecal samples, my research collaborators at Texas A&M University found that raccoons and Virginia opossums had the highest mean CFU/gram of fecal material of sampled species. Overall, I estimated that raccoons potentially deposited the most *E. coli* per km², followed by feral hogs, Virginia opossums, and white-tailed deer.

Significance

Free-ranging mammals in my study area were significant contributors of *E. coli* into floodplains. Raccoons were larger potential contributors than mammals like feral hogs and white-tailed deer. This is exacerbated by the fact that raccoons stay near water and are known to defecate in water sources. Feral hogs are known for a high degree of coprophagy likely further reducing their fecal contribution. White-tailed deer defecated frequently and in relatively large amounts; however, they had relatively low *E. coli* concentration in their fecal material.

Sources and Risks of Waterborne Pathogens in the El Paso del Norte Region

Basic Information

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Principal Investigators:	Joy Archuleta-Truesdale, George D Di Giovanni

Publications

1. Truesdale, J. A., K. M. Barrella, E. A. Casarez and G. D. Di Giovanni, 2010, Challenges and considerations for bacterial source tracking in Texas, Abstracts of the International Symposium on Waterborne Pathogens, May 2-4, 2010 [on CD-ROM].
2. Truesdale, J. A., Barrella, K. M., E. A. Casarez and G. D. Di Giovanni, 2010, Challenges and considerations for bacterial source tracking in Texas, Abstracts of the Annual Meeting of the Rio Grande Branch American Society for Microbiology, February 27, 2010, El Paso, Texas.

REPORT

Title: Sources and Risks of Waterborne Pathogens in the El Paso del Norte Region

Project Number: 2009TX322B

Primary PI: Joy Archuleta-Truesdale

Other PIs: George Di Giovanni, PhD.

Abstract:

Vigilant water quality monitoring is very important for compliance with government standards and in the interest of the public. The Rio Grande river is the natural boundary between the U.S. and Mexico and is the only source of surface water for the El Paso, Texas and Ciudad Juarez, Mexico area known as the El Paso del Norte region. Agriculture, farming, domestic activities, and effluent from local wastewater treatment plants increase the contamination potential of water supplies along the region. Monitoring of selected sites along the Rio Grande river has showed the occurrence of *Cryptosporidium* and *Giardia*. Higher pathogen levels were observed during the non-irrigation season when the river flow is dominated by wastewater effluents. This indicates that there could be an increased risk of using the river water as a source of drinking water during the winter if it is not properly treated. Therefore, the objective of this research is to determine the sources and risks of contamination in the Rio Grande river and assess the potential impact to human health. These efforts will aid our understanding of effective treatment of wastewater and drinking water. With this increased understanding, we will be able to make recommendations for wastewater and drinking water treatment, and aid in developing cost effective treatment strategies.

Problem and Research Objectives:

The Rio Grande River is the primary surface water resource for the Paso del Norte region. It is heavily utilized for agriculture and as a drinking water supply, but has been poorly characterized for its microbiological quality. Winter return flows during the non-irrigation season (typically November through April) contain significantly higher levels of pathogens due to agricultural return flows and wastewater treatment plant effluents. It is assumed that higher pathogen levels in winter return flow water leads to increased health risk in utilizing the winter return flows for drinking water. The objectives of this research are to: 1) *define the sources and risks of contamination in the Rio Grande river;* 2) *determine the infectivity of Cryptosporidium in wastewater effluents;* and, 3) *perform a microbial risk assessment for Rio Grande river winter return flows as a source of drinking water.*

Materials/Methodology:

To assess the sources and magnitude of human and animal fecal pollution sources impacting the Rio Grande river during the summer irrigation and winter return flow seasons, *Bacteroidales* quantitative PCR (qPCR) is being utilized to identify key points in the watershed of possible contamination. Importantly, the impact of *Bacteroidales* fecal pollution markers present in wastewater effluents on estimates of pollution is being investigated. The potential risk to public health from wastewater effluents is being determined by analyzing the infectivity of *Cryptosporidium* oocysts using a cell culture method. Levels of infectious *Cryptosporidium* are being determined using human ileocecal adenocarcinoma cells (HCT-8 cells) labeled with an indirect antibody procedure and examined with epifluorescence microscopy. For both *Cryptosporidium* and *Giardia*, total levels of (oo)cysts are being determined using standard microscopy, and genotype analysis is being performed. Finally, data generated from this study will be incorporated into a risk assessment of the Rio Grande river.

Principal Findings:

The *Bacteroidales* PCR method is a culture-independent molecular method which targets genetic markers of *Bacteroides* and *Prevotella* spp. fecal bacteria that are specific to humans, ruminants (including cattle and deer) and pigs (including feral hogs) (Bernhard and Field 2000; Dick, Bernhard et al. 2005). There is also a general *Bacteroidales* marker (GenBac) that can be used as a general indicator of fecal pollution.

For this project, most of the activity involved method development focusing on *Bacteroidales* qPCR. Previous work in our lab revealed that Rio Grande river water samples were positive for the GenBac marker using *Bacteroidales* conventional PCR. This indicated that there is a presence of fecal contamination at all sampling sites. It was also noted that several samples tested positive for the human and hog markers. However, conventional PCR is only a presence/absence test of fecal pollution and is not quantitative. In order to estimate the relative abundance of host-specific *Bacteroidales* we are now using qPCR.

1. *A novel Bacteroidales quantitative PCR (qPCR) was applied to determine relative abundance of human and animal fecal pollution*

In theory, the GenBac marker detects the majority of the *Bacteroidales* in the samples, including those detected with the host-specific markers. Using river water samples from a concurrent project, GenBac standard curves were developed using 10^0 , 10^{-1} , and 10^{-2} dilutions of each water sample DNA. Since the actual copy number of GenBac target sequences in each sample was unknown, arbitrary values of 1,000, 100, and 10 were assigned to the dilutions, respectively. The hog, human and ruminant host-specific markers were quantified using the GenBac standard curve for each water sample and results are expressed as semi-quantitative marker abundance as determined by quantitative PCR (qPCR). This attempted to make the marker quantitation data for different water samples comparable by accounting for sample-to-

sample variation in *Bacteroidales* DNA concentration and any effects of PCR inhibitors on quantitation. This approach makes it possible to compare the relative abundance of each marker between stations or at the same station over time. The developed approach is being used to identify key locations in the Rio Grande River that may be contributing to fecal contamination.

2. *Human marker persistence through wastewater treatment*

As stated previously, analysis of Rio Grande river samples indicated the presence of the human and hog *Bacteroidales* marker. There are very few hogs in this region, and based on analysis of wastewater samples, our results suggest that human sewage presents a low level of hog marker cross-reactivity. More importantly, we have found that the human and hog *Bacteroidales* markers were present in chlorine and UV disinfected wastewater effluents. This is an important observation because it shows that *Bacteroidales* bacteria can persist through the wastewater treatment process. The presence of the human *Bacteroidales* marker in treated effluents could impair our ability to differentiate between river water influenced by properly treated wastewater and untreated, raw sewage. However, it is still unclear if the *Bacteroidales* bacteria found in the treated effluents are viable or non-viable. In order to address this issue, we are collecting effluents from wastewater treatment plants that utilize chlorine disinfection only or chlorine and UV disinfection. We can then characterize the human marker using the current qPCR method which detects both viable and nonviable *Bacteroidales*. A new approach using propidium monoazide (PMA) and qPCR to differentiate viable from non-viable *Bacteroidales* will be applied. Final results are anticipated by the end of summer 2010.

3. *Cryptosporidium genotyping training*

I received training and participated in a technology transfer workshop on a *Cryptosporidium* genotyping method that includes the use of forensic DNA sample purification techniques combined with a single round of multiplex PCR targeting the *Cryptosporidium* genes for 18S ribosomal RNA (18S rDNA) and heat shock protein 70 (hsp70). This genotyping method is being applied to characterize the total (viable and non-viable) and infectious *Cryptosporidium* spp. present in wastewater effluents.

4. *Microbial risk assessment for Rio Grande river winter return flows as a source of drinking water.*

A substantial amount of data from our lab was provided to Dr. Kristina Mena, U.T. Houston School of Public Health, El Paso Regional Campus, and will be incorporated into a quantitative microbial risk assessment for *Cryptosporidium* in the Rio Grande. Additional results from this project will be incorporated into the risk model in the future.

Significance:

This research will provide data necessary for understanding the sources of pathogen contamination in the Rio Grande river. Determining the infectivity of *Cryptosporidium* and levels of *Giardia* in wastewater effluents and their impact on river water quality will help identify the sources and health risks associated with using the Rio Grande river as a source of drinking water. In conclusion, the developed risk assessment will include important data generated by this project to properly address *Cryptosporidium* and *Giardia* risks and in the implementation of effective water treatment. Results will be broadly disseminated among stakeholders to effectively address surface water treatment and appropriate management of water resources.

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Economic analysis of proposed seawater desalination facility in Brownsville, TX

Basic Information

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Principal Investigators:	Andrew J Leidner, Ron Lacewell, M Edward Rister

Publications

There are no publications.

Final Report

Title

Economic analysis of proposed seawater desalination facility in Brownsville, Texas

Project Number

(2009TX323B)

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Abstract

A seawater desalination project is being actively pursued by the Brownsville Public Utilities Board, municipal power and water supplier to the City of Brownsville located in the Texas Lower Rio Grande Valley. Seawater desalination provides a means to expand and diversify the region's water supply offering protection against water delivery shortfalls and periodic droughts. This research will compile economic and financial cost data from desalination facilities similar to the facility being proposed for Brownsville (to be located on the Port of Brownsville). The analysis will compare the projected costs of water production via desalination at the Port of Brownsville with the costs of alternative potable water supplies, including conventional surface water treatment, brackish groundwater desalination, and seawater desalination at other locations, controlling for water quality, energy costs, time value of money, etc. Cost analysis will use DESAL ECONOMICS®, a cost model developed by Texas A&M AgriLife Research and AgriLife Extension Service economists, along with cost models used in the industry, e.g., Reverse Osmosis Desalination Cost Model (RODCM) published by Water Resource Associates, and WTCost© II published by I. Moch and Associates.

Problem and Research Objectives

Water scarcity has been an issue for community managers in the arid parts of the world for many years. As population levels increase across the globe, even areas that are traditionally thought of as non-arid or semi-arid must be prepared to engage the reality of increasing levels of water scarcity. Competition among a diverse set of ever-growing consumers motivates interest in both non-traditional water supply projects and non-traditional water demand management strategies. This research addresses the several inter-related issues by looking at one such non-traditional water supply project for a semi-arid region which consistently ranks high among the fastest-growing parts of the country. For many years, the Rio Grande Valley of south Texas has relied heavily, essentially primarily, on river diversions from the Rio Grande and conventional surface water treatment technologies to provide its population with potable water supplies. In recent years, the water suppliers of the Valley have expanded their water supply portfolio to include brackish groundwater desalination. This research investigates another potential technology to harness an as yet untapped potential source of freshwater for the region. Municipal-scale, seawater desalination is a novel technology for the Valley, and for that matter, much of the US. Two municipal-scale seawater desalination facilities currently in operation in the US include one located in Tampa Bay, Florida and another in North Dighton, Massachusetts. The objective of this research is to estimate life-cycle facility segment and component costs for a hypothetical seawater desalination facility that would be located in the Valley, with the costs grounded in the real world experiences of engineers and water managers who have already undertaken projects which employ the technology of seawater desalination, such as those facilities in Florida and Massachusetts.

Materials/Methodology

The approach taken is essentially that of a two-stage case study, with the first stage encompassing a study of existing seawater desalination facilities to acquire *in situ* life-cycle facility segment and component costs. In the second stage, segments and components which would be appropriate for a hypothetical facility in the Valley are identified, and results from the first stage are modified to approximate the most likely costs for a Valley facility.

Principal Findings

Of the two seawater desalination facilities mentioned above located in the US, neither, without substantial and possibly disencumbering modifications, would provide an accurate approximation for costs for a

facility in the Rio Grande Valley of Texas. Each facility has different upsides and downsides relative to providing accurate cost information towards the hypothetical Valley facility; a discussion of these pros and cons follows.

In terms of output capacity, the Tampa Bay facility more closely matches the size of the fully built-out facility described in the Final Pilot Study Report (NRS Consulting Engineers, 2008), which is 25 million gallons per day. However, the Tampa Bay facility has recently undergone rehabilitation following undesirable production results during the early years of its operations. Additionally, the Tampa Bay facility was constructed adjoining a power generation facility, to take advantage of the power facility's cooling water infrastructure; doing so provided for more readily accessible and less expensive source water than if the desalination facility had to independently construct and operate its own raw water intake extraction and concentrate discharge outfall systems. Such an independent construction and operation is a likely outcome for a facility in the Valley; therefore, the complications during the startup phases and the absence of an independent intake and outfall system made the Tampa Bay facility seem less desirable as a model for the first stage of this project.

Initially, the facility in Massachusetts seemed more promising since that facility did construct an independent intake and outfall system. Also, the facility has a current operating capacity of 4 million gallons per day which, while smaller than the full build-out recommendation from the Brownsville pilot study, was considered near enough to the range of the initial build-out capacity from the pilot study recommendation, i.e., 2.5 million gallons per day. Additionally, the Massachusetts facility was known to employ a membrane pretreatment system, which is similar, though not identical, to the membrane pretreatment system recommended from the Brownsville pilot study. The downsides of the Massachusetts facility were discovered to be the source of raw water is not very similar to that which is expected to be found in the Valley. In addition to the likely differences due to seasonal differences from Massachusetts and south Texas, the facility is located not on the ocean but rather on a tidal river. The facility managers, wisely, take advantage of the river's tidal influences and extract raw water when the salinity is at a minimum, because treating the less saline water requires less energy. This characteristic of facility operations results in much lower treatment costs than would be experienced if the facility treated undiluted seawater, as will likely be the case for the Valley facility.

Significance

This project took an important step towards identifying a reasonable first-stage case study project to use to evaluate likely life-cycle segment and component costs for a seawater desalination facility located in the Texas Lower Rio Grande Valley. Although neither facility in the U.S. seems ideal for the first stage of this project, during the site visit and subsequent follow up consultation with the engineers and managers, who built the Massachusetts facility, a third prospective facility was introduced to the authors. A 20 million gallon per day facility, located in Baja California, Mexico, equipped with an independent intake and outfall system, may be the ideal first-stage case study project that will ultimately provide the information necessary to construct an acceptable estimate of the costs for a seawater desalination facility in south Texas.

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NRS Consulting Engineers. "Final Pilot Study Report: Texas Seawater Desalination Project." *Brownsville Seawater Desalination Pilot Project*. October 2008.

Lake Houston Watershed Water Quality Prediction System

Basic Information

Title:	Lake Houston Watershed Water Quality Prediction System
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Descriptors:	None
Principal Investigators:	Aarin Teague, Philip B. Bedient

Publications

There are no publications.

Final Report

Lake Houston Watershed Water Quality Prediction System

Project Number 2009TX324B

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Keywords : Hydrologic Models, Land Use, Watershed Protection

Abstract

The increased degradation of influent to Lake Houston is causing increased water treatment cost for the City of Houston's Drinking Water Operations and has severe public and environmental health implications. The watersheds flowing into Lake Houston are impaired for bacteria and have concerns for nutrients. Therefore hydrologic models and water quality predictions concerning the influent from the watersheds to the lake are key to the operation of the City of Houston drinking water treatment plant. A water quality modeling system based on a distributed hydrologic model (*Vflo*TM) that uses NEXRAD RADAR rainfall input, was proposed. The system is being tested in Cypress Creek Watershed as part of a wider Basin effort. Cypress Creek is an urbanizing watershed with significant agricultural activity. As such historic water quality data will be analyzed for loading relationships in conjunction with a wider literature review of land use pollutant loading rates for determination of water quality parameters. Then pollutant washoff and transport is modeled using land use parameters and hydrologic output from *Vflo*TM. This output will then be evaluated using water quality sampling during storm events collected as part of the proposed project.

1. Introduction

Lake Houston is an important source of drinking water for the City of Houston, with approximately 300 million liters of water withdrawn daily (Chellam, 2008).

Unfortunately, the lake experiences seasonal algal blooms and stratification during warm weather. This eutrophication is associated with nutrient inflow from the seven watersheds draining into the lake. Increasing urbanization within the watersheds is expected to increase urban runoff with loads of nutrients, suspended solids, and bacteria. The combination of nutrient enrichment combined with bacterial impairment increases the cost of water treatment for the drinking water purification plant on Lake Houston.

In order to address the rising water treatment costs, source protection measures need to be implemented within the watersheds draining into the lake. Source protection measures are designed structures and procedures devised to maintain the quality of a water resource and can include detention basins, vegetated stream buffers, pet waste pickup programs, and resident education programs. Seven watersheds, encompassing 1,939 mi², drain into the lake (See Figure 1). Cypress Creek, the most highly urbanized of these watersheds, is impaired for bacteria (TCEQ, 2008a) and listed on the 2008 303-d concerns list for nutrient enrichment (TCEQ, 2008b). Because of its contribution of urban and agricultural runoff to the lake, knowledge of the water quality in Cypress Creek is necessary for improved operation of the drinking water purification plant and future protection of the City of Houston's water supply.

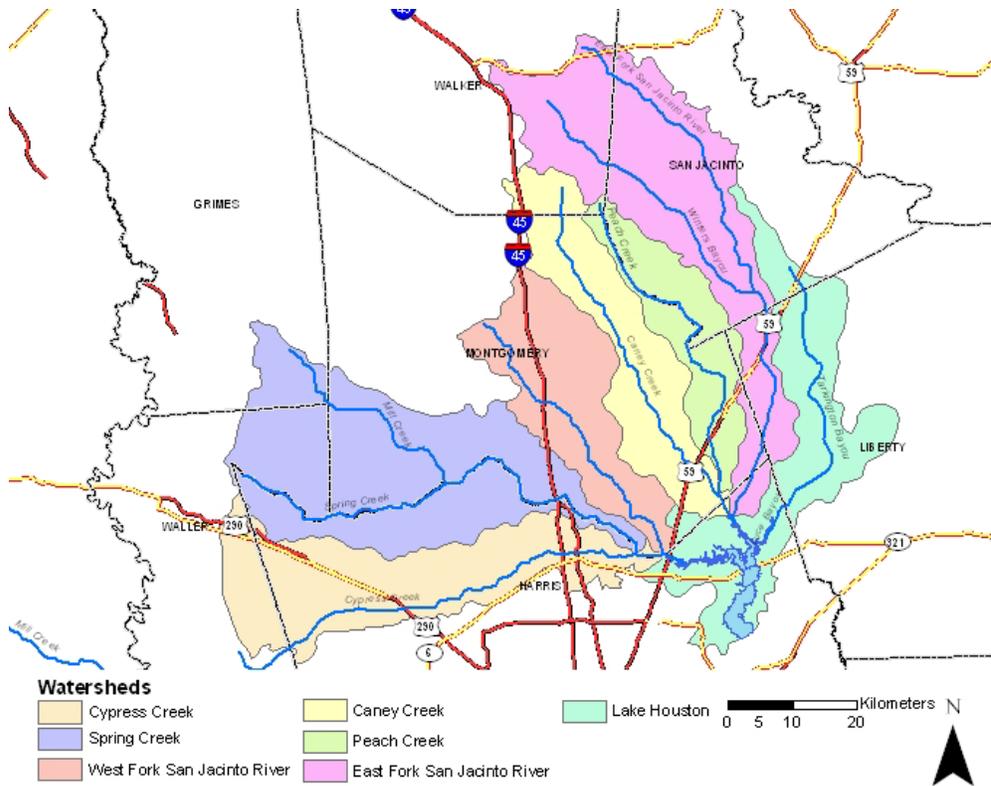


Figure 1 .Watersheds Flowing into Lake Houston

Efficient operation of the drinking water plant can be assisted by advance warning of pollutant loads entering Lake Houston from Cypress Creek. A predictive model that incorporates RADAR rainfall in real time and provides hydrologic and water quality output would provide information to the water treatment plant operators to use as a decision aid in the management of water purification processes.

2. Objectives

The goal of the proposed project was to develop a water quality management system based on a distributed hydrologic model for simulation and prediction of pollutant loads from Cypress Creek watershed to Lake Houston. The system can be expanded and

applied to other watersheds, notably the other watersheds flowing into Lake Houston, for a comprehensive management plan for Lake Houston.

3. Study Area

Cypress Creek is a 308 mi² watershed north of the city of Houston in north Harris County with the upstream, western portion in Waller County. It flows 50 river miles to Lake Houston. The western upstream part of the watershed is undeveloped primarily as cultivated agricultural fields. The eastern portion of the watershed has primarily residential development and is home to most of 216,000 residents (ESRI, 2000). Based on the 2002 Land Cover analysis performed by the Houston-Galveston Area Council, low and high intensity development accounted for approximately 16% of the watershed. This development increased to approximately 39% by 2008. Additionally, forested and woody wetland decreased from 23% in 2002 to 11% in 2008 whereas grasslands decreased from 51% to 11% (See Figure 2). As such, the watershed has experienced rapid urban development in the past decade. Cypress Creek watershed is relatively flat with sandy loam soils. With sandy loam soils, there is greater infiltration potential and less erosion potential. As a result, increases in impervious cover would increase runoff and thus create greater loading of pollutants to the stream.

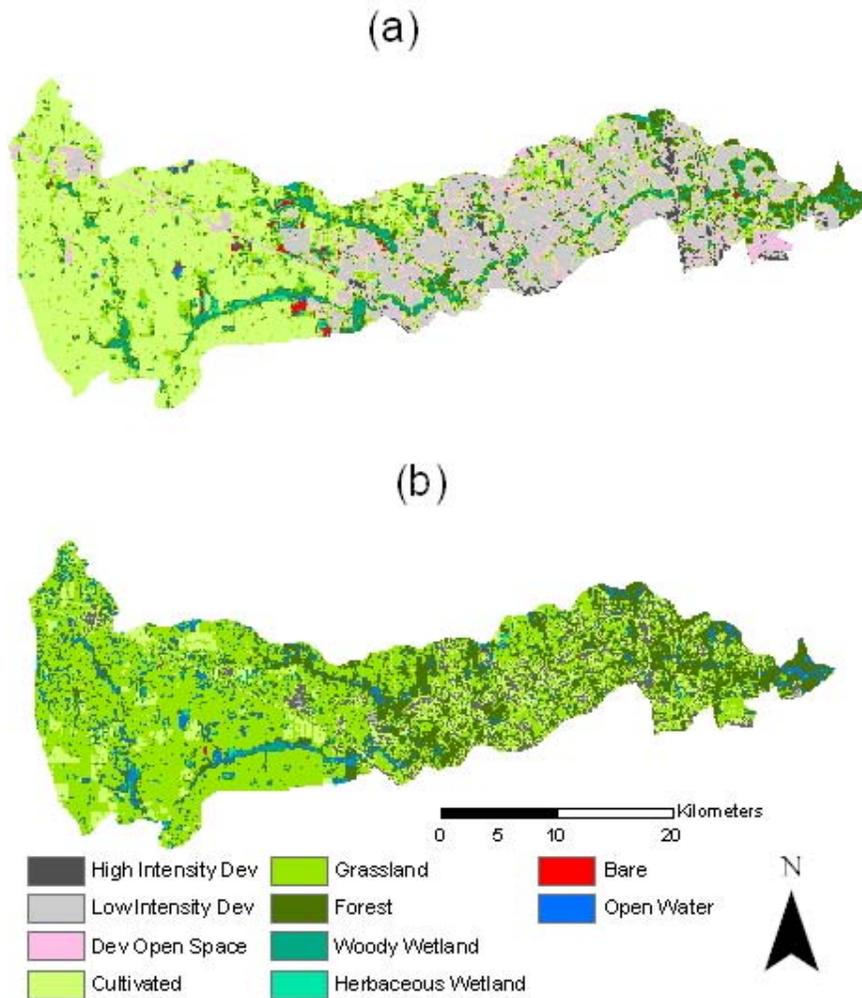


Figure 2. Land Cover for Cypress Creek in (a) 2008 and (b) 2002

4. Literature Review

The proposed water quality prediction system requires the development of a hydrologic model and a pollutant washoff and transport model using the output from the hydrologic model. The hydrologic model background as well as fundamental pollutant buildup, washoff, and transport relationships were reviewed in support of the project development.

4.1 *Vflo*TM model

*Vflo*TM is a distributed hydrologic model developed by Vieux et al. as a refinement of *r.water.fea* (Vieux and Gauer, 1994). The model uses finite element solutions of the kinematic wave equation for runoff routing. The solution for both overland and channel flow were derived from Saint Venant equations for unsteady free surface flows. It is derived from the continuity and momentum equations (Borah et al., 2007). The one-dimensional continuity equation is

$$\frac{\partial Q}{\partial x} + \frac{\partial A}{\partial t} - q = 0 \quad (1)$$

Where Q is the flow rate, A is the cross-sectional area, and q is the lateral inflow, x is length, and t is time. The momentum equation is simplified to

$$S_0 = S_f \quad (2)$$

Where S_0 is the slope and S_f is the friction slope. The continuity and momentum equations are used to solve for discharge through

$$q = \alpha Q^\beta \quad (3)$$

Where β for overland flow is assumed to be 5/3 and the conveyance factor α is

$$\alpha = \frac{k_m}{n} \sqrt{S_0} \quad (4)$$

Where n is the Manning's coefficient, and k_m is the dimensionless kinematic flow number. Overland flow is calculated from the surface flow modeled by Manning's equation as

$$v = \frac{1}{n} S_f^{1/2} B h^{5/3} \quad (5)$$

Where v is the flow velocity, S_f is the overland slope, B is the width of flow, h is the depth of flow, and n is the Manning's coefficient which is based on surface characteristics.

Runoff moves from overland cells into channel cells. Open channel flow is simplified to the form

$$q = \frac{\partial Q}{\partial t} + \alpha\beta Q^{\beta-1} \left(\frac{\partial Q}{\partial t} \right) \quad (6)$$

which takes into account the change in portion of flow depth to flow width. This formulation can then be solved by finite element analysis, which is an efficient way to transform partial differential equations into ordinary differential equations in time (Vieux, 2004). By translating the 2-D grid into 1-D finite elements, or partial discretization, the system becomes computationally more efficient. The result is a system of equations for each element incorporating the boundary conditions of the grid cell, which can then be solved in matrix form by numerical methods.

The *Vflo*TM model solves Green-Ampt infiltration and saturation excess equations for runoff generation (Bedient et al., 2003). Geospatial data representing elevation, soils, and land use are incorporated as parameters for the solution of these relationships. Precipitation input can be RADAR rainfall data, interpolated from rain gage data, or simulated design storms. The model is used to simulate runoff and other hydrologic quantities at any location within the study area, which supports the generation of hydrographs for the selected locations in the watershed.

*Vflo*TM has been used to model multiple watersheds in Houston, Texas, including Brays Bayou, Whiteoak Bayou (Safiolea, 2006), and Cypress Creek (Zimmer, 2007). Previous applications in the Houston region have focused on flood prediction. Notably, a real-time

flood alert system was developed for the Texas Medical Center using a Brays Bayou *Vflo*TM model and NexRAD RADAR rainfall input (Fang et al., 2008). Furthermore the model has been applied to numerous other watersheds including the Yuna River in Dominican Republic (Robinson et al., 2009), Namgang and Yongdam River Basins, Korea (Vieux et al, 2009), and Blue River Basin, Oklahoma (Gourley and Vieux, 2006). It has been found that *Vflo*TM produces highly accurate prediction of peak flows and simulation of the hydrograph (Bedient et al, 2003).

4.2 Pollutant Loading and Buildup Estimation

The type and rate of pollutant buildup is dependent on land use, human activities, and season (Overton and Meadows, 1976). The buildup of a pollutant on a surface can be modeled by different relationships such as linear, power, exponential, and Michaelis-Menton function (Barbe et al., 2006). Among the different modeling options, the first order relationship is the most commonly used and is integrated to an exponential form.

The rate of accumulation of a pollutant can be modeled as

$$\frac{dP}{dt} = C - kP \quad (7)$$

Where P is the pollutant load, C is the constant rate of pollutant deposition, and k is rate of pollutant removal.. This can be solved (Haiping and Yamada, 1998) to the form

$$P = P_i \exp(-k * t) + C(1 - \exp(-k * t)) \quad (8)$$

which models the pollutant buildup behavior over time.

An alternative to assigning a general land use pollutant loading factor is to estimate potential loading through pollutant producing populations. For example, Paul et al.

(2006) estimated *E. coli* loads by spatially distributing the population of agricultural animals, wildlife, pets, septic systems, and sewage treatment. Based on this population distribution, a production rate is applied to the population. This produces a spatial distribution of *E. coli* potential loads. This is formalized through the Spatially Explicit Load Enrichment Calculation Tool (SELECT) methodology (Teague, 2009), which automates the process of spatial distribution of key populations, land use specific loading, and application of production rates. The SELECT method involves the steps of :

- (1) Identify the potential sources of the pollutant
- (2) Assess the population(s) of the pollutant sources
- (3) Spatially distribute the population(s) of the pollutant sources to appropriate land use areas in order to determine the population densities
- (4) Apply a loading rate or production rate to the population densities to calculate the average daily potential load.

The result is spatially distributed average daily potential load data, or a grid of the rate of load buildup in terms of mass per time for each grid cell.

4.3 Washoff and Transport Calculation

Pollutant washoff is the process of removal of soluble and particulate pollutants by rainfall and runoff (Vaze and Chiew, 2003). Falling raindrops create turbulence and overland flow loosens particles from the surface so that the particles can be transported through the watershed with water flow. Storm water quality models have traditionally conceptualized the washoff process as driven by the energy of raindrop impact or overland flow shear stress flow (Brodie, 2007).

The most common pollutant washoff model developed by Sartor and Boyd, assumes the mass of pollutant washed off is proportional to the runoff intensity (Patry, 1989) and has been incorporated into the SWMM and STORM models. The model is a first order equation describing the pollutant mass that remains on the surface at time t with the onset of a storm that can be simplified to exponential relationship between the pollutant washoff and runoff volume (Millar, 1999) and adequately describes the first flush phenomenon.

A variation of the Sartor and Boyd model assumes that shallow overland flow is satisfactorily approximated by assuming that washoff is proportional to the bottom shear stress of overland flow and the distribution of the pollutant (Nakamura, 1984). These assumptions were used to expand the model describing washoff by Akan (1987) and further elucidated by Singh (2002a; 2002b). Washoff is described by the model

$$\frac{\partial P}{\partial t} = -kShP \quad (9)$$

Where P is the mass of pollutant on the surface, S is the slope of the land surface, h is the depth of flow, and k is the washoff rate constant. The washoff rate constant is constant and is considered to depend only on pollutant characteristics with the dimensions Mass Length⁻³ Time⁻¹.

Pollutants can be transported through convection, dispersion, or diffusion. In addition, biochemical reactions degrade the pollutant. However, due to the time scale of a single storm, solutes are transported by shallow overland flow. This may not accurately

represent the natural environment, where pollutants could be present in runoff in non-solute forms, such as adsorbed to particulates and organic matter. Despite these limitations, it is assumed that pollutant transport by diffusion and dispersion as well as biochemical reactions are negligible (Singh, 2002). Therefore, transport can be modeled based exclusively on convection. As such pollutant transport by overland flow can be represented by the dynamic equations of free-surface flow, the Saint Venant series of equations.

Convective transport in shallow overland flow can be adequately approximated by the kinematic wave analogy. The kinematic wave analogy is a mass balance that takes into account pollutant movement in runoff, run-on, rainfall deposition, and flux from the land surface as well as accumulation of pollutant in the overland flow. Mathematically this takes the form:

$$\frac{\partial(Ch)}{\partial T} + \frac{\partial(CQ)}{\partial X} + \frac{\partial P}{\partial T} = C_R I \quad (10)$$

Where C is the concentration of the pollutant in runoff, C_R is the concentration in rainfall, Q is the overland flow rate, h is the depth of runoff, P is the mass of pollutant on the surface of the land, and I is the intensity of rainfall (Akan, 1987). The first term is the change in mass flux of the pollutant in the runoff overtime. The second term is the net flux of pollutant in the runon and runoff. The third term is the change in mass of pollutant per area of land surface over time. The term on the right hand side is the mass of pollutant falling on the land surface in rainfall.

The transport relationship is solved for the pollutant concentration at each time step in each cell of the watershed grid through the following:

$$\begin{aligned}
0 = & \frac{C(x, y, t)h(x, y, t) - C(x, y, t-1)h(x, y, t-1)}{\Delta T} \\
& + \frac{\sum Q_{in}(x, y, t-1)C(x, y, t-1) - \sum Q_{out}(x, y, t-1)C(x, y, t-1)}{\Delta X} \\
& - Zh(x, y, t)P(x, y, t-1)
\end{aligned} \tag{11}$$

Where Q_{in} is the runoff discharge entering a grid cell from the adjacent cell and Q_{out} is the discharge leaving the cell. Further details on the implementation of this solution are given in the Methods section.

5. Methods

The basic setup of the project is illustrated in Figure 3. The water quality management system is comprised of hydrologic modeling using RADAR rainfall input and pollutant loading and buildup using SELECT which are used to model pollutant washoff and transport. Each of these water quality processes is calculated for each grid cell in the watershed model for simulation of pollutant concentration in runoff at each time-step of the modeled rainfall event.

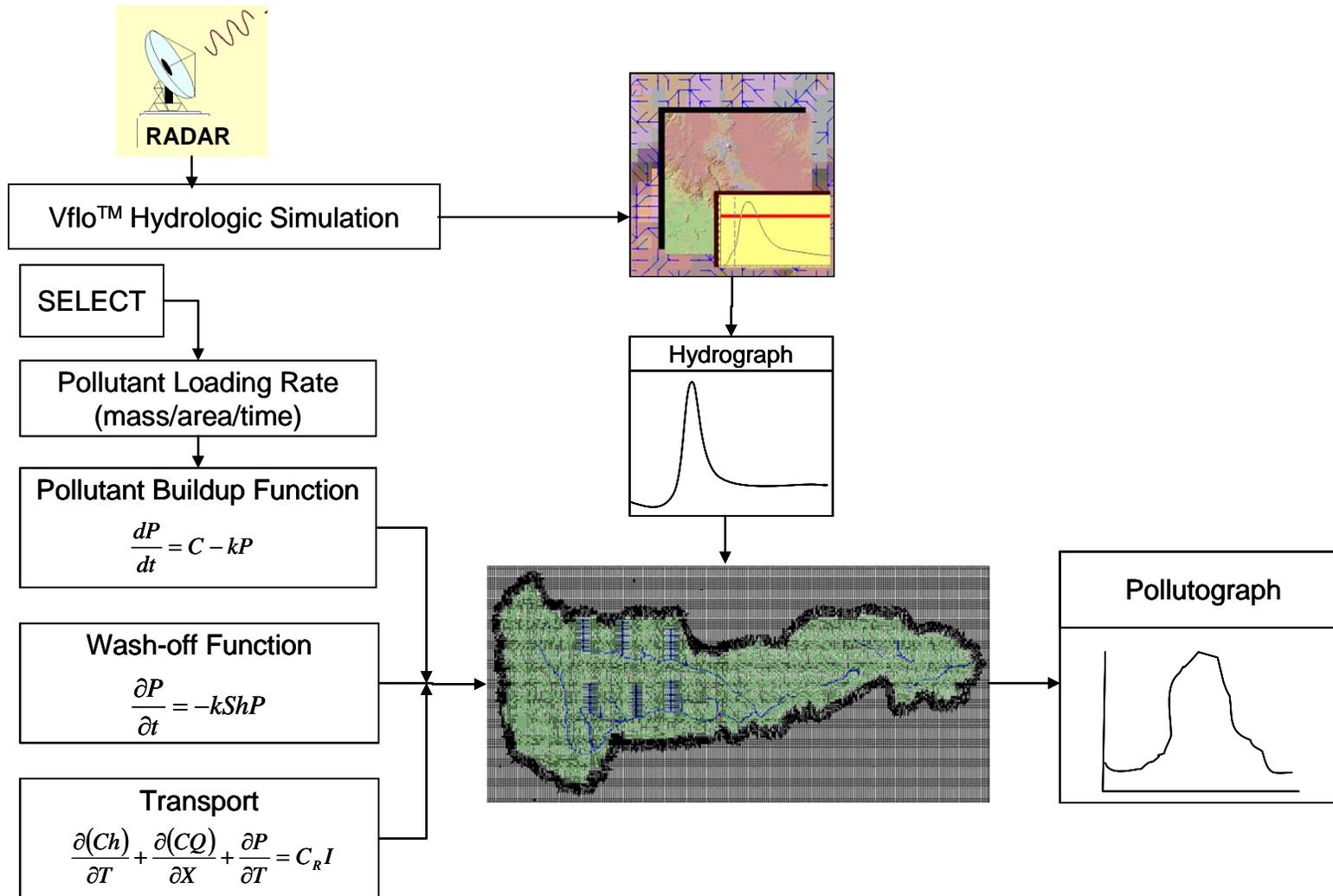


Figure 3. Flowchart of *Vflo*™ Water Quality Application

5.1 Hydrologic Model

A *Vflo*TM model developed by Zimmer (2007) was created in order to assess flooding in Little Cypress Creek, a sub-watershed of Cypress Creek (Fang et al., 2009). Geospatial inputs to the model include slope and flow accumulation grids that were derived from Lidar data gathered by the Tropical Storm Allison Recovery Project (TSARP) in 2006. Soil roughness and conductivity were taken from values associated with the soil types present according to the STATSGO soil survey. Channel cross sections were inserted for each of the 71 sub-watersheds of Cypress Creek. The channel cross sections were taken from HEC-RAS model developed as a part of TSARP. Model inputs and data sources are shown in Table 1.

Table 1. Cypress Creek Vflo Model Data Sources

Data Type	Source	Data Processed
<i>Elevation Data</i>	Lidar -TSARP	Slope Flow Direction Flow Accumulation
<i>Soils Data</i>	Statsgo	<u>Infiltration</u> Hydraulic Conductivity Wetting Front Soil Depth Initial Saturation Impervious
<i>Land Use Data</i>	TSARP	Roughness
<i>HEC RAS Cross Sections</i>	TSARP	Channel Geometry
<i>TWDB Lake Evaporation</i>	TWDB	Evapotranspiration
<i>Baseflow</i>	H-GAC Permitted Outfalls, WWTP	

A grid consisting of 22 acre cells (or 300 meter on a side) was used to spatially represent the watershed (See Figure 4). The 308 mi² watershed is represented by a total of 25,070 cells. A digital elevation model (DEM) created from Lidar topographic data was processed in ArcView using the Spatial Analyst Toolbox to create a slope grid and

ArcHydro (Maidment, 2006) to create a flow direction grid. Land use data collected through the TSARP project (2006) was used to determine the Manning's overland roughness, n . In addition, each land use category was assumed to have a percent impervious value.

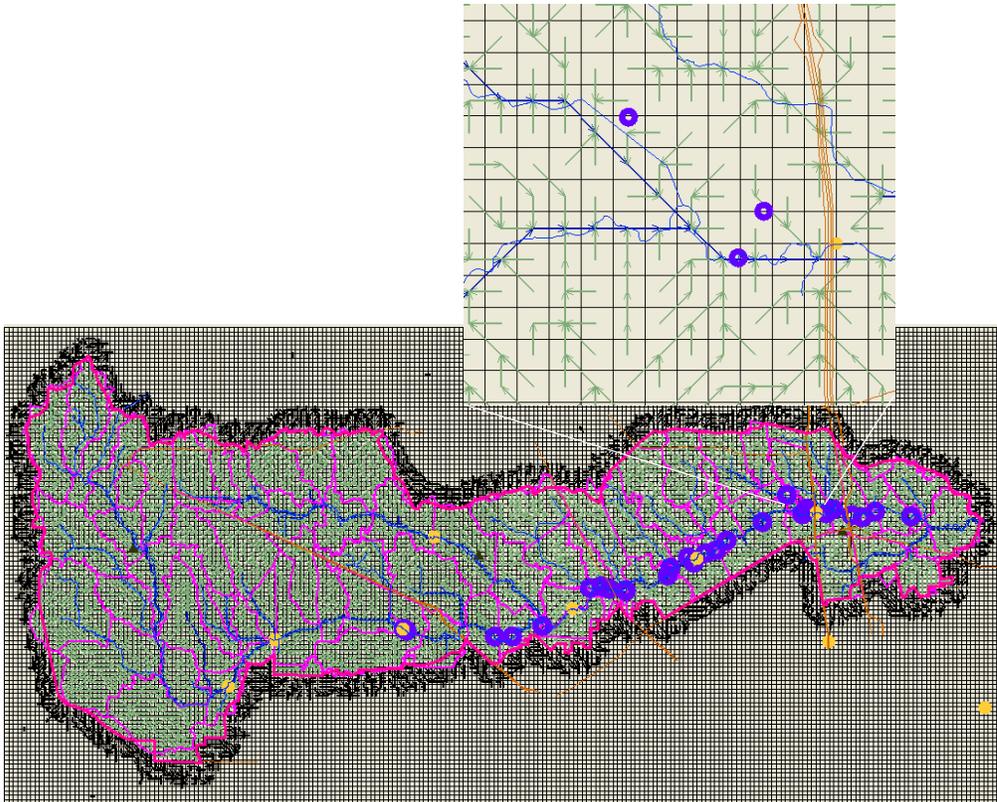


Figure 4. $Vflo^{TM}$ Grid and Grid Details of Cypress Creek

The rainfall runoff model, $Vflo^{TM}$, was run with NEXRAD rainfall data, delivered by Vieux and Associates in 10 minute intervals at a 1km resolution. The RADAR data was collected from the National Weather Service RADAR at Dickinson, Texas and calibrated by Vieux and Associates to the 12 rain-gauges within and around the watershed.

5.2 Pollutant Loading

Average daily pollutant loading was estimated using SELECT (Spatially Explicit Load Enrichment Calculation Tool). The identified *E. coli* sources within Cypress Creek are waste water treatment plants (WWTP), pet waste, urban runoff, septic system failure, wildlife, and agricultural animals. The population estimates for cattle and sheep were taken from the 2002 U.S. Department of Agriculture Census (USDA-NASS, 2002). The population estimates for feral hogs and dogs were derived from literature values as outlined in Teague et al. (2009). The population estimates are in Table 2.

Table. 2 Cypress Creek Population Estimates

Populations	Description	Estimate
Beef Cattle	2002 USDA NASS	11,610
Dairy Cattle	2002 USDA NASS	153
Sheep	2002 USDA NASS	265
Feral Hogs	5/km ² distributed to Riparian Corridor	3,156
Pets	0.8 dogs/ Household	123,680

Nutrients, including total phosphorus and total nitrogen have associated sources including waste water treatment plants, agricultural fertilizer, urban fertilizer application, and agricultural, pet, and wildlife wastes. The potential loading of nutrients has been estimated based upon the EPA suggested pollutant loading rates for different land uses.

5.3 Water Quality Modeling of Pollutant Washoff and Transport

The mass of pollutant in the runoff leaving each grid cell is calculated by the kinematic wave equation for the selected pollutant in each grid cell at each time step. This mass

balance approach accounts for the washoff, deposition, and pollutant runoff from other cells, so that the pollutant discharge from each cell can be calculated (See Figure 5).

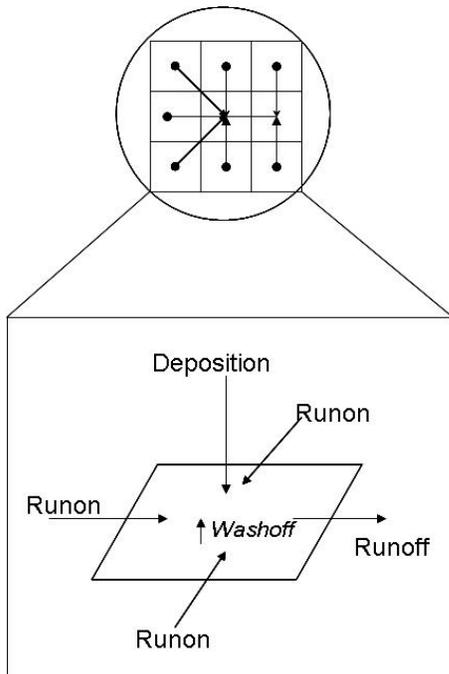


Figure 5. Schematic Representation of Pollutant Runoff in Grid-based Finite Element Model Solutions

The algorithm to accomplish this is conceptualized within the following steps for overland flow:

- (1) Calculate the mass of pollutant washed from the surface for every grid cell at the initial time step.
- (2) Calculate the mass of pollutant in the runoff leaving each grid cell.
- (3) Assign the runoff from each grid cell as the runoff to the receiving grid cell.
- (4) Use conservation of mass and momentum (kinematic wave equation) to calculate the mass of pollutant in each grid cell.
- (5) Repeat for the next time step.

5.4 Washoff Calculation

The mass of pollutant washed off the land surface is calculated for each time step using the depth of the flow, washoff coefficient, and the mass of pollutant from the previous time step. Because the mass of pollutant washed off the land surface is independent of the concentration of the pollutant concentration in the overland flow, the pollutant washoff can be calculated independently of the transport, thus simplifying the calculation. The results of the $Vflo^{TM}$ simulation, distributed discharge, can be used in ArcGIS to calculate the washoff, using Spatial Analysis: Raster Calculator as:

$$\frac{P(x, y, t) - P(x, y, t - 1)}{\Delta t} = -kSh_i(x, y, t)P(x, y, t - 1) \quad (12)$$

The calculation requires slope S , the washoff factor k , depth of flow, h , from the $Vflo^{TM}$ model output, and P , the mass of pollutant per cell from the previous timestep. The $P(x, y, 0)$ is taken from the loading and buildup calculation.

5.5 Simulation of Transport

The transport of the pollutant using kinematic wave equation (see equations 10 and 11) then requires calculation of concentration of pollutant in the runoff from each grid cell (See Figure 6) with

$$\begin{aligned}
0 = & \frac{C(x, y, t)h(x, y, t) - C(x, y, t-1)h(x, y, t-1)}{\Delta T} \\
& \left[\begin{aligned}
& Q_{in}(x-1, y-1, t-1)C(x-1, y-1, t-1) + Q_{in}(x, y-1, t-1)C(x, y-1, t-1) \\
& + Q_{in}(x+1, y-1, t-1)C(x+1, y-1, t-1) + Q_{in}(x-1, y, t-1)C(x-1, y, t-1) \\
& + Q_{in}(x+1, y, t-1)C(x+1, y, t-1) + Q_{in}(x-1, y+1, t-1)C(x-1, y+1, t-1) \\
& + Q_{in}(x, y+1, t-1)C(x, y+1, t-1) + Q_{in}(x+1, y+1, t-1)C(x+1, y+1, t-1)
\end{aligned} \right] - \\
& \left[\begin{aligned}
& Q_{out}(x-1, y-1, t-1)C(x-1, y-1, t-1) + Q_{out}(x, y-1, t-1)C(x, y-1, t-1) \\
& + Q_{out}(x+1, y-1, t-1)C(x+1, y-1, t-1) + Q_{out}(x-1, y, t-1)C(x-1, y, t-1) \\
& + Q_{out}(x+1, y, t-1)C(x+1, y, t-1) + Q_{out}(x-1, y+1, t-1)C(x-1, y+1, t-1) \\
& + Q_{out}(x, y+1, t-1)C(x, y+1, t-1) + Q_{out}(x+1, y+1, t-1)C(x+1, y+1, t-1)
\end{aligned} \right] \\
& + \frac{\quad}{\Delta X} \\
& - ZY_i(x, y, t)P(x, y, t-1) +
\end{aligned} \tag{13}$$

Where Q_{in} is the discharge from one cell into the target cell and Q_{out} is the discharge leaving the target grid cell and entering the other cells. It should be noted that most of these cells will have a Q_{in} or Q_{out} of zero. This simulation will require exporting to matrix solver software that can support the large number of grid cells required by the simulation. In this project, this was accomplished using ArcObjects programming in ArcGIS.

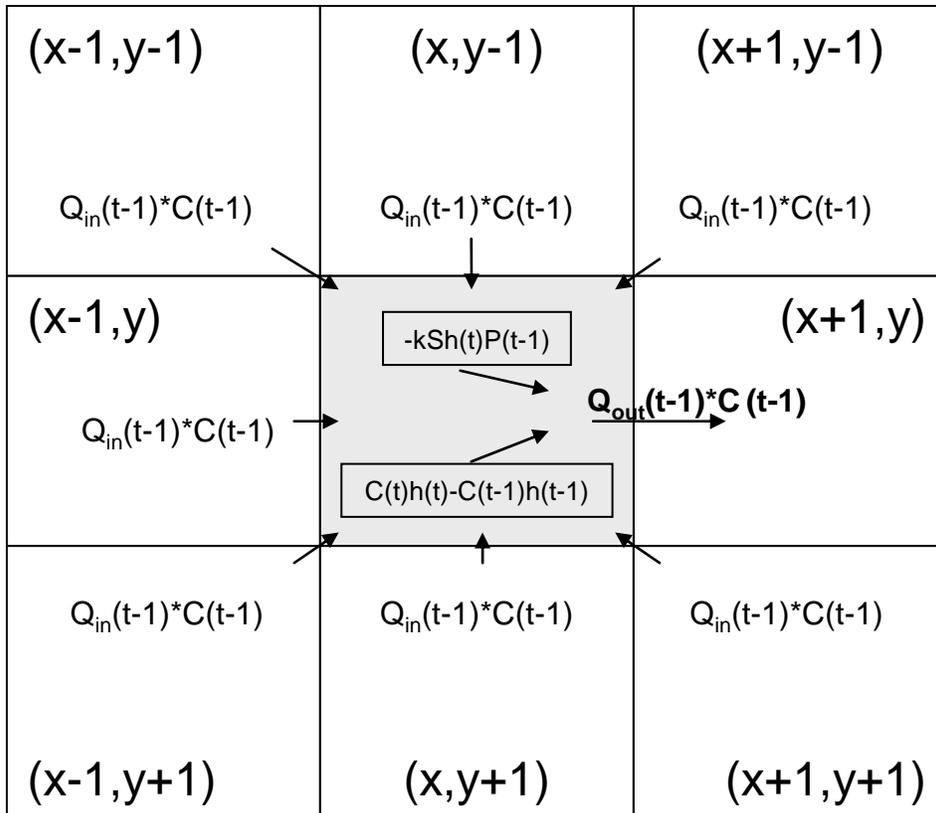


Figure 6. Grid Based Calculation of Pollutant Transport

6. Results

The proposed water quality management system is currently in development. Thus far the system is in the process of application for two rainfall events for which corresponding water quality data has been collected at the water quality monitoring station at IH45. The *VfloTM* hydrologic model was applied for July 7, 2009 and September 22, 2009 rainfall events using delivered RADAR rainfall. The modeled versus observed discharge at the IH45 from the hydrologic model are shown in Figure 7 for July 7, 2009 and Figure 8 for September 22, 2009. Distributed discharge, or the modeled runoff for each grid cell of the watershed model, from a sample of time-steps, are shown in Figures in Appendix A.

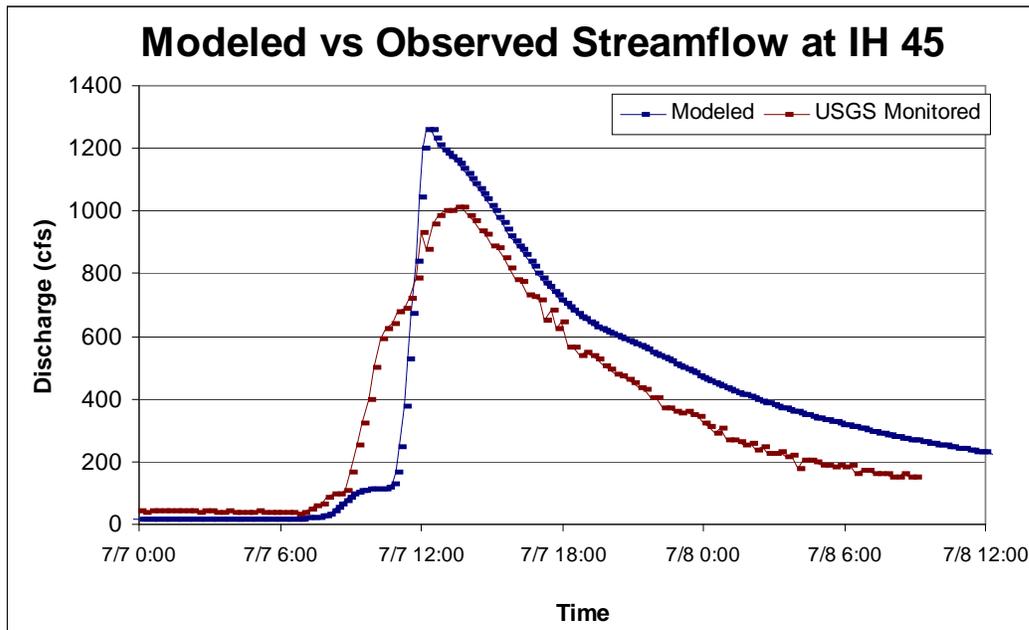


Figure 7. *Vflo*TM Simulation of July 7, 2009 Storm

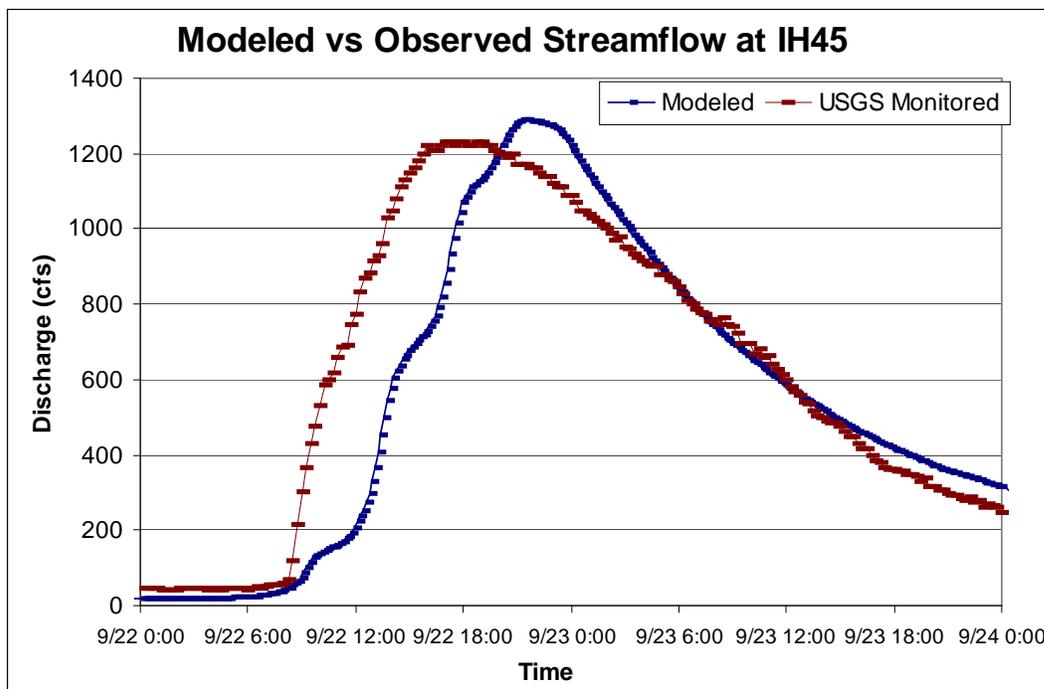


Figure 8. *Vflo*TM Simulation of September 22, 2009 Storm

The previously discussed storms have been sampled to assess storm water quality of Cypress Creek at IH-45. The timing of the water quality observations are shown in Figures 9 and 10 with associated water quality data in Tables 3 and 4.

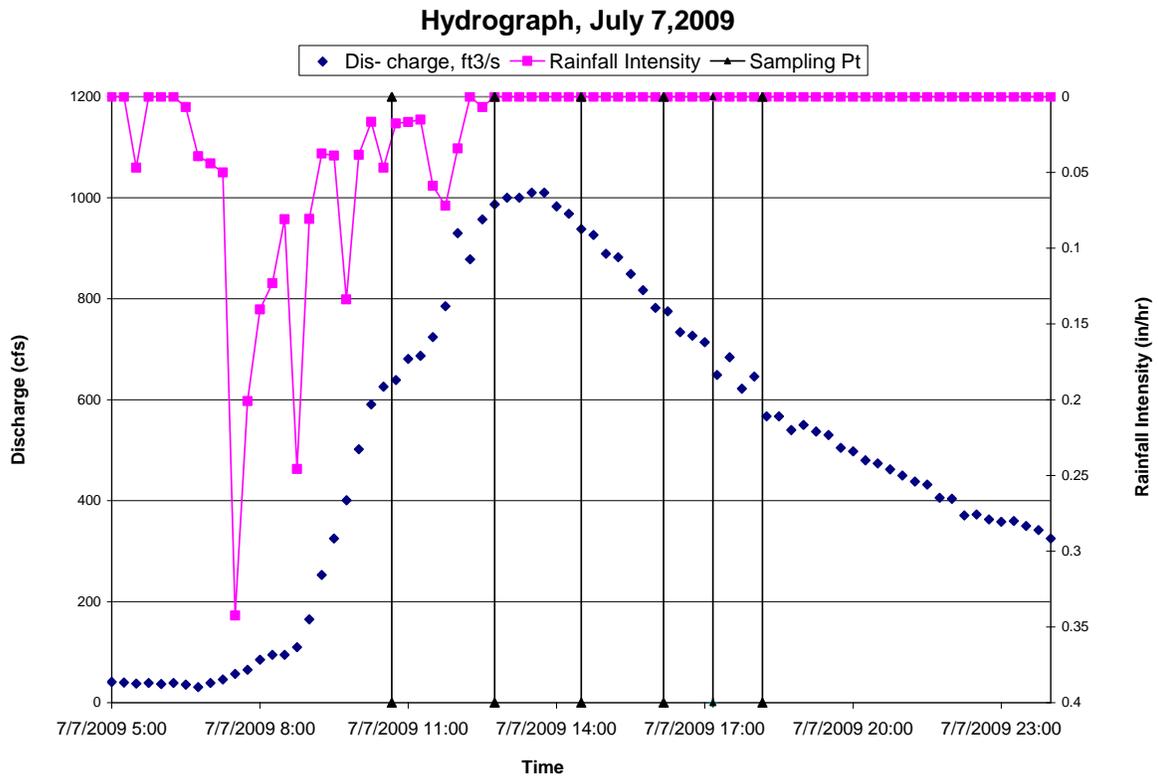


Figure 9 . Storm Water Quality Sampling from July 7, 2009

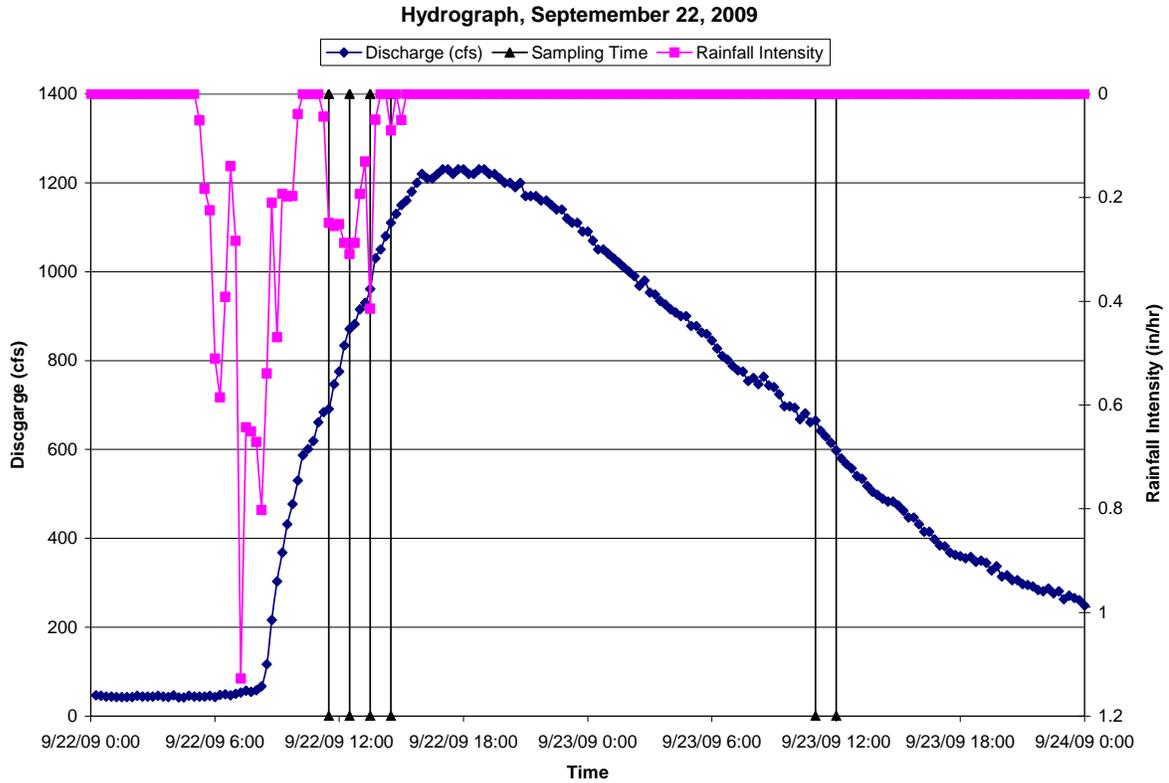


Figure 10 . Storm Water Quality Sampling from September 22, 2009

Table 3. Water Quality Data for July 7, 2009 Storm

Time	Streamflow (cfs)	<i>E.coli</i> (MPN/dL)	Nitrite (mg/L)	Nitrate (mg/L)	TP (mg/L)	OP (mg/L)	NH3 (mg/L)	TSS (mg/L)
7/7/2009 10:40	626	10,265	0.11	5.44	1.82	1.59	0.716	107
7/7/2009 12:45	987	49,657	0.048	2.68	1.31	0.968	0.911	213
7/7/2009 14:30	938	60,480	0.06	2.7	0.99	0.99	0.826	192
7/7/2009 16:10	782	49,657	0.064	2.34	0.904	0.904	0.862	155
7/7/2009 17:10	714	60,492	0.067	2.36	0.929	0.929	0.765	149
7/7/2009 18:10	646	60,492	0.061	2.09	0.841	0.841	0.777	125
Min	626	10,265	0.05	2.09	0.84	0.84	0.72	107.00
Max	987	60,492	0.11	5.44	1.82	1.59	0.91	213.00
Median	748	55,069	0.06	2.52	0.96	0.95	0.80	152.00
Std Dev	151	19,472	0.02	1.25	0.37	0.28	0.07	39.88
EMC		49,706	0.07	2.87	1.12	1.02	0.82	163.15

Table 4. Storm Sampling from Sept. 22, 2009

Time	Streamflow (cfs)	<i>E.coli</i> (MPN/dL)	Nitrite (mg/L)	Nitrate (mg/L)	TP (mg/L)	OP (mg/L)	NH3 (mg/L)	TSS (mg/L)
9/22/09 11:30	629	12,210	0.041	4.672	1.414	1.344	0.411	107
9/22/09 12:30	871	38,827	0.028	3.192	1.128	1.003	0.484	134
9/22/09 13:30	961	27,996	0.044	4.811	1.411	1.358	0.436	157
9/22/09 14:30	1,110	43,322	0.037	4.479	1.4	1.281	0.508	173
9/23/09 11:00	665	14,485	0.035	1.246	0.935	0.681	0.883	99
9/23/09 12:00	598	14,485	0.036	1.155	0.885	0.691	0.92	88
Min	598	12,210	0.03	1.16	0.89	0.68	0.41	88.00
Max	1,110	43,322	0.04	4.81	1.41	1.36	0.92	173.00
Median	768	21,241	0.04	3.84	1.26	1.14	0.50	120.50
Std Dev	207	13,567	0.01	1.70	0.25	0.32	0.23	33.96
EMC		27,883	0.04	3.48	1.23	1.10	0.58	133.51

7. Discussion

The hydrologic modeling results for the two storms shown in Figures 7 and 8 show that the $Vflo^{TM}$ rainfall runoff model performs adequately on average with varying performance for each rainfall event. The spatially distributed results of hydrologic modeling of the July 7, 2009 rainfall event shown in Appendix A, show the format of the $Vflo^{TM}$ hydrologic modeling. The hydrologic results, in the form of modeled runoff from each grid cell at each time step can be used in the modeling of pollutant washoff and transport. Examination of the hydrographs at IH45 (Figures 7 and 8) show that at the beginning of rising streamflow, the modeled flow is less than the observed streamflow. Near the peak in streamflow, the modeled flow is greater than the observed flow. Despite this, the modeled results are considered within an acceptable range. Further modeling of additional storms, including further calibration efforts, will improve the model performance.

The July 7, 2009 storm followed after 51 days of dry weather, where as the September 22, 2009 storm followed after 9 days of dry weather. Corresponding to a longer period of buildup, the median and Event Mean Concentration (EMC) (See Tables 3 and 4) of *E.*

coli and total suspended solids are larger for the July 7 storm. In contrast, the median and EMC for nitrate, total phosphorus, and orthophosphorus were higher for the September 22nd storm than the July 7th storm. For the July 7, 2009 storm, concentrations of nitrate and total phosphorus at the beginning of the rising limb of the hydrograph are higher than the observed concentrations at the end of the falling limb of the hydrograph. This indicates the presence of a first flush phenomenon. In contrast, *E. coli* observations were higher at the falling limb of the hydrograph. This could possibly be attributed to greater buildup on areas of the watershed that contribute to streamflow at this time or to overflows at the wastewater treatment plants. The September 22nd storm also exhibited higher concentrations of nitrate and total phosphorus in the rising limb of the hydrograph, displaying first flush phenomenon. The observations of *E. coli* start low and increase with the rising limb of the hydrograph, with a decrease on the falling limb. This displays a lack of first flush phenomenon. This data will be used to calibrate the water quality model with future storms used for further calibration and validation.

Future efforts needed to further develop the proposed water quality management system include :

- 1) Estimation of Pollutant Loading using SELECT
- 2) Simulate the selected storms using *Vflo*TM with RADAR Rainfall input
- 3) Calculate pollutant washoff at each time step
- 4) Calculate pollutant discharge at each time step
- 5) Process the simulation results to produce pollutographs at the Cypress Creek at IH-45 gauge.

- 6) Calibrate the model based upon comparison of simulated results with measured pollutant loads.

8. Conclusion

The proposed project to develop a water quality prediction system was composed of three primary components including hydrologic modeling, pollutant buildup, washoff, and transport modeling, and water quality data collection. The hydrologic model *VfloTM* has been calibrated for use of RADAR rainfall input. Currently the rainfall-runoff modeling results are being used for development of the pollutant washoff and transport modeling. Water quality data have been collected for two rainfall events and the data used for development and calibration of the pollutant washoff and transport model.

Future efforts will include continuation of water quality data collection during selected rainfall events with the goal of capturing information on bacterial and nutrient loads during the rising and falling limb of the hydrograph. Further development of the water quality prediction model will include the estimation of pollutant buildup with SELECT, and automated calculation of pollutant washoff and transport.

This project is the basis for building a continuous, real time alert system for on-demand prediction of influent pollutant loading to Lake Houston. The intent is for this study to be the first phase of a wider project encompassing the Lake Houston Basin. Overall, the expected outcome of the proposed project is an advance in water quality modeling capabilities. It will extend current models by producing a fully distributed water quality

model simulating pollutant buildup, washoff, and transport. Specifically it will provide valuable management information to the City of Houston Northeast Water Purification Plant Operations Manager for improved efficiency of water quality treatment.

Acknowledgements

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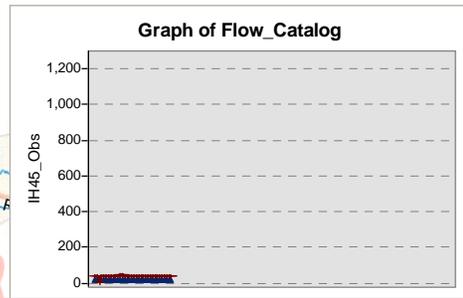
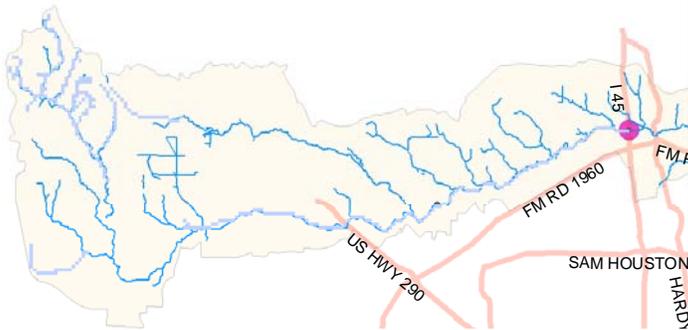
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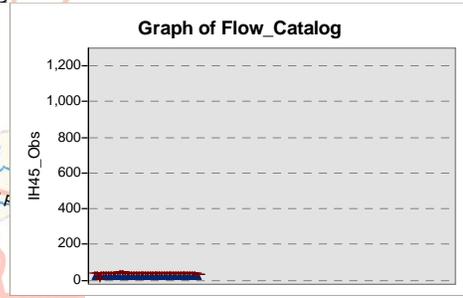
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Appendix A: Spatially Distributed Results of Rainfall-Runoff Modeling

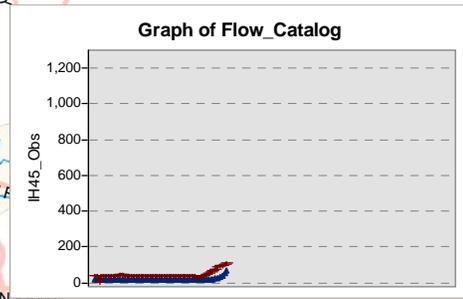
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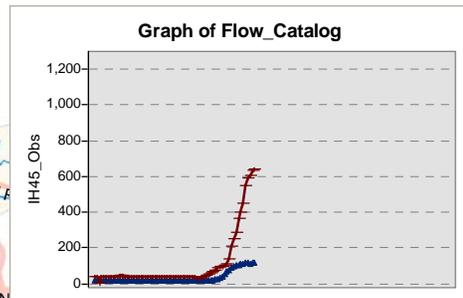
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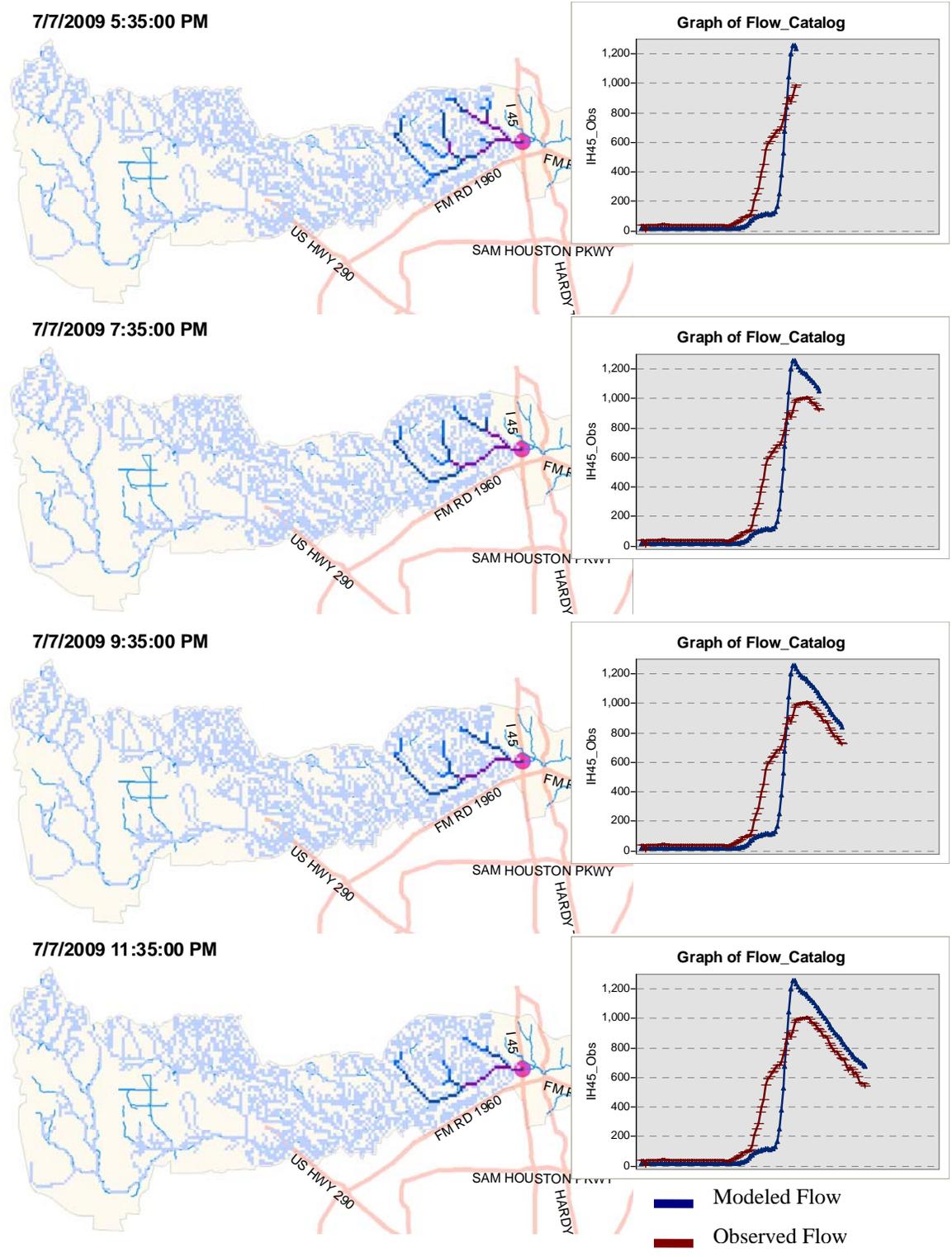


Runoff (CFS)



■ Modeled Flow
■ Observed Flow

Figure A-1. Spatially Distributed Results of Rainfall-Runoff Modeling of July 7, 2009 Rainfall Event



Runoff (CFS)



Figure A-2. Spatially Distributed Results of Rainfall-Runoff Modeling of July 7, 2009 Rainfall Event

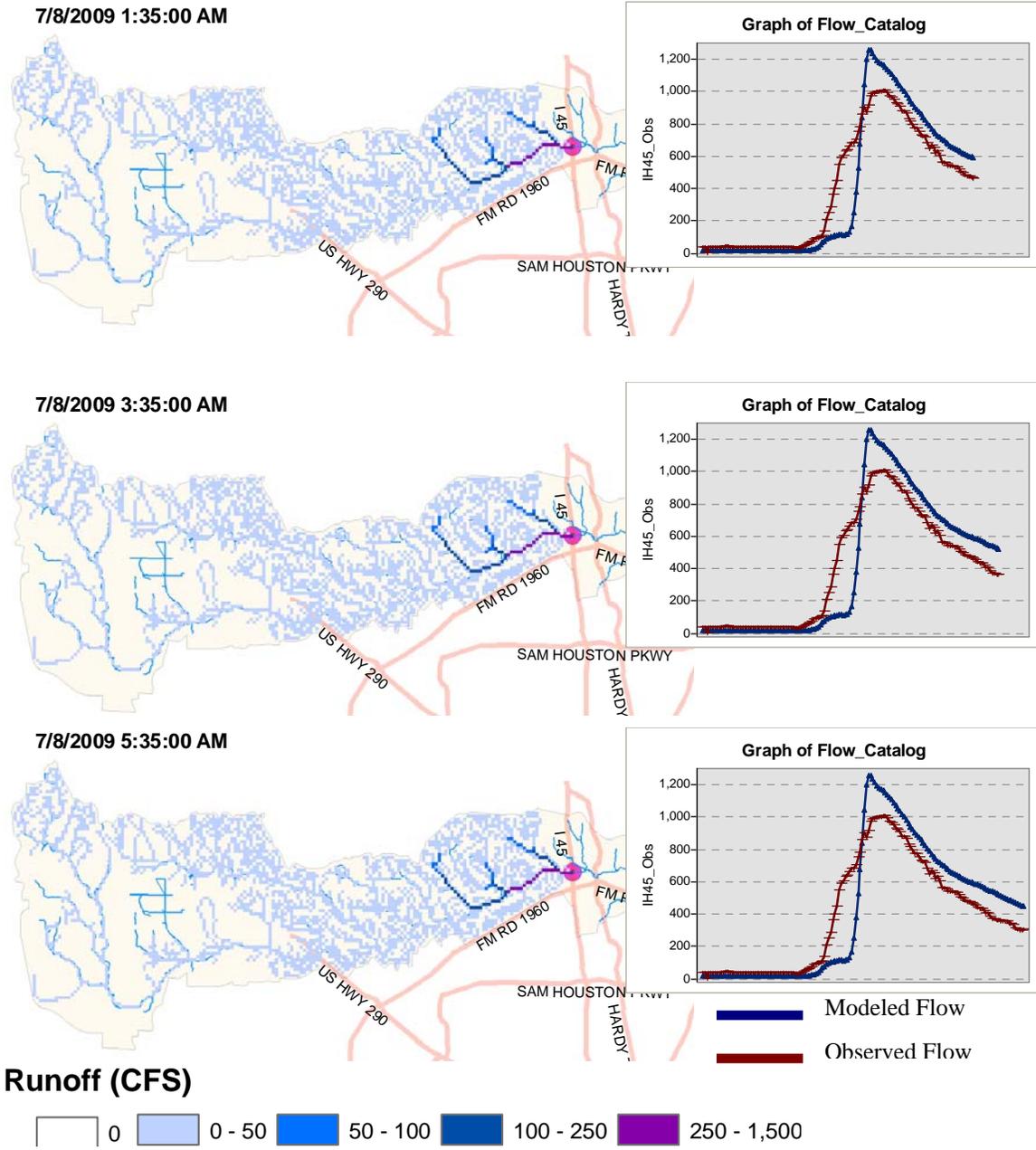


Figure A-3. Spatially Distributed Results of Rainfall-Runoff Modeling of July 7, 2009 Rainfall Event

Biotransformation of pharmaceuticals and personal care products (PPCPs) at an effluent land application site

Basic Information

Title:	Biotransformation of pharmaceuticals and personal care products (PPCPs) at an effluent land application site
Project Number:	2009TX325B
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End Date:	2/28/2010
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Focus Category:	Treatment, Wastewater, Water Quality
Descriptors:	None
Principal Investigators:	Deborah Carr, Todd Anderson

Publications

1. Carr, D.L., Morse, A.N., Zak, J.C., and Anderson, T.A. Microbially Mediated Degradation of Common Pharmaceuticals and Personal Care Products in Soil under Aerobic and Anaerobic Conditions. (in revision), Water Air & Soil Pollution.
2. Carr, D.L., 2009, Biotransformation of estrogens and synthetic pharmaceuticals and personal care products in a sandy loam soil, "MS (Ph.D.) Dissertation," Environmental Toxicology, College of Arts and Sciences, Texas Tech University, Lubbock, TX, 117pp.
3. Carr, D.L., Morse, A.N. and Anderson T.A., 2009, Biotransformation of estrogens and synthetic pharmaceuticals and personal care products in a sandy loam soil. SETAC North America Annual Meeting
4. Carr, D.L., Morse, A.N. and Anderson, T.A. Biotransformation of micropollutants in sandy loam soil. SC-SETAC Annual Spring Meeting, 2009
5. Carr, D. L. and Anderson, T. A Biotransformation of two synthetic micropollutants in soils. Toxicology Research Exposé, Texas Tech University, 2009.

REPORT

Title Biotransformation of pharmaceuticals and personal care products (PPCPs) at an effluent land application site

Project Number 2009TX325B

Primary PI Deborah L. Carr

Other PIs Todd A. Anderson

Abstract

Biological degradation rates of estrogen compounds and common pharmaceutical and personal care products (PPCPs) were examined in soils with a long history of exposure to these compounds through wastewater effluent and in soil not previously exposed.

Biological degradation rates over 14 d were compared under aerobic and anaerobic conditions. Autoclaved soils were used as controls for chemical and physical interactions between the tested compounds and the soil matrix. Estrogen compounds including estrone, β -estradiol, estriol, and 17α -ethinylestradiol exhibited rapid degradation by soil microorganisms in both aerobic and anaerobic conditions. The most rapid degradation rates for estrone, estriol, and 17α -ethinylestradiol occurred in pre-exposed soil under aerobic conditions; half-lives calculated under these conditions were 0.6 d, 0.7 d, and 0.8 d, respectively. Unexposed soil showed similar or slightly longer half-lives than pre-exposed soil under aerobic conditions. β -estradiol was the exception; in all treatments, degradation in unexposed soil resulted in a shorter half-life (2.1 d versus 2.3 d).

Anaerobic soils exhibited high biological degradation of estrogens as well. Half-lives of all estrogens ranged from 0.7 d to 6.3 d in anaerobic soils. Triclosan degraded faster under aerobic conditions with half-lives of 5.9 d and 8.9 d in exposed and unexposed soil. Under anaerobic conditions, triclosan half-lives were 15.3 d in unexposed and 28.8 d in exposed soil. Ibuprofen showed the least propensity toward biological degradation compared to the other chemicals tested. Biological degradation of ibuprofen was only observed in the unexposed soil; a half-life of 41.2 d was determined under anaerobic conditions and 121.9 d under aerobic conditions. Interestingly, the unexposed soil exhibited a greater ability under anaerobic conditions to biologically degrade all tested compounds than soil with previous exposure to PPCPs.

Problem and Research Objectives

Several recent media accounts have focused attention on prescription, over the counter drugs, and personal care products showing up in the nation's drinking water sources. While PPCPs have been identified in the environment for several decades (Kummerer, 2001), the fates and persistence of these compounds are not well known. These compounds are considered micropollutants and can be found in wastewater and surface and groundwater near wastewater discharge areas. They can include birth control hormones, antibiotics, antimicrobials, pain relievers, insect repellants, and caffeine to name only a few. In general these are compounds with known pharmacological actions in humans and animals and, although quantities of these contaminants in wastewater may be

low, they are continuously present and constitute a constant exposure. In most cases, no regulatory limits have been set for these compounds and their discharge from WWTPs.

Natural and synthetic estrogens have become one of the emerging contaminants of concern because of their ability to disrupt the endocrine system and their potential to cause long-term impacts to wildlife and human health (Lee and Liu, 2002; Hermanowicz and Wozei, 2002; Norris and Carr, 2006). Investigations into the removal of endocrine disrupting chemicals (EDCs) from water in WWTPs have shown that bacteria in activated sludge systems can reduce concentrations of natural and synthetic estrogens and their breakdown products (Hermanowicz and Wozei, 2002; Andersen *et al.*, 2003). Sorption to sludge particulate matter and biodegradation appear to be the most important removal processes for EDCs in wastewater treatment systems, though microbial populations vary in their ability to degrade estrogens (Layton *et al.*, 2000). While studies have confirmed the ability of EDCs to partition to solids in WWTPs (Gomes *et al.*, 2004), less than 3 percent of the estrogenic activity was found in the sludge (Körner *et al.*, 2000) and only 5 percent of the estrogens were adsorbed onto digested wastewater sludge (Anderson *et al.*, 2003). This implies a significant fraction may be susceptible to microbial degradation.

Several studies have detected antibiotics such as ciprofloxacin (Alder *et al.*, 2000) in WWTP effluents at ng/L to µg/L concentrations. According to a study by the U.S. Geological Survey (Kolpin *et al.*, 2002), out of 31 antibiotics and antibiotic metabolites measured 17 were detected, indicating a strong need for information regarding the fate and transport of antibiotics through waste treatment plants and in the environment.

Many PPCPs other than antibiotics and EDCs have been detected in surfacewater and wastewater effluents. Triclosan, an antimicrobial disinfectant found in a wide array of personal care cleansers and household cleaning products and plastics, has been identified as one of the most commonly occurring chemicals in effluent fed surfacewaters (Kolpin *et al.*, 2002; Focazio *et al.*, 2008). Ibuprofen, a non-steroidal anti-inflammatory drug (NSAID) has been identified as the third most popular drug in the world both by sales and use. It is one of the most common PPCPs occurring in the aquatic environment and has been shown to persist up to 6 months in groundwater aquifers (Drewes *et al.*, 2003).

As water supplies become more limiting (especially in the arid Southwest) and water re-use practices increase, PPCPs in municipal water supplies and the level of effluent treatment become an important human and environmental health issue. Land application as a tertiary treatment for wastewater is an efficient method for many communities because of its low cost and as an alternative to potable water for agriculture and maintaining green spaces in the community. To our knowledge, information about the fate of PPCPs contained in secondary effluent once they are applied to a soil environment is non-existent. Complex soil structure including varying aggregate and soil pore sizes provide multiple niche environments and support a large and varied microbial community (Beare *et al.*, 1995). Difficulty in isolating and culturing the vast majority of these organisms inhibits our understanding of the scope and rates of microbially mediated biochemical processes that may occur within the soil profile (Buckley and Schmidt, 2003). This study attempted to broadly address potential microbial soil environments and their contributions to degrading PPCPs.

Materials/Methodology

Site Description

The Lubbock land application site (LLAS), a component of the Lubbock wastewater treatment plant (LWWTP) was the site of interest for this study. The LLAS receives effluent after secondary treatment from the LWWTP and has been in continual operation since 1915. LLAS soils are classified as Friona loam of the Estacado series. The soil is a slightly alkaline brown clay loam of weak granular structure, with permeability of 1.5 to 5.0 cm/hr (USDA, 2007). Depth to the water table exceeds 200 cm with a moderately high to high hydraulic capacity (9-28 $\mu\text{m/s}$). Sampling occurred from exposed soils – soils under an irrigation pivot receiving effluent, and from unexposed soil – soil at the same site but never having been irrigated. The two sample sites have very similar soil characteristics which are summarized in Table 1.2. The reduced cation exchange capacity (CEC) in the exposed soil (22.9 meq/100 g) versus 36.7 meq/100 g CEC in the unexposed soils may reflect effluent nitrogen levels. Soil pH in the unexposed soil was 7.9 and is typical for soils of the Friona Loam series (USDA, 2007). The soil pH of 7.3 in the exposed soil may indicate high nitrate levels and a degree of nitrogen saturation. The effluent exposed soils have less than half the soluble salts content as the unexposed soils due to leaching of the salts through frequent irrigation of secondary treated effluent at a rate of 3-4 cm/week (M. Gonzales, LWWTP, personal communication).

Soil Collection

Samples were collected from the top 5-18 cm topsoil from three locations within the irrigation pivot area (exposed) or outside the irrigation range (unexposed). The soils were mixed to form a composite of wastewater effluent exposed or unexposed control soil, and stored in the dark at 4°C until needed. Prior to experimental set-up, the soils were coarse sieved (4.0 mm) to achieve a degree of homogeneity while maintaining meso- and micro-aggregate soil structure. Soil aliquots to serve as abiotic controls were autoclaved twice for 1 hour, at 24 h intervals, to ensure that the microbial community was killed.

Experimental design

Ten grams of soil was added to 40 mL clear glass vials with Teflon® silica septa in polypropylene lids. Soil samples were spiked with 25 $\mu\text{g/mL}$ micropollutant standard. Sterile Milli-Q water was added to achieve 30% field capacity v/w (Table 1.2). The headspace of each vial was sparged with either compressed, breathing quality air (aerobic) or compressed nitrogen ultra-high purity (anaerobic) equal to five volume replacements. Triplicate samples were incubated in the dark at 22 °C under aerobic or anaerobic conditions. Killed controls under aerobic and anaerobic conditions were also monitored in triplicate for each chemical. All efforts were made to maintain starting oxygen conditions by allowing a slight positive pressure in the vials and incubating them upside down. Upon opening the vials for extraction, vials maintained a slight positive pressure, confirming that gas exchange had not occurred. Samples were extracted after incubation periods of 0, 3, 7 and 14 d with 20 mL high-performance-liquid chromatography (HPLC)-grade acetonitrile (ACN) (Fisher Scientific, Suwanee, GA)

(Golet, 2003). Preliminary studies indicated 98 % recovery of E1, E2 and EE2 compounds, 52 % of E3, 96 % of ibuprofen, and 93 % of triclosan by this method. Extracts were filtered through 0.45 μm nylon filters (Whatman International Inc., Florham, NJ, USA) into 2 mL amber glass HPLC auto-sampler vials, sealed with PTFE/rubber septa and stored frozen until analysis.

Test Chemicals and Analysis

Estrogens

Three natural steroid estrogens, estrone (E1), β -estradiol (E2) and estriol (E3), and synthetic steroid estrogen, 17 α -ethinylestradiol (EE2) were used in this study. All estrogens were HPLC grade (> 98%) and obtained from Sigma Aldrich (St. Louis, MO, USA). Spiking solutions were made up in 100 percent ACN at 25 $\mu\text{g}/\text{mL}$. Stock solutions at 100 mg/L were made for each chemical and diluted for analytical standards using HPLC grade ACN. Estrogens from soil extractions were determined by reverse phase HPLC equipped with Chemstation analytical software (HP series 1100, Hewlett-Packard, Avondale, PA, USA). Sample injection volume was 50 μL , eluent flow was 0.8 mL/min through a C-18 column (Alltech Platinum 250 X 4.6 mm, 5 μm , Deerfield, IL, USA), and detection wavelength was 200 nm. An acetonitrile:water mobile phase was used for analysis, but the ratio was adjusted for each compound; E1 was 85:15, E2 and EE2 was 80:20, and E3 was 50:50 ACN: water. Reporting limit was 0.02 $\mu\text{g}/\text{g}$ soil

Triclosan

Triclosan as HPLC-grade (Irgasan) (EC 3380-34-5) was obtained from Sigma Aldrich (St. Louis, MO, USA). The solution for initial spiking was made up in 100 percent ACN at 25 $\mu\text{g}/\text{mL}$. A stock solution of 100 mg/L was diluted for analytical standards using HPLC-grade ACN. Standards and extracted samples were analyzed by reverse phase HPLC with a sample injection volume of 25 μL , 1.0 mL/min eluent flow, through a C-18 column (Alltech Platinum 250 X 4.6 mm, 5 μm , Deerfield, IL, USA), with detection at $\lambda = 200$ nm. The mobile phase was 80:20 ACN:water. Reporting limit was 0.02 $\mu\text{g}/\text{g}$ soil.

Ibuprofen

HPLC-grade ibuprofen (EC 51146-56-6) was obtained from Sigma Aldrich (St. Louis, MO, USA). The solution for initial spiking was made up in 100 percent ACN at 1.5 $\mu\text{g}/\mu\text{L}$. A standard stock solution at 100 mg/L was diluted for analytical standards using HPLC-grade ACN. Standards and extracted samples were analyzed by reverse phase HPLC with a sample injection volume of 50 μL , 0.8 mL/min eluent flow through a C-18 column (Alltech Platinum 250 X 4.6 mm, 5 μm , Deerfield, IL, USA), and detection at $\lambda = 200$ nm. The mobile phase was 90:10 MeOH:0.04M H_3PO_4 . Reporting limit was 0.1 $\mu\text{g}/\text{g}$ soil.

Ciprofloxacin

HPLC-grade ciprofloxacin (EC 85721-33-1) was obtained from Sigma Aldrich (St. Louis, MO, USA). The solution for initial spiking was made up in ACN with 0.1 % acetic acid at 1.5 $\mu\text{g}/\mu\text{L}$. A standard stock solution at 100 mg/L made up in ACN plus 0.1 % acetic acid was diluted for analytical standards using HPLC-grade ACN. Standards and extracted samples were analyzed by reverse phase HPLC with a sample injection volume of 25 μL , 0.8 mL/min eluent flow through a C-18 column (Alltech Platinum 250 X 4.6 mm, 5 μm , Deerfield, IL, USA), and detection by fluorescence with excitation $\lambda =$

278 nm and emission $\lambda = 445$ nm. The mobile phase was 50:50 ACN:5 mM mono-phosphate buffer KPO_4 at pH 3. Reporting limit was 0.02 $\mu\text{g/g}$ soil.

Data analysis

Sample concentrations at various time points were normalized as percent of the day 0 concentrations and plotted by treatment on a scatter diagram. Best fit regression curves were fit to the scatter diagrams and analyzed by ANCOVA in R version 2.7.2.

Principal Findings

Loss of target compounds in the following results section has been interpreted to be due to biological processes in the soil because there was no loss of compound over time observed in the samples that contained killed soil resulting from autoclave sterilization.

Estrogens

Estrone

Estrone exhibited biological degradation under all experimental conditions as indicated by no loss of compound over time in the killed (autoclaved) controls (Figure 1). Biological degradation was most rapid under aerobic conditions. Half-lives calculated from best-fit regression equations were 0.6 d and 1.1 d in exposed and unexposed soil, respectively. Half-lives under anaerobic conditions were slightly longer: 6.3 d in exposed and 3.4 d in unexposed soil (Table 1). The calculated half-life under aerobic conditions was half that of unexposed soil. That finding was reversed under anaerobic conditions, where the unexposed soil exhibited a shorter half-life for estrone than in exposed soil. Regression lines of biodegradation rate for each treatment were significantly different from each other ($p < 0.001$) by ANCOVA analysis.

β -Estradiol

Biological degradation was responsible for more than 96% loss of β -Estradiol in 14 d under both aerobic and anaerobic conditions and regardless of prior exposure to wastewater effluent (Figure 2). Calculated half-lives from biodegradation (regression fit) under aerobic conditions were 2.3 d and 2.1 d in exposed and unexposed soil, respectively. Anaerobic conditions resulted in half-life calculations of 1.9 d in exposed soil, and 1.6 d in unexposed soil (Table 1). β -Estradiol exhibited slightly shorter half-lives in unexposed soil than in soil with prior exposure. All treatments regressions were significantly different ($p < 0.001$) by ANCOVA analysis.

Estriol

There was no loss of estriol in killed control treatments except under anaerobic conditions in the exposed soil where an 18% loss was seen over the 14 d incubation. Rapid loss of estriol was seen in all live treatments over the 14 d incubation period (Figure 3). Calculated half-lives by regression fit were 0.7 d for aerobic conditions in both exposed and unexposed soil and under anaerobic conditions in unexposed soil.

Anaerobic conditions in exposed soil resulted in a significantly higher ($p < 0.001$) half-life of 1.7 d (Table 1).

17 α -Ethinylestradiol

Biological degradation of 17 α -Ethinylestradiol under aerobic conditions was significantly faster ($p < 0.001$) than biological loss under anaerobic conditions. No loss of 17 α -Ethinylestradiol was observed in the killed controls (Figure 4). The half-life of 17 α -Ethinylestradiol was calculated as 0.8 d in aerobic soil. Anaerobic soil conditions resulted in half-lives of 3.0 d in exposed soil and 2.0 d in unexposed soil (Table 1). Regression analysis indicated significant differences between the exposed and unexposed anaerobic treatments ($p < 0.001$) though not between the aerobic exposed and unexposed treatments

Triclosan

Biological degradation of triclosan occurred in all live treatments over the 14 d study. There was no significant loss of triclosan in the killed controls (Figure 5). Biotic degradation of triclosan was fastest in exposed soil under aerobic conditions, with a 5.9 d half-life. Unexposed soil under aerobic conditions resulted in a half-life of 8.9 d for triclosan. The half-life of triclosan under anaerobic conditions was 15.3 d in unexposed soil and 28.8 d in effluent exposed soil (Table 1). Regressions analysis by treatment (ANCOVA) showed significant differences between all treatment conditions on degradation rate ($p < 0.001$).

Ibuprofen

Ibuprofen only exhibited biological degradation in unexposed soils (Figure 6). Exposed soils under both aerobic and anaerobic conditions exhibited no significant differences between killed controls, thus no half-lives could be calculated by regression. Over the 14 d study only 21% or less ibuprofen was degraded biologically. In the unexposed soils half-lives were calculated as 121.9 d under aerobic soil conditions and 41.2 d in anaerobic soil (Table 1). The rates in unexposed soils were shown to be significantly different ($p < 0.001$ and $p < 0.05$) between aerobic and anaerobic conditions, and aerobic from exposed and killed controls.

Ciproflaxacin

No degradation data were obtained for ciprofloxacin under aerobic and anaerobic conditions.

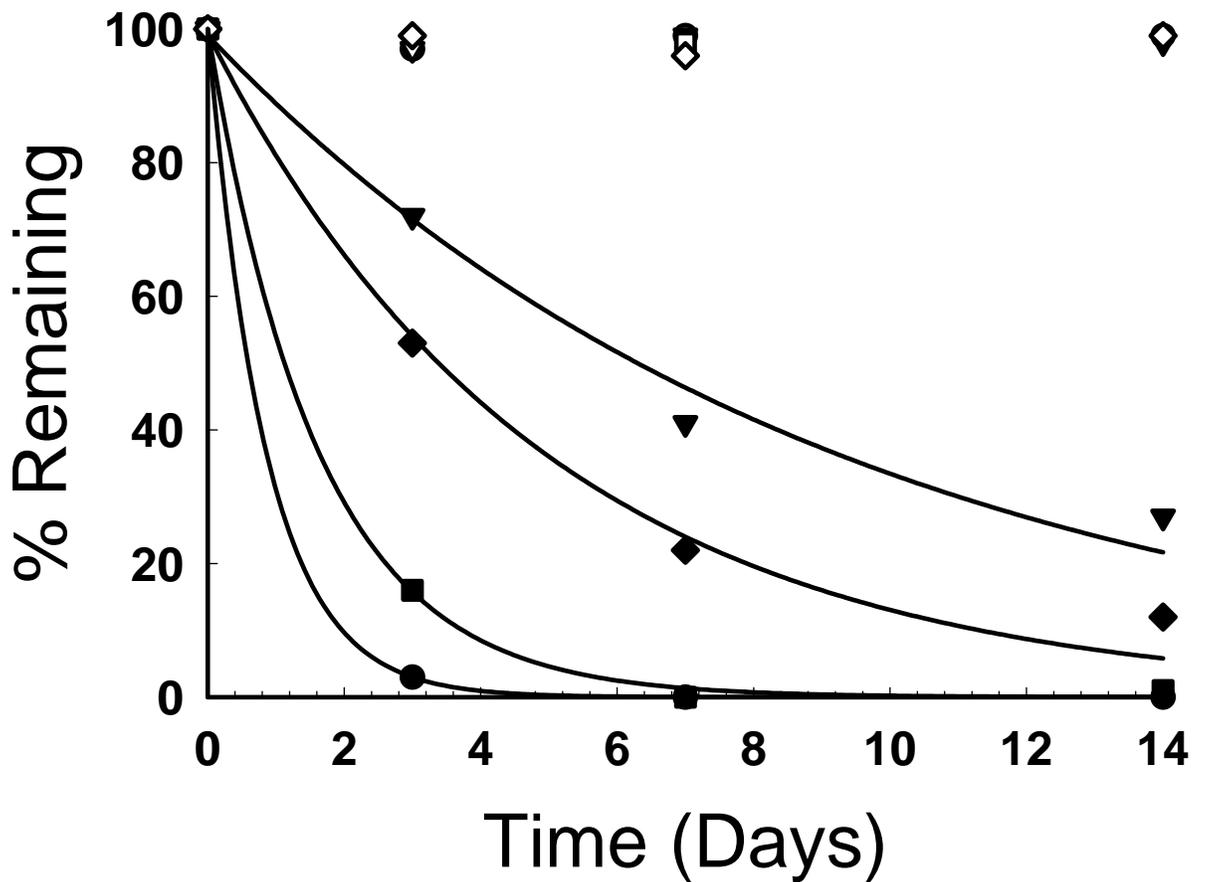


Figure 1. Aerobic and anaerobic degradation of estrone in soil. Data points represent triplicate measured values. Aerobic effluent exposed (●), aerobic unexposed (■), anaerobic effluent exposed (▼), anaerobic unexposed (◆). Killed controls are represented by open symbols. Vertical bars represent \pm standard error of the means ($n=3$). Bars not visible fall within the dimensions of the symbols. Lines represent best fit regression equations.

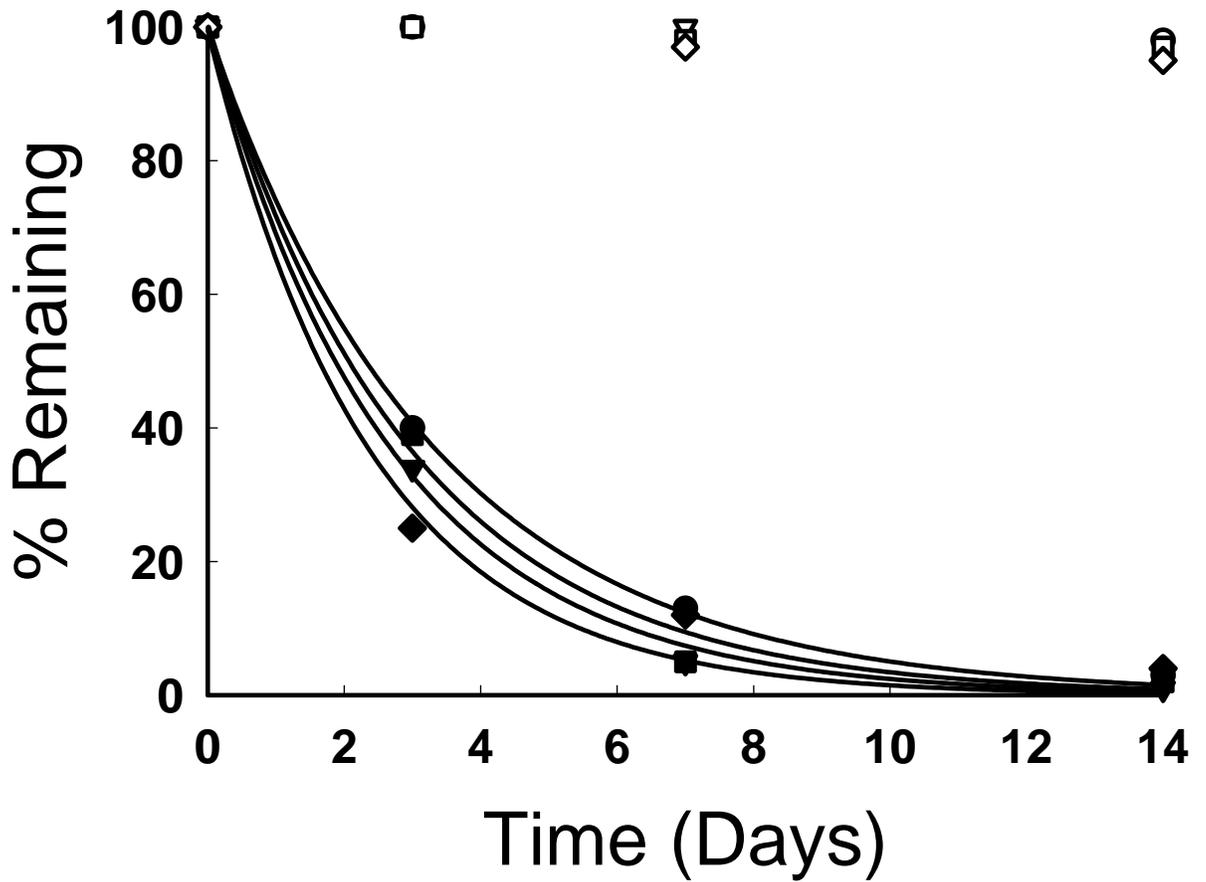


Figure 2. Aerobic and anaerobic degradation of β -estradiol in soil. Data points represent triplicate measured values. Aerobic effluent exposed (\bullet), aerobic unexposed (\blacksquare), anaerobic effluent exposed (\blacktriangledown), anaerobic unexposed (\blacklozenge). Killed controls are represented by open symbols. Vertical bars represent \pm standard error of the means ($n=3$). Bars not visible fall within the dimensions of the symbols. Lines represent best fit regression equations.

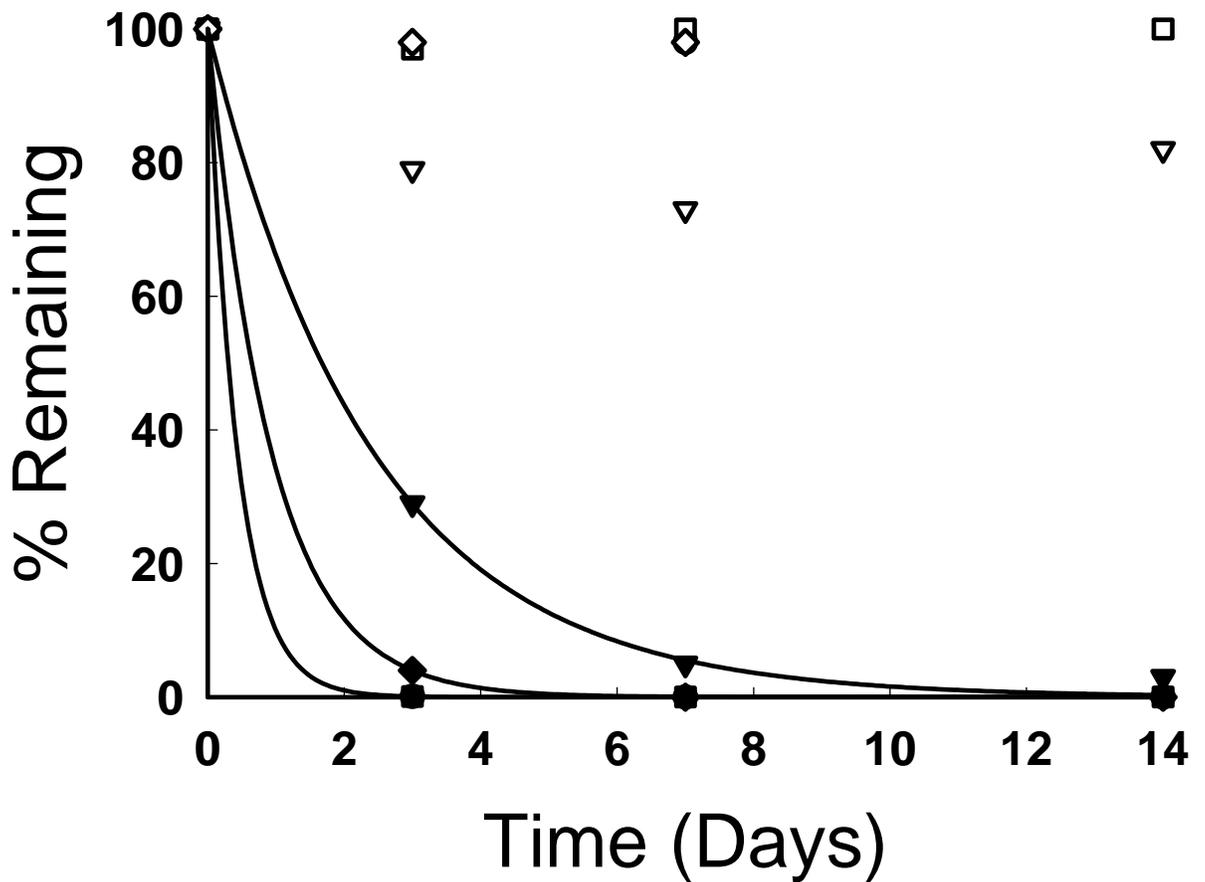


Figure.3. Aerobic and anaerobic degradation of estriol in soil. Data points represent triplicate measured values. Aerobic effluent exposed (●), aerobic unexposed (■), anaerobic effluent exposed (▼), anaerobic unexposed (◆). Killed controls are represented by open symbols. Vertical bars represent \pm standard error of the means (n=3). Bars not visible fall within the dimensions of the symbols. Lines represent best fit regression equations.

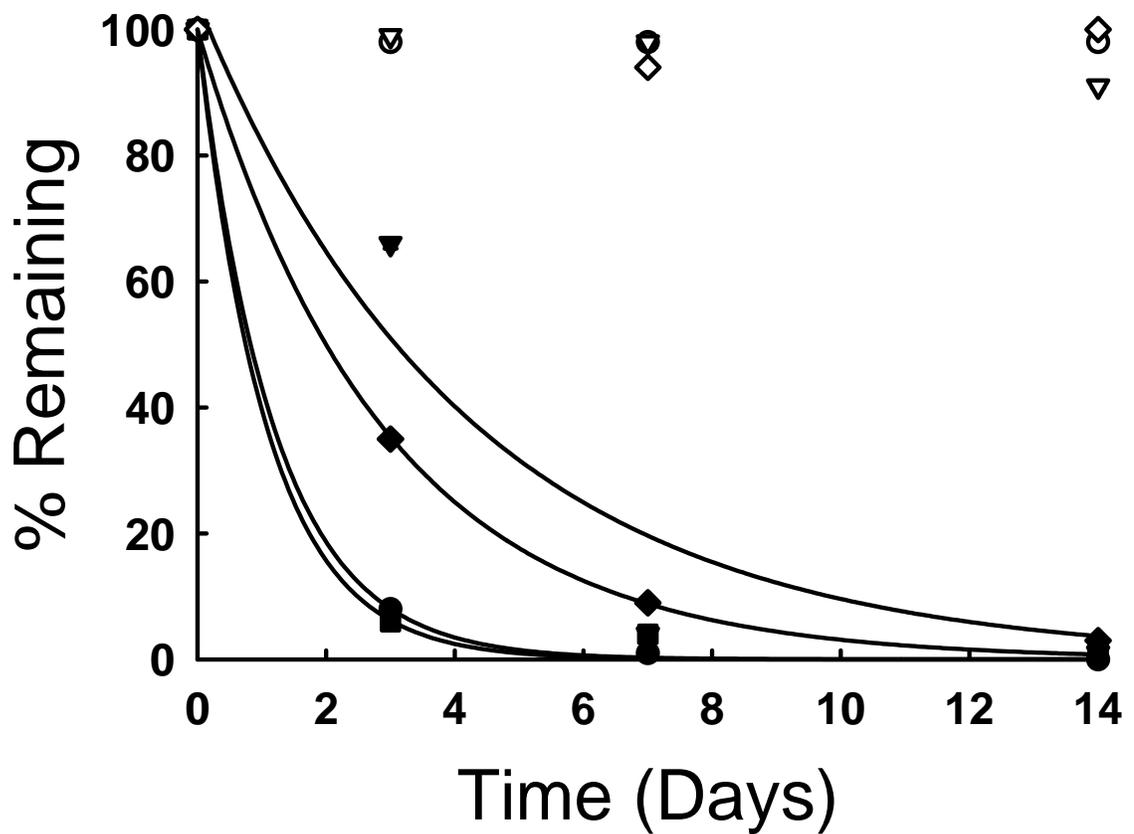


Figure 4. Aerobic and anaerobic degradation of 17 α -ethinylestradiol in soil. Data points represent triplicate measured values. Aerobic effluent exposed (●), aerobic unexposed (■), anaerobic effluent exposed (▼), anaerobic unexposed (◆). Killed controls are represented by open symbols. Vertical bars represent \pm standard error of the means (n=3). Bars not visible fall within the dimensions of the symbols. Lines represent best fit regression equations.

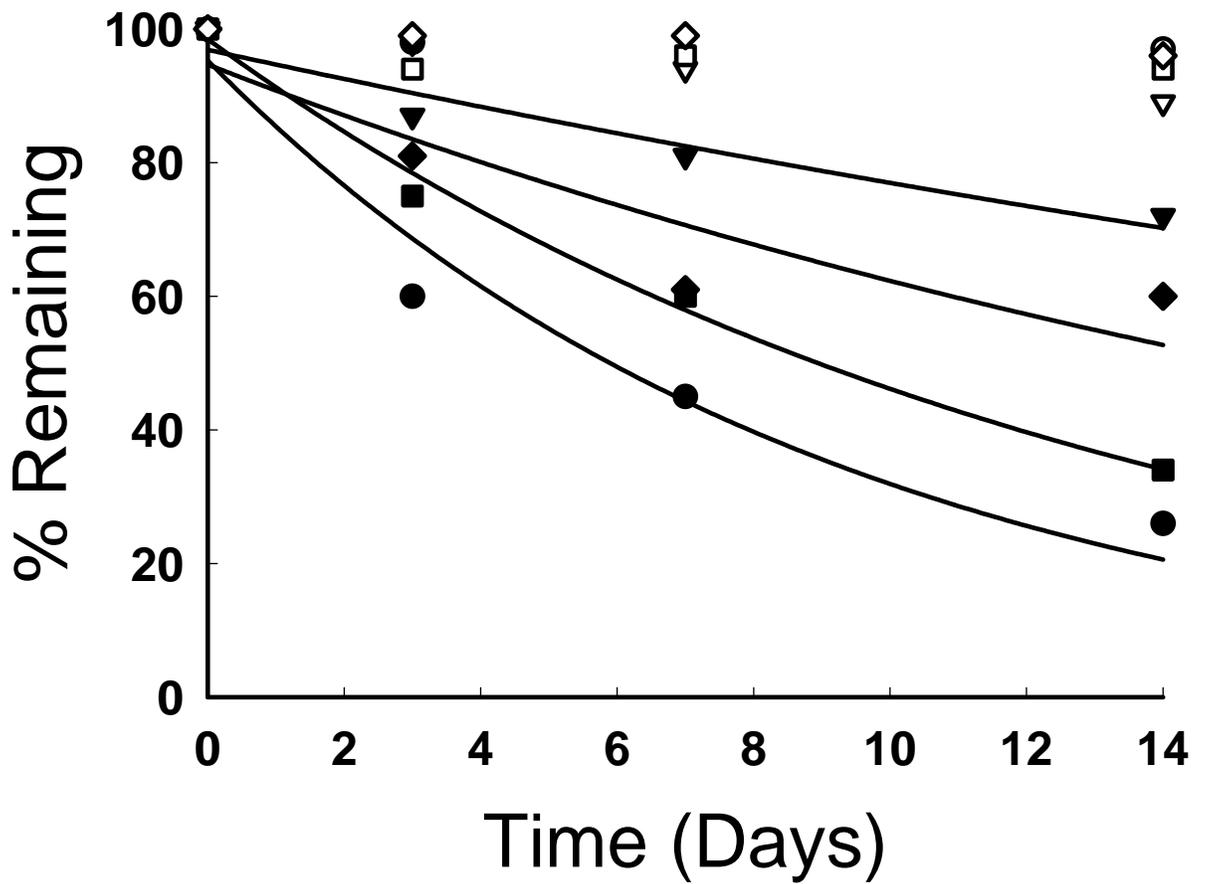


Figure 5. Aerobic and anaerobic degradation of triclosan in soil. Data points represent triplicate measured values. Aerobic effluent exposed (●), aerobic unexposed (◆), anaerobic effluent exposed (▼), anaerobic unexposed (◊). Killed controls are represented by open symbols. Vertical bars represent \pm standard error of the means (n=3). Bars not visible fall within the dimensions of the symbols. Lines represent best fit regression equations.

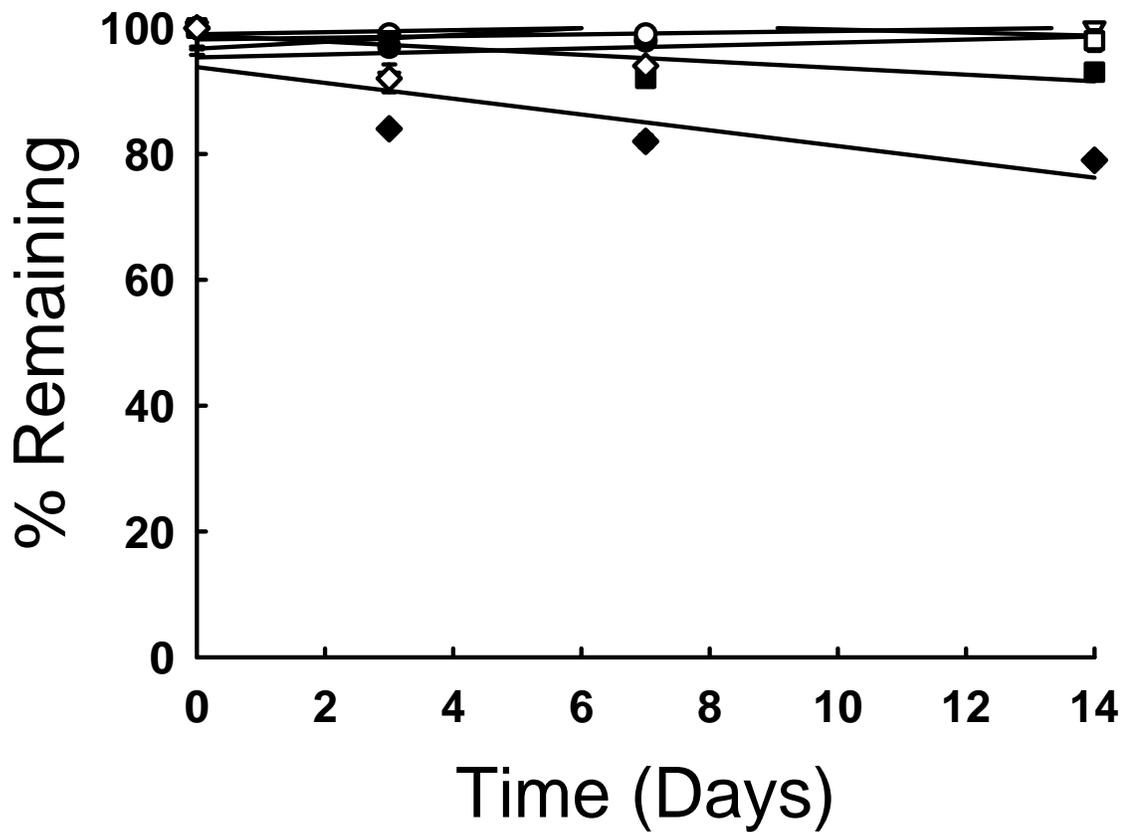


Figure 5. Aerobic and anaerobic degradation of ibuprofen in soil. Data points represent triplicate measured values. Aerobic effluent exposed (●), aerobic unexposed (■), anaerobic effluent exposed (▼), anaerobic unexposed (◆). Killed controls are represented by open symbols. Vertical bars represent \pm standard error of the means (n=3). Bars not visible fall within the dimensions of the symbols. Lines represent best fit regression equations.

Table 1 Calculated half-lives (days) of selected PPCPs in soil under aerobic and anaerobic conditions.

The r^2 for the regression fit is indicated parenthetically.

Treatment	Calculated Half-life					
	Estrone	B-Estradiol	Estriol	17 α -Ethinylestradiol	Triclosan	Ibuprofen
Aerobic Exposed	0.6 (0.999)	2.3 (0.999)	0.7 (0.999)	0.8 (0.999)	5.9 (0.957)	NC
Aerobic Unexposed	1.1 (0.999)	2.1 (0.996)	0.7 (0.999)	0.8 (0.997)	8.9 (0.992)	121.9 (0.692)
Anaerobic Exposed	6.3 (0.982)	1.9 (0.999)	1.7 (0.999)	3.0 (0.930)	28.8 (0.935)	NC
Anaerobic Unexposed	3.4 (0.991)	1.6 (0.988)	0.7 (0.999)	2.0 (0.999)	15.3 (0.833)	41.2 (0.679)

NC – not calculated

Significance

Estrogens

Under aerobic conditions natural and synthetic estrogen are efficiently degraded by soil microorganisms within 14 d, with half-lives of less than 1 to 2 d. Prior exposure of these soils to these chemicals does not seem to be an important factor in the ability of the endogenous soil microbial community to degrade estrogens. While there were statistical differences ($p < 0.05$) between aerobic and anaerobic treatments, the half-lives are short enough to question whether this would be an environmentally significant factor. Apparently a robust anaerobic bacterial community exists in the upper 15 cm of soil as we saw rapid degradation of estrogens under anaerobic conditions as well. In most cases the half-lives under anaerobic conditions were not so different from aerobic half-lives as to be an important factor in the environment. The significant differences we report by comparison of regressions for best fit by ANCOVA relate to the shape of the curves and the high efficiency of the extraction methods which resulted in small standard error of the means. The endpoint measurements of estrogens at 14 days were less than 3 percent of the concentration initially added. Estrone was the exception to this pattern. Under aerobic conditions estrone behaved as the other estrogen compounds, however, under anaerobic conditions degradation was significantly slower and the half-life was 2 to 3 times longer than other estrogens under the same conditions and 3 to 6 times longer than estrone in aerobic conditions. Estrone was the only estrogen tested that had measurable concentrations remaining at the end of 14 days (12-17%) when incubated in an anaerobic environment.

In general, results from this study concur with natural estrogen degradation and removal rates found in other studies. While degradation of estrogens was slower under anaerobic conditions, our observed half-lives from 0.7 d to 6.3 d do not suggest that any of the estrogens tested would be persistent in the soil environment. In a slow rate land application scenario where effluent irrigation occurs rotationally so the soil can maintain unsaturated conditions and return to aerobic conditions, it is unlikely that estrogen degradation would be exceeded by input of new estrogen substrate.

Several studies suggest that 17α -ethinylestradiol is more resistant to degradation under aerobic conditions and resistant under anaerobic conditions in wastewater treatment plants and sediments (Layton *et al.*, 2000; Jürgens *et al.*, 2002; Ying *et al.*, 2003; Braga *et al.*, 2005; Furuichi, *et al.*, 2006). Results presented here suggest that soil environments contain bacterial assemblages capable of rapidly degrading 17α -ethinylestradiol under aerobic and anaerobic conditions. Reports by Coombe *et al.*, (1966) and Shi *et al.*, (2004) suggest that nitrifying bacteria such as *Nocardia sp.* and ammonia oxidizing bacteria like *Nitrosomonas spp.* are capable of rapid degradation of natural estrogens as well as 17α -ethinylestradiol through the oxidation of C4 at the A ring followed by complete mineralization. Both families of these bacterium are well represented in soils; they may be the primary degraders of these compounds including the synthetic estrogen 17α -ethinylestradiol.

Triclosan

This study demonstrated that triclosan was degraded by microbial populations in soils under both aerobic and anaerobic conditions. The half-life of triclosan in aerobic soil was slightly lower in unexposed soil than in exposed soil (5.9 d vs. 8.9 d). These half-lives are shorter than the 18 d reported by Ying *et al.*, (2007) and by Christensen as reported in Reiss *et al.*, (in press). Another study reported as unpublished (Reiss *et al.*, in press) was a Swiss study

by D. Adam in which triclosan had half-lives ranging from 2.5 d to 10.7 d in aerobic loamy soils. The calculated half-lives for triclosan under aerobic conditions in this study appear to fall in the middle of half-life ranges reported previously.

Ying *et al.*, (2007) reported no degradation of triclosan under anaerobic conditions. In contrast, we observed reasonable rates of microbially mediated degradation and half-lives between 15.3 and 28.8 d in anaerobic soils. Over the 14 d study, between 27 percent and 40 percent of the added triclosan was lost due to microbial activity. Other factors such as nutrient availability, microbial population, and soil structure could influence degradation under anaerobic conditions. By allowing a larger aggregate size in the experimental soils, a greater potential for degradation by fungal hyphae networks was encouraged. Fungal systems, like animal systems, use a different fatty acid synthesis pathway; type I FAS rather than the bacterial type II FAS (Wright, and Reynolds, 2007). Bacteria such as *Staphylococcus aureus* that over express *FabI*, the target of triclosan antibacterial action, may exhibit low level resistance to triclosan (Slater-Radosti *et al.*, 2001), other bacteria with multi-drug efflux pumps actively pump triclosan out of the bacterial cell providing resistance such as seen in *Pseudomonas aeruginosa* (Chuanchuan *et al.*, 2003). Still other bacteria such as *Bacillus spp.* have the *FabK* gene rather than the *FabI*. Both *Bacillus spp.* and *Pseudomonas spp.* are commonly isolated from soils. *Pseudomonas aeruginosa* is a denitrifying chemoheterotroph and a facultative anaerobe. In the absence of oxygen it utilizes nitrate as the terminal electron acceptor during anaerobic respiration. Changing between aerobic and anaerobic respiration occurs within hours for facultative anaerobes (Paul, 2007). The ability to quickly adapt to anaerobic conditions would explain the lack of a lag period in anaerobic degradation rates in our observations.

Ibuprofen

This study observed only slight potential for ibuprofen to undergo biological degradation by soil microbial communities. Only in the unexposed soil could we calculate a half-life for ibuprofen. The most efficient biological degradation occurred under anaerobic conditions when a half-life of 41.2 d was calculated. In aerobic soil, the half-life increased to 121.9 d. Previous studies suggest that ibuprofen is inherently biodegradable (Richardson and Bowron, 1985; Ternes, 1998). This would suggest that ibuprofen would degrade under high bacterial activity found in activated sludge sewage treatment plants, but not necessarily under lower bacterial concentrations found in the environment, including soil. *Nocardia sp.*, a commonly occurring soil actinomycete, has been shown in the laboratory to degrade ibuprofen producing alcohol and ester metabolites (Chen and Rosazza, 1994). Ibuprofen has gram-positive antibacterial (Chowdhury *et al.*, 1996) as well selective antifungal properties (Sanyal *et al.*, 1993; Clausen, 1996). Clausen (1996) demonstrated morphological changes, growth inhibition to fungicidal effects in several brown-rot fungal species, and morphological changes but no inhibitory effects in white rot fungi, both of which are widespread in soils associated with decaying wood and organic matter. Taken together these studies might explain the slow but significant biological degradation we observed in this study. Differences in the exposed and unexposed sites might be due to different microbial community composition.

One of the most surprising observations in this study was the faster degradation rate under anaerobic conditions in the unexposed soils rather than the exposed soils. It is a widely held belief that bacteria capable of anaerobic degradation processes such as de-chlorination, require pre-exposure to the chemical or an adaptation period before active degradation can be measured (Brahushi *et al.*, 2004; Middeldorp *et al.*, 2005). This is not the pattern observed in this

study for triclosan, any of the estrogen compounds, or ibuprofen. In all cases, under anaerobic conditions, the unexposed soil produced shorter half-lives. At this time there is not an explanation for this pattern except to propose that soil tillage as part of agricultural crop management in the exposed soil may have lead to a less favorable or less diverse anaerobic bacterial community from that seen in the nearby unexposed soil.

Ciprofloxacin

Degradation of ciprofloxacin in soils was not able to be determined. Although a robust analytical method was developed, we were unable to detect ciprofloxacin in any extracts from the soils. Preparation of ciprofloxacin standards required 0.1 % acetic acid in the ACN solvent to aid in dissolution of the crystallized compound. Initial soil extractions were done with a 2:1 solvent:soil ratio that was used for all other extractions. While extraction efficiency in sand was good (98.04 % \pm 1.86), extraction efficiency from the soils in the study was only 4.4 % \pm 0.82. Extraction with ACN containing 0.1 % acetic acid resulted in an extraction efficiency of 4.4 % \pm 0.66. The soils in this study are somewhat basic with high buffering capacity. These physical characteristics make it likely that a much higher acid concentration would be required to re-solubilize the ciprofloxacin to allow it to be extracted from the soil. An extract with a pH low enough to allow reasonable extraction efficiency would require further treatment and method development before it could be analyzed by HPLC. Further tests for extraction and method development for ciprofloxacin were not pursued at this time. The goal of this study was to examine the fate of pharmaceuticals, in this case ciprofloxacin, once they reach the soil environment. In this study it appears that ciprofloxacin becomes immobilized in these soils and is unlikely to move through the soil profile where it can enter groundwater. The ability of soil microorganisms to degrade ciprofloxacin cannot be addressed in these soils nor should the fate of ciprofloxacin in other more acidic soils be assumed.

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Influence of Land Use and Terrain on Surface Hydrology in Shrink-Swell Soils.

Basic Information

Title:	Influence of Land Use and Terrain on Surface Hydrology in Shrink-Swell Soils.
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Principal Investigators:	Takele M Dinka, Cristine Morgan

Publications

1. Dinka, Takele M., Cristine L. S. Morgan, Andrea Sz. Kishné, 2009, Soil Characteristics and Cracking Behavior of a Vertisol Catena, "ASA-CSSA-SSSA Joint Annual International Meeting", Pittsburgh, PA.
2. Dinka, Takele M., Cristine L. S. Morgan, Andrea Sz. Kishné, and Kevin J. McInnes, 2010, Land Use and Spatial Cracking Dynamics of a Vertisol, "46th Annual Soil Survey and Land Resource Workshop", Texas A&M University, College Station, TX.

REPORT

Title: Influence of Land Use and Terrain on Surface Hydrology in Shrink-Swell Soils

Project Number: 2009TX327B

Primary PI: Takele M. Dinka

Other PIs: Dr. Cristine Morgan (Major Professor)

Abstract

Understanding the dynamics of cracking and swelling of clayey soils improves the ability to predict the impact of land use on the hydrologic response of watersheds containing shrink-swell soils. The objective of this research was to characterize the impact of land use on spatial and temporal shrink-swell dynamics of a Vertisol. The hypothesis of this research is there is a variation in soil shrinkage on different land uses. This is because variations of soil properties, topography, and land use modify local infiltration, runoff, and storage in cracking and swelling soil. Cracking and swelling, in turn, influence infiltration, runoff, and storage, creating a feedback loop. In situ measurements of vertical soil movement and soil water content along with analysis of soil properties were made on fields under three land uses. The land uses were grazing land (GL), native prairie (NP), and cropland (CL). The research was conducted at the USDA-ARS Grassland, Soil and Water Research Laboratory near Riesel TX. The soil at the site was Houston Black (Fine, smectitic, thermic Udic Haplustert). To monitor vertical soil movements, five measurement sites on a GL and NP and four measurement sites on a CL (corn) were selected. Bi-weekly measurements of soil subsidence and soil water were made beginning in June 2008. The change in absolute heights of rods anchored at 0, 30, 60 and 90 cm was used to track the temporal trends in thickness of soil layers. Near each set of rods, soil water content was measured using a neutron moisture meter. The study showed that maximum soil subsidence and the time of its occurrence varied with land use. The maximum soil subsidence ranged from 91 to 112 mm in the sites of GL; from 70 to 75 mm in the sites of NP, and from 67 to 76 mm in the sites of CL. The maximum soil subsidence in the cornfield (CL) was within the same range as that of the prairie (NP), but the maximum occurred in mid July of 2008 in the prairie whereas maximum shrinkage did not occur until mid August of 2009 in the cornfield. In addition, there were differences in relative subsidence of soil layers within and among land use. Grass roots, size, and shape of gilgai likely influence the observed variation and further studies are underway. Knowledge gained in these studies may be used to modify and refine hydrology models that simulate runoff, infiltration and solute transport across different land uses in a Vertisol landscape.

Problem and Research Objectives

Seasonal cracking of shrink-swell soils is mainly driven by the change in soil moisture; however, temporal interactions with antecedent soil moisture and plant roots associated with land use are also assumed to affect crack opening and closure. This indicates that shrink-swell behavior of soil may change depending on land use system and vegetation cover.

Several methods, including field and laboratory have been applied to understand the shrink-swell behavior of soil. Some of these are measuring the Coefficient of Linear Extensibility (COLE) in the laboratory (e.g; Vaught et al., 2006; Grossman et al., 1968) , measuring height change of a soil in the field as a result of shrink-swell (e.g; Arnold et al., 2005; Bronswijk et al., 1991), and direct measurement of cracks in the field (Kishne et al., 2008). However, little has been done to characterize and quantify the spatial and temporal variation of soils shrink-swell activities under different land use systems. Understanding the impact of land use on soil shrink-swell activities help improve the knowledge of shrink-swell dynamics and in turn the study of hydrology in shrink-swell landscapes. The overall objective of this research is to determine if there is any difference in a Vertisol subsidence under different land use systems and to quantify the spatial and temporal shrink-swell activities under different land use systems.

Materials/Methodology

The research was conducted at the USDA-ARS Grassland, Soil and Water Research Laboratory near Riesel TX. In situ measurements of vertical soil movement and soil water content along with analysis of soil properties were made on fields under three land uses. The land uses are grazing land (GL), native prairie (NP), and cropland (CL). The soil at the site was Houston Black (Fine, smectitic, thermic Udic Haplustert). To monitor vertical soil movements, five measurement sites on a GL and NP and four measurement sites on a CL (corn) were selected based on topographic information and apparent soil electrical conductivity. At each site, soil from cores was described, and soil texture and inorganic carbon were analyzed. Bi-weekly measurements of soil subsidence and soil water were made beginning in June 2008. Particle size analysis, inorganic carbon and total carbon analysis were done. Measurements of soil subsidence and soil water were done to characterize the shrink-swell activities of Vertisols. The soil subsidence is estimated by taking the difference between the maximum soil height and the current soil height. Soil water loss from a soil layer was also estimated to study its relationship with soil subsidence. Soil water loss is estimated by taking the difference between the maximum soil water in the layer and the current soil water.

Principal Findings

- The study showed that maximum soil subsidence and the time of its occurrence varied with land use.
- The maximum soil subsidence ranged from 91 to 112 mm in the sites of GL; from 70 to 75 mm in the sites of NP, and from 67 to 76 mm in the sites of CL. The graph of soil subsidence of one site for each land use in shown in figure 1.
- The maximum soil subsidence in the cornfield (CL) was within the same range as that of the prairie (NP), but the maximum occurred in mid July of 2008 in the prairie whereas maximum shrinkage did not occur until mid August of 2009 in the cornfield.
- In addition, there were differences in relative subsidence of soil layers within and among land use.
- Soil subsidence varies yearly, spatially and with a landuse.
- Grass roots and gilgai presence and shape could be a reason for variation in soil subsidence within and among landuse.

- Maximum subsidence occurred at the same time in grazing land and native prairie, but in a different year in cropland.
- Observations do not always follow the mechanics of equidimensional shrinkage during a normal shrinkage.
- Development of a mechanistic model that relates soil water, antecedent soil moisture and soil subsidence is underway.

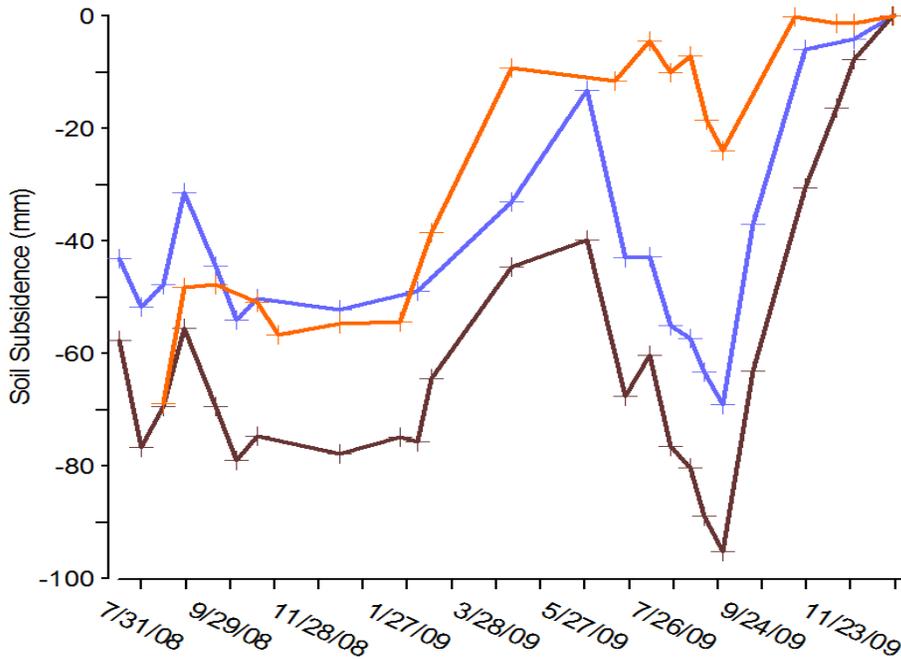


Figure 1. Soil subsidence on each land use, **native prairie**, **corn**, and **grazing land**.

Significance

The result of this study provides the information necessary for understanding watershed hydrology and improving hydrology models applied in watersheds with shrink-swell soils. The graph below is attached to demonstrate how soil subsidence is correlated with runoff at the native prairie land (Figure 2). Assuming equidimensional soil shrinkage, when the maximum soil subsidence measured in the different land use is converted to crack volume, it gives an idea of how much runoff can be trapped by the volume of cracks. In this study, the maximum crack volume estimated during the study period was 114, 98 and 99 mm/m² in GL, NP and cornfield. An improved understanding of how soil cracking affects watershed hydrology will lead to improved simulation of water, solute and particulate movement in watersheds and to more sound estimates of the effect of land management practices on surface and groundwater quality and quantity. The result will also help modify hydrological models that are developed for shrink-swell soils based on theory for non- shrink/swell soils.

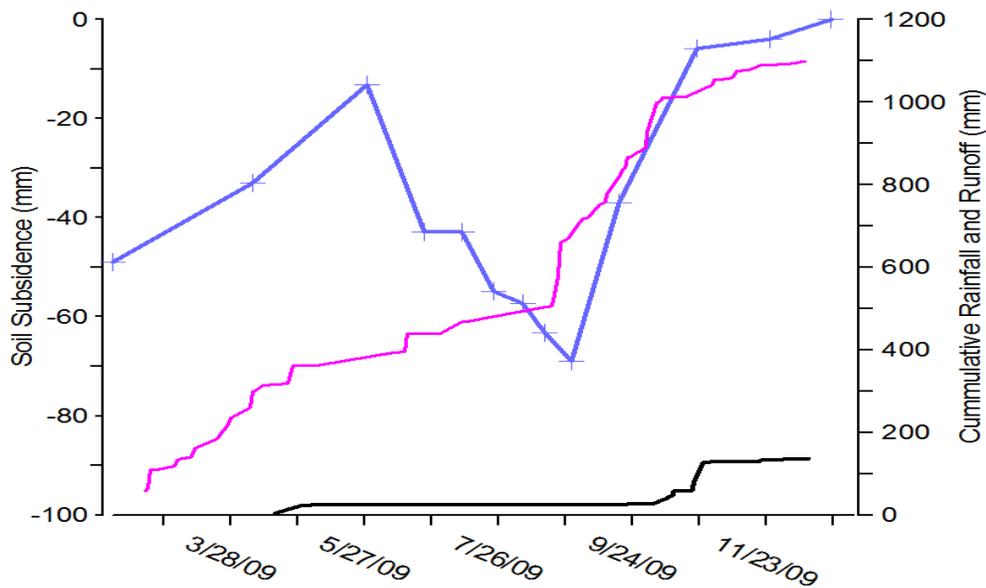


Figure 2. Soil subsidence, cumulative rainfall and runoff at the native prairie.

Regulated Deficit Irrigation Application and Cotton Production in SW Texas

Basic Information

Title:	Regulated Deficit Irrigation Application and Cotton Production in SW Texas
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Principal Investigators:	Yujin Wen, Tom Cothren

Publications

1. Wen, Yujin, 2010, The physiological responses, lint yields and fiber quality of cotton (*Gossypium hirsutum* L.) under several fixed and dynamic deficit irrigation schemes in Southwest Texas, "Ph.D. Dissertation", Dept. Soil and Crop Sciences, College of Agricultural and Life Sciences, Texas A&M University, College Station, Texas.
2. Wen, Yujin, Giovanni Piccinni, J. Tom Cothren, Daniel I. Leskovar, Diane L. Rowland and Armen R. Kemanian, 2010, Regulated deficit irrigation application and the physiological responses of cotton (*Gossypium hirsutum* L.) in Southwest Texas. In: Proc. 2010 Beltwide Cotton Conferences, New Orleans, LA, Jan. 4-7, 2010.
3. Wen, Yujin, Giovanni Piccinni, J. Tom Cothren, Daniel I. Leskovar, Diane L. Rowland and Armen R. Kemanian, 2010, The lint yield and fiber quality of cotton (*Gossypium hirsutum* L.) under several regulated deficit irrigation schemes in Southwest Texas. In: Proc. 2010 Beltwide Cotton Conferences, New Orleans, LA, Jan. 4-7, 2010.
4. Wen, Yujin, Giovanni Piccinni, J. Tom Cothren, Daniel I. Leskovar, Diane L. Rowland and Armen R. Kemanian, 2009, Regulated deficit irrigation application and cotton production responses in Southwest Texas. In: Proc. Of the 5th USCID Irrigation and Drainage International Conference, Salt Lake City, UT, Nov. 3-6, 2009.

REPORT

Title: Regulated Deficit Irrigation Application and Cotton Production in SW Texas

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Abstract

The urban water demand in Southwest Texas has grown rapidly in recent years due to large population increase. An improved irrigation scheme is in need to support a better water use plan. Regulated deficit irrigation (RDI) is one important measure for saving water for other usage, while maintaining crop yield or farmers' net benefit. An field experiment of deficit irrigation, including five fixed-ratio (100X, 80X, 70X, 60X and 50X) and two RDI (70D and 50D) schemes was conducted at the Texas AgriLIFE Research and Extension Center at Uvalde in the summers of 2008 and 2009 to examine the water saving potential in Southwest Texas. Four varieties were assigned to the experimental field each year as a second factor, to test both deficit irrigation and genotype effects on seed cotton yield, lint yield and fiber quality measurements.

The research showed that the threshold of the replacement ratio for fixed ratio irrigation schemes is between 0.7 and 0.8. Considering the previous study in the same area, 0.7-0.75 is considered to be the practical range to produce non-reduced lint yield and save irrigation water. The newly developed dynamic irrigation scheme demonstrated higher potential to save water, establish deeper cotton plant root system, produce more lint yield per unit water input, and maintain fiber quality. However, further study on optimal deficit ratios of each growth stage is suggested before RDI is applied in cotton production in southwest Texas.

Student is not able to release entire report until their dissertation is approved by the Office of Graduate Studies and the thesis office, to avoid any potential conflicts. Therefore only page 1 was uploaded.

In Situ Groundwater Arsenic Removal using Iron Oxide Coated Sand

Basic Information

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Principal Investigators:	Hongxu Yu, Yongheng Huang

Publication

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1. Proposal Title: *In Situ* Groundwater Arsenic (As) Removal using Iron Oxide-Coated Sand

2. USGS Project #: 2009TX329B

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5. Abstract

Iron oxide-bearing minerals have long been recognized as an effective reactive media for arsenic (As) remediation. A simple iron oxide coating process was developed to employ a sustainable and cost-effective *in situ* coating technique for treating contaminated groundwater. To *in situ* emplace iron oxide coatings on soil particles, ferrous salt and dissolved oxygen solutions were periodically injected into a sand matrix following a specially designed injection scheme. The resulting adsorption, diffusion, and redox reactions could continuously deposit large quantities of ferric oxide onto the surface of soil particles, thus creating a constantly-refreshed reactive surface for the continuous adsorption and co-precipitation of arsenic and other heavy metals.

6. Statement of Critical Regional Water Problems and Current Solutions (Need for Research)

Arsenic, a naturally-occurring groundwater toxicant, has been linked to illnesses such as liver dysfunction, gangrene, and skin tumors (Hutton, 1978). Furthermore, a study focusing on the carcinogenic risks associated with arsenic-laden water concluded that cancers in the lung, kidney, bladder, and liver may result from consumption (Smith et al., 1992). There are many sources of arsenic in the environment that are transported by water. Soil erosion and leaching are suspected of depositing dissolved and suspended arsenic into the oceans (Mackenzie et al., 1979). Industrial effluents from metallurgy, petroleum, fertilizer, glassware, pesticides, chemical, and coal-power facilities are major causes of point source pollution. On January 23, 2006, the United States Environmental Protection Agency (USEPA) lowered the maximum concentration level (MCL) of As in drinking water to 10 micrograms per liter ($\mu\text{g/L}$) (USEPA, 2006). The American Water Works Association (AWWA) conducted a survey for inorganic contaminants in water supply regions in the United States that identified 34 cases where As levels exceeded the MCL (American Water Works Association Committee, 1985) and the USEPA identified 541 superfund sites with As being the contaminant of concern in groundwater (USEPA, 2009). The majority of the violations were documented in New Mexico, Oklahoma, and Texas while separate cases were reported in Alaska, Illinois, New Hampshire, North Carolina, and Virginia (Viraraghavan et al., 1999).

Interest in the development of dissolved metal removal technology has been triggered by USEPA regulation of inorganic contaminants in drinking waters. Some volatile metals in the water are highly hydrophilic and cannot be easily removed through oxidation, precipitation, or biological treatment while maintaining low operating costs and environmental sustainability. Major problems with the treatment technology for dissolved metals are complex operations, mono-functionality, use of expensive and dangerous chemicals, and lack of re-usability.

7. Objective and Scope of Research

Objective

With an emphasis on economics and sustainability, this study aims to develop and optimize the iron coating of sand under submerged conditions to simulate an aquifer environment. Lab-scale column tests will be performed to verify feasibility and assess iron oxide-coated sand regeneration capabilities. Dissolved oxygen will be used as the only Fe^{2+} oxidant.

Scope of Work (Methodology)

The range of work for this applied research encompasses coating design, coating optimization, and coating regeneration of iron oxide-coated sand. Contaminant treatment will only be analyzed as part of the regeneration assessment.

• Stoichiometry, Calculations, and Chemical Preparation

- **Stoichiometry** - The basis of the calculations and chemical preparation in this experiment resulted from the following oxidation-reduction reactions between Fe^{2+} and dissolved oxygen:



where the resulting equation below represents the overall production of ferric oxide:



The formation of ferric oxide by oxygen requires the addition of alkalinity (OH^-) to resist the significant reduction in pH caused by the hydrogen ion (H^+). The source of alkalinity used in this study to maintain a high Fe^{2+} oxidation rate was NaOH. To compensate for the fixed elevated temperature, the rate of oxygen flow into the system was adjusted to exceed the stoichiometric requirements.

- **Calculations** – Fe^{2+} source: anhydrous ferrous chloride 4-hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), $\text{MW}_{\text{FeCl}_2 \cdot 4\text{H}_2\text{O}} = 198.81$ grams per mole
 Fe^{2+} oxidant: compressed oxygen (O_2) dissolved in tap water @ 21 °C, $\text{MW}_{\text{O}_2} = 32$ grams per mole
 O_2 saturation = 8.24 mg/L in ambient air @ 21 °C (21% composition of air)
 Alkalinity (OH^-) source: sodium hydroxide (NaOH), $\text{MW}_{\text{NaOH}} = 40.00$ grams per mole
 Acid (H^+) source: hydrochloric acid (HCl), $\text{MW}_{\text{HCl}} = 36.46$ grams per mole
 Water source: **tap water**, $\text{V}_{\text{Fe(II)}} = 10$ L, $\text{V}_{\text{O}_2} = 10$ L, $\text{V}_{\text{water buffer}} = 20$ L

$$\text{O}_2 \text{ (mM)} = \frac{8.24 \frac{\text{mg}}{\text{L}}}{(21\%) \cdot (3.2 \frac{\text{mg}}{\text{mmole}})} = 1.226 \text{ mM O}_2 \text{ (39.24 mg/L) dissolved in 10 L tap H}_2\text{O}$$

$$\text{Alkalinity (O}_2\text{)} = [1.226 \text{ mM O}_2] \cdot [10 \text{ L}] \cdot [0.040 \frac{\text{g NaOH}}{\text{mM NaOH}}] \cdot [4 \frac{\text{g NaOH}}{\text{mM NaOH}}] = 1.962 \text{ g NaOH dissolved in 10 L tap H}_2\text{O}$$

$$\text{M}_{\text{Fe(II)}} \text{ (g)} = [1.226 \text{ mM O}_2] \cdot [4 \frac{\text{mM Fe(II)}}{\text{mM O}_2}] \cdot [10 \text{ L H}_2\text{O}] \cdot [0.19881 \frac{\text{g Fe(II)}}{\text{mM Fe(II)}}] = 9.75 \text{ g Fe}^{2+} \text{ dissolved in 10 L tap H}_2\text{O}$$

$$[\text{Fe}^{2+}] \text{ (mM)} = [1.226 \text{ mM O}_2] \cdot [4 \frac{\text{mM Fe(II)}}{\text{mM O}_2}] = 4.905 \text{ mM Fe}^{2+} \text{ dissolved in 10 L tap H}_2\text{O}$$

○ **Preparation of sand cleaning agents**

Acid water: 20 L of de-ionized water (DI H_2O) was acidified to 0.5 mM HCl.

Base water: 0.5 mM NaOH was made by mixing 10 L DI H_2O with 5 mL of 1 M NaOH.

Salt water buffer: 3 L of DI H_2O was fortified to 0.5 mM NaCl

○ **Preparation of iron oxide coating agents**

Dissolved Oxygen: 10 L of tap H_2O was oxygenated under ambient conditions to 1.23 mM (39.2 mg/L) using a compressed oxygen tank. The oxygenated water was supplied with 4.92 mM of NaOH to provide extra alkalinity.

Iron source: Equation 3 was used to determine the proper amount of Fe^{2+} sufficient for DO saturation in water in a submerged environment. 9.75 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 10 L of tap H_2O to produce a stock solution of 4.92 mM Fe^{2+} (274.7 mg/L Fe^{2+}). 0.3 mM HCl was used to adjust the pH and prevent Fe^{2+} precipitation in the storage tank.

Acid water buffer: 20 L tap H_2O was used as a buffer between the Fe^{2+} and the oxygen water to prevent precipitation in the conveyance system in the coating procedure. The pH of the acid water was adjusted using 0.5 mM of HCl.

• Iron Oxide-Coated Sand (IOCS) Research Approach (page 4)

- **Phase 1: In Situ Coating** – wet-pack and pre-clean sand, determination of optimum coating pH range, ascertain applicable *in situ* injection schematic, optimize coating procedure through the control of the pH and acid water buffer, and assess iron oxide accumulation through Fe^{2+} breakthrough curves and concentration profiles. Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) for describing iron oxide crystallization. Chemical production costs will be compared to conventional IOCS production costs.

- **Phase 2: In Situ Treatment and Regeneration** – filter design via As batch isotherms from Phase 1 IOCS, synthetic pollutant (As of various species and concentrations) removal and iron oxide regeneration, evaluate for feasibility of regeneration using Fe^{2+} and pollutant breakthrough curves. Re-dissolution of iron oxides and pollutant will be explored and analyzed via SEM. Iron oxide-coated sand usage rates (IOCSUR) and specific throughputs (ST) for each contaminant will also be estimated. Repeat phase 2 for real groundwater spiked with targeted toxicant.
- **Phase 3: In Situ Pilot Study** – construction of simulated sub-surface groundwater aquifer with gravity-driven injection wells incorporating data and details from Phases 1 and 2, evaluate using real groundwater spiked with As.

• **Iron Oxide-Coated Sand (IOCS) Analytical Process (Figure 1)**

- **Characterization** – collect sand samples before wet-packing, after pre-cleaning, and after iron oxide coating for SEM imaging. Obtain Fe^{2+} breakthrough curves to assess the distribution of the iron oxide crystals on the sand surface throughout the filter. Air-dry sand samples for 5 days before undergoing imaging. Mix 6 5-gram samples of dried, coated sand placed in separate vials with 9.5 mL strong acid for 48 hours to obtain aqueous iron oxide solutions. Analyze for Fe^{2+} and total Fe to quantify the Fe^{3+} accumulation on the sand at various depths of the filter.

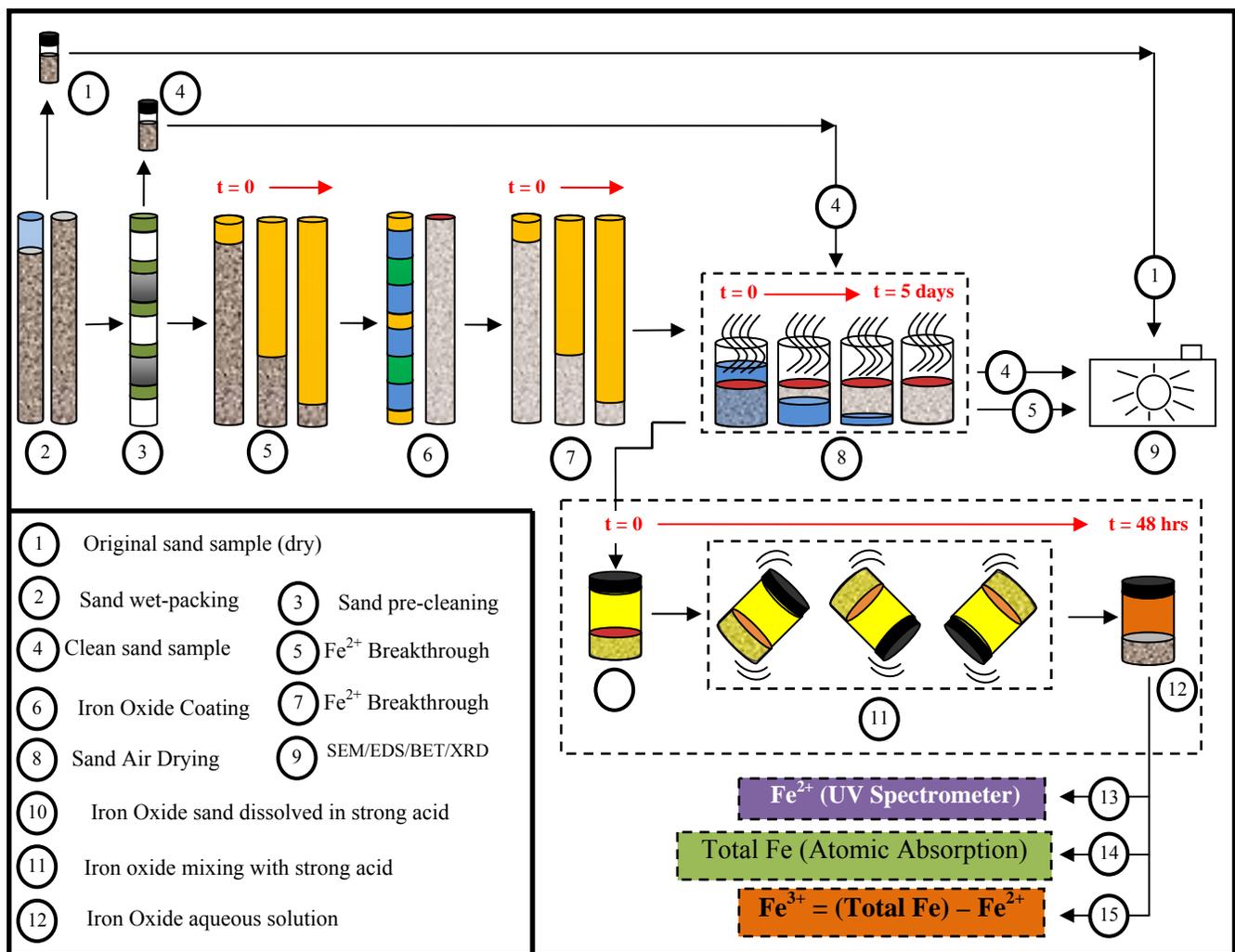
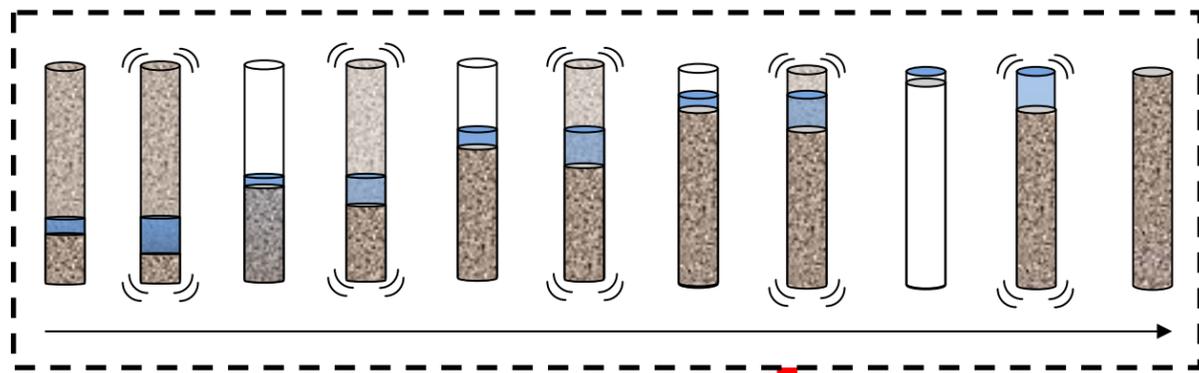
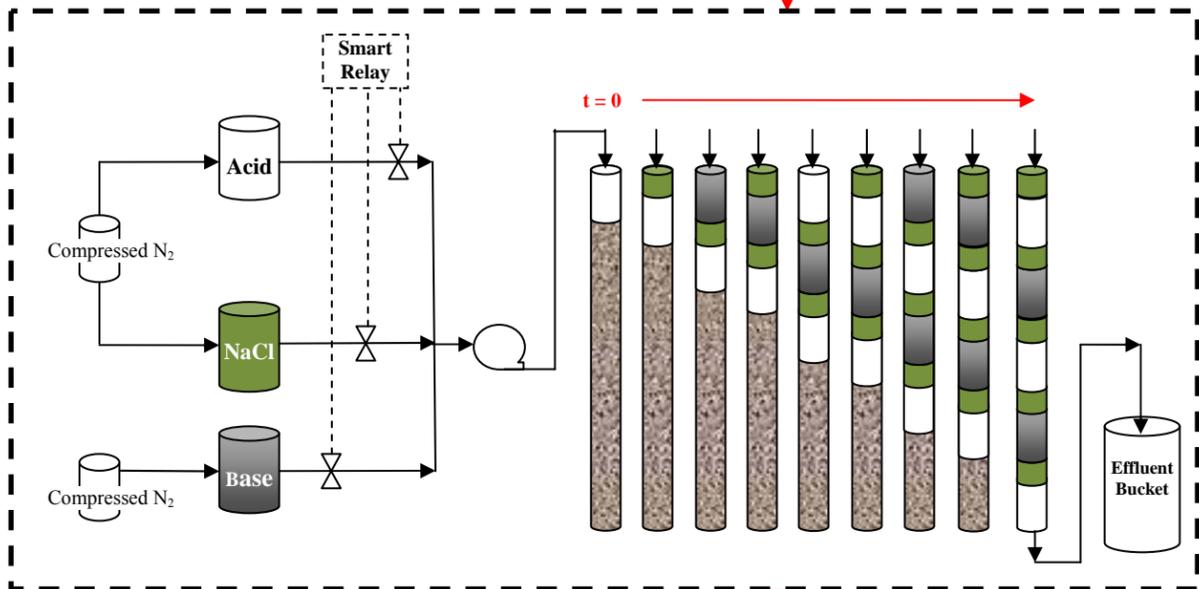


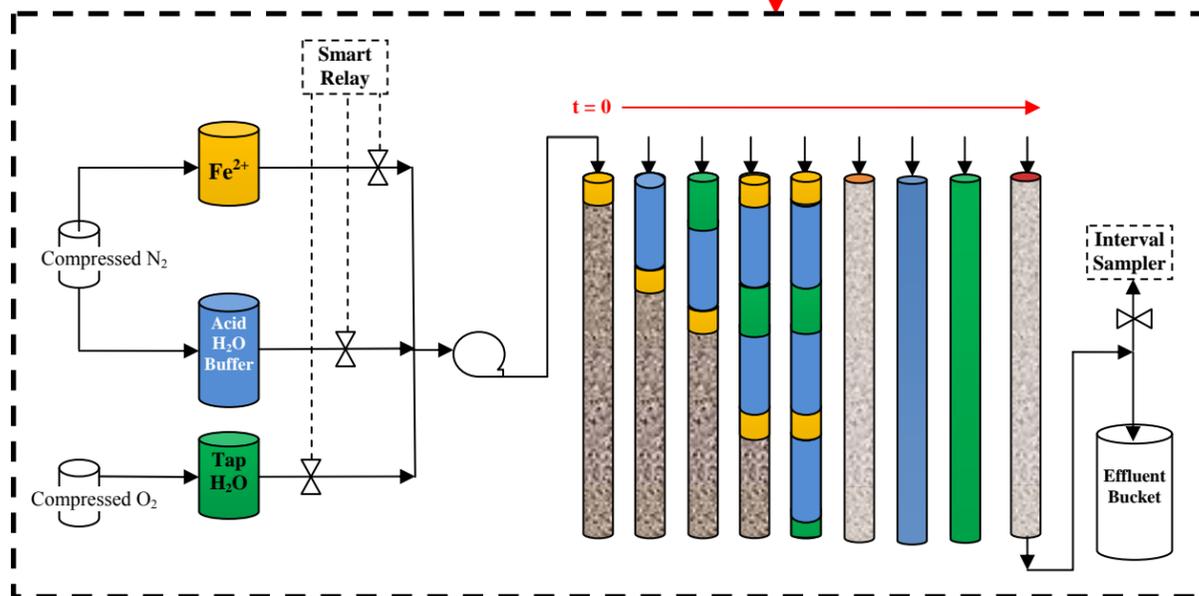
Figure 2: IOCS Analytical Process Diagram



Step 1: Sand Wet-packing

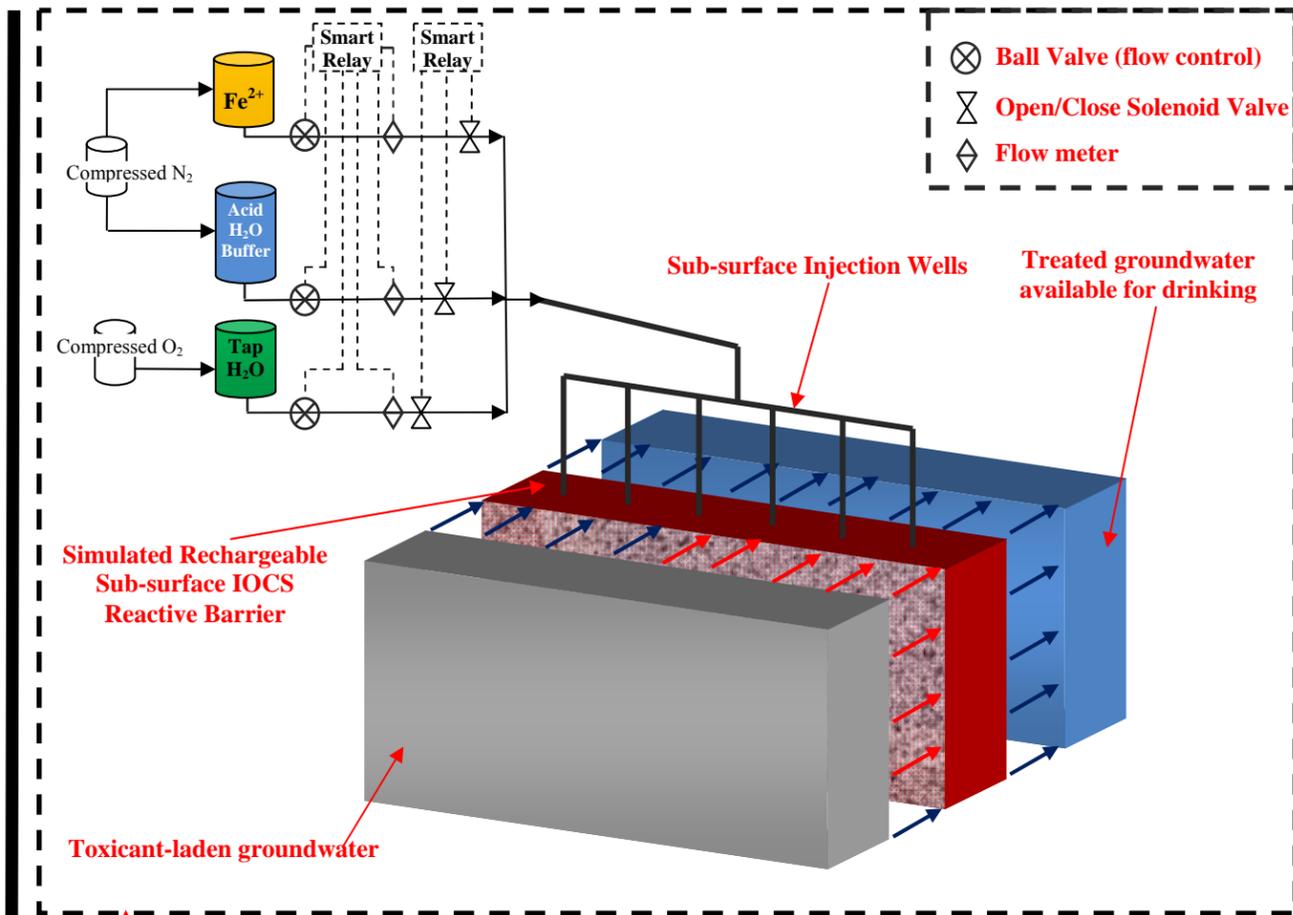


Step 2: Sand Pre-cleaning

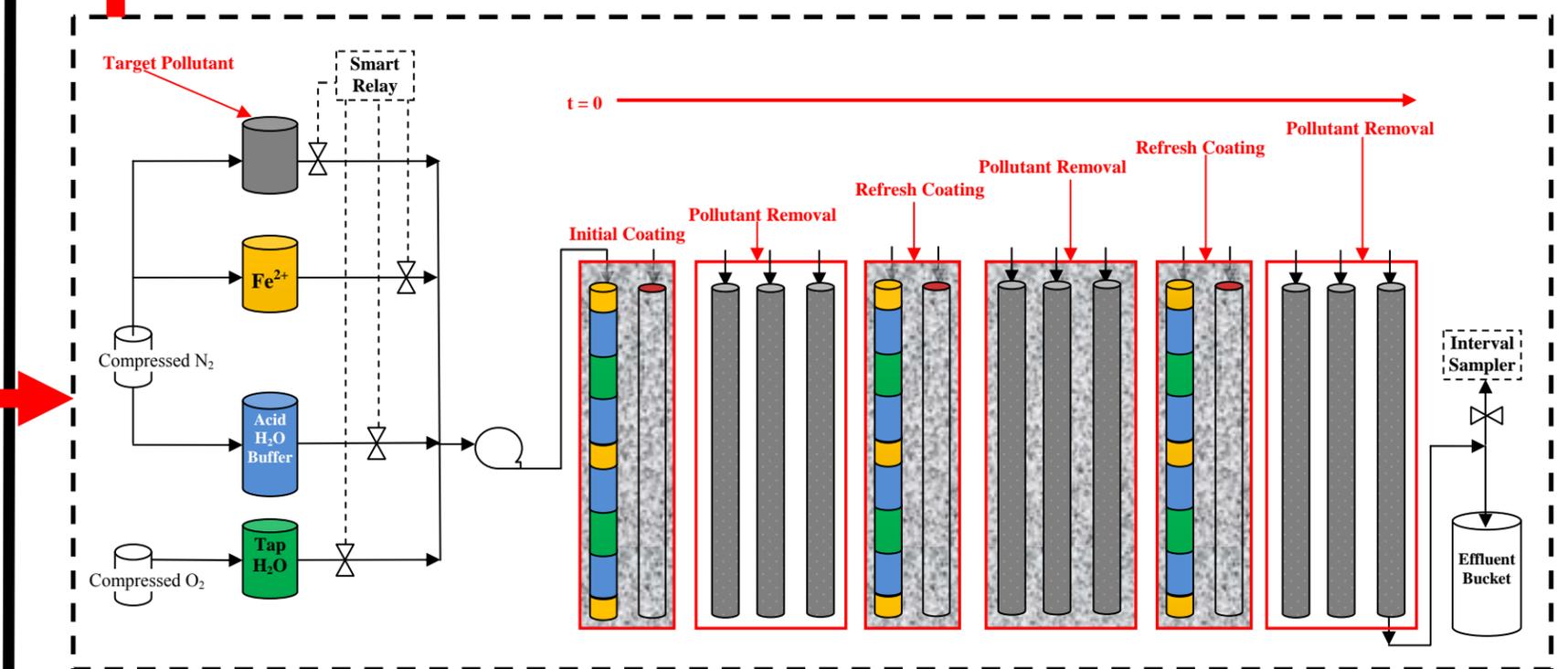


Step 3: Iron Oxide Coating

PHASE 1: *In Situ* Coating (June 2009 – March 2010)



PHASE 3: *In Situ* Pilot Study (September 2010 – April 2011)



PHASE 2: *In Situ* Treatment & Regeneration (March 2010 – August 2010)

RESEARCH STATUS

PHASE 1

- Step 1: Complete
- Step 2: Complete
- Step 3: Complete
- Publication: **In Progress**

PHASE 2

- 1st run: **In Progress**
- 2nd run: Stand-by
- 3rd run: Stand-by
- Publication: **In Progress**

PHASE 3

- Design: Stand-by
- Construction: Stand-by
- Operation: Stand-by
- Publication: **In Progress**

8. Analytical Equipment

Effluent samples were collected using a Spectrum Chromatography IS-95 Interval Sampler, Model 141200, Houston, Texas, United States. pH measurements were made on a pH meter, Model Thermo Scientific No. 5000, Singapore. Arsenic and total iron analyses were performed using an Atomic Absorption Spectrometer; Model PerkinElmer No. B3150080, Shelton, Connecticut, United States. The spectrometer was also used to analyze ions and metals that were believed to be detected at the parts per billion (ppb or ppm x 10⁻³) level. Fe²⁺ was analyzed using a UV/IVS Spectrometer; Model PG Instruments T80+, Wibtoft Lutterworth, Leicestershire, United Kingdom via Standard Methods 3500-Fe (Standard Methods, 1998).

9. Significant Findings

The injection schematic designed in the Research Approach accommodates the demand for numerous trials using a variety of configurations to determine the best feed sequence. Tables 1 and 2 provide the operations for sand cleaning and Fe-O coating.

Table 1 - Sand Pre-cleaning Operation ^a				
Agent	Strength	Units	Time ^{b, c}	Units
HCl	0.5	10 ⁻³ mol/L	180	minutes
NaCl	0.5	10 ⁻³ mol/L	60	minutes
NaOH	0.5	10 ⁻³ mol/L	180	minutes
NaCl	0.5	10 ⁻³ mol/L	60	minutes
^a	7-day operation			
^b	injection time during a single cycle			
^c	hydraulic retention time of 60 minutes			

Table 2 - Iron Oxide Coating Operation ^a				
Agent	Strength	Units	Time ^{b, c}	Units
Fe ²⁺	4.92	10 ⁻³ mol/L	4 - 5	minutes
HCl	0.5	10 ⁻³ mol/L	8 - 10	minutes
O ₂	1.23	10 ⁻³ mol/L	6 - 7	minutes
HCl	0.5	10 ⁻³ mol/L	8 - 10	minutes
^a	3-day operation			
^b	injection time during a single cycle			
^c	hydraulic retention time of 30 minutes			

Figure 3 depicts a scanning electron method (SEM) angled view of a sand particle surface before and after acid/base cleaning. The acid treatment degraded the bonds between the impurities, colloids, and the sand surface while the base removed the impurities and colloids from the sand filter. The saltwater buffer was used to keep the acid and base from reacting with each other in the conveyance system prior to sand application.

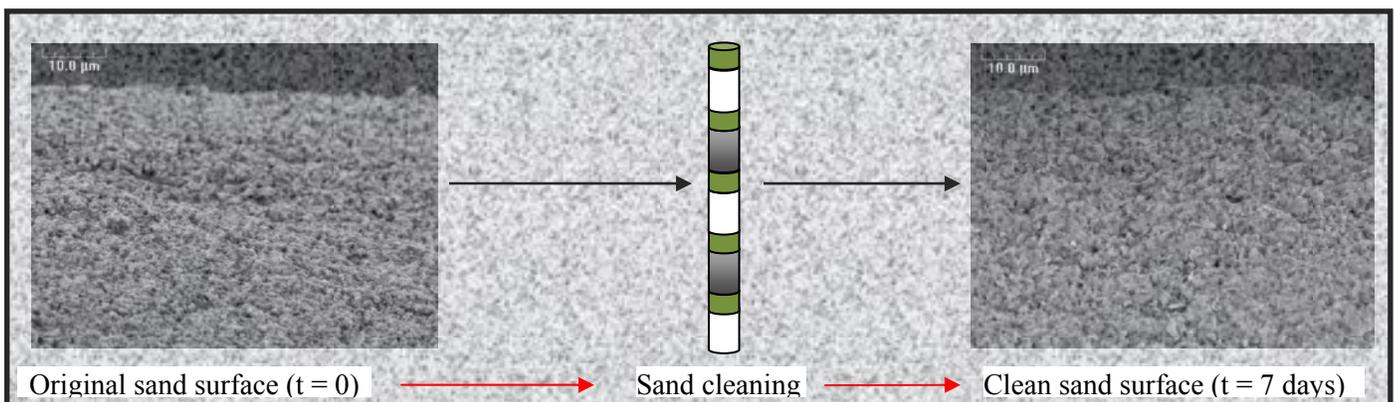


Figure 3 – Sand Pre-cleaning Results

There was a great deal of speculation during the pre-planning stages of this project that the sand cleaning would provide a more uniform sand surface for the iron oxide to form; thus promoting a uniform coating process throughout the filter rather than coating one specific region at a time. Furthermore, this process has slightly improved the porosity of the sand by, minimizing the effect of significant head loss induced by clogging. The removal of the impurities and

colloids on the sand surface increased the space between the sand particles; allowing water to flow through the filter with less resistance.

As a result of the improved sand surface from the acid/base treatment, the iron oxide coating was successful. After 40 hours of intermittent injection with the chemicals described in Table 2, uniform coating was observed (Figure 4). The coating sequence was employed for a little while longer in an attempt to accumulate more iron oxide on the sand. The acid water buffer was then injected for 30 minutes to flush the filter of excess solids and suspended Fe^{2+} before applying a 9-hr oxygen blanket to strengthen the iron oxide crystallization on the sand. This method was intended to oxidize any excess Fe^{2+} that was adsorbed onto the sand surface. An x-ray diffraction analysis (XRD) revealed that the iron oxide crystals were consistent with hematite and lepidocrocite.

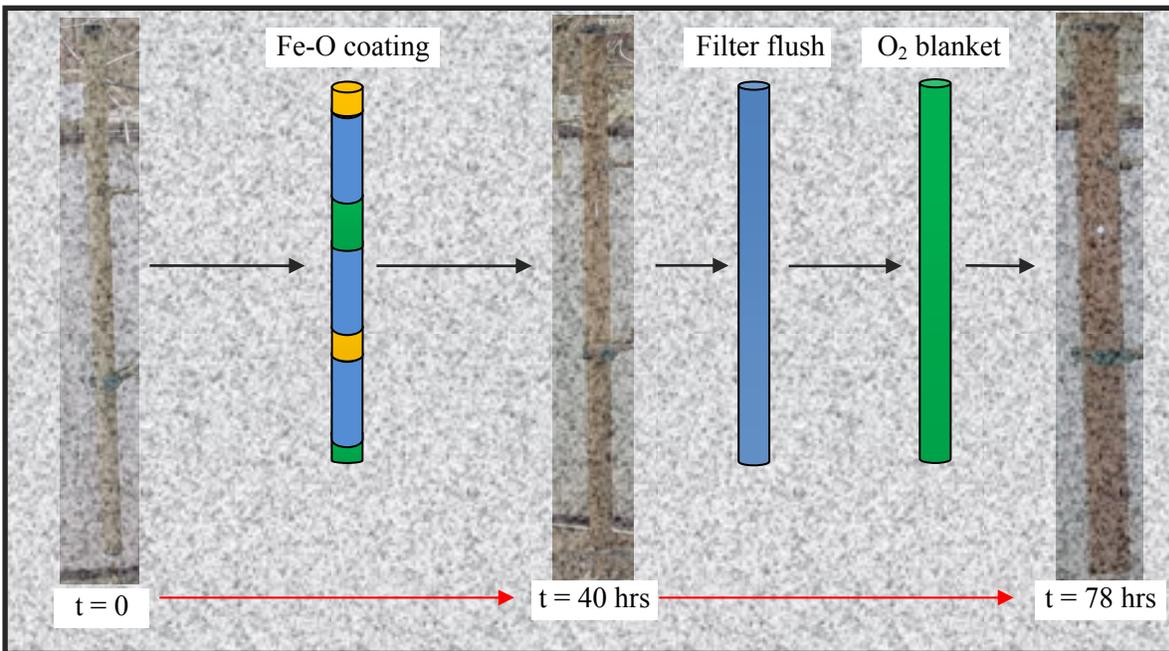


Figure 4 – Iron Oxide Coating

Two trials were performed to evaluate the performance of the coating method by quantifying the iron oxide accumulation on the sand surface. The sand was broken into six segments when coating was complete after it was assumed that the accumulation was not homogeneous throughout the filter. The second trial shows more accumulation after elongating the coating procedure and applying the oxygen blanket (Figure 5). The second trial resulted in clogging and it was determined that the suspended particles were not flushed out of the system and produced a thick slurry in the top 18" of the filter that induced significant head loss. The coating procedure was then modified to intermittently flush the filter with acid water to prevent any excess solids from being suspended between the sand particles.

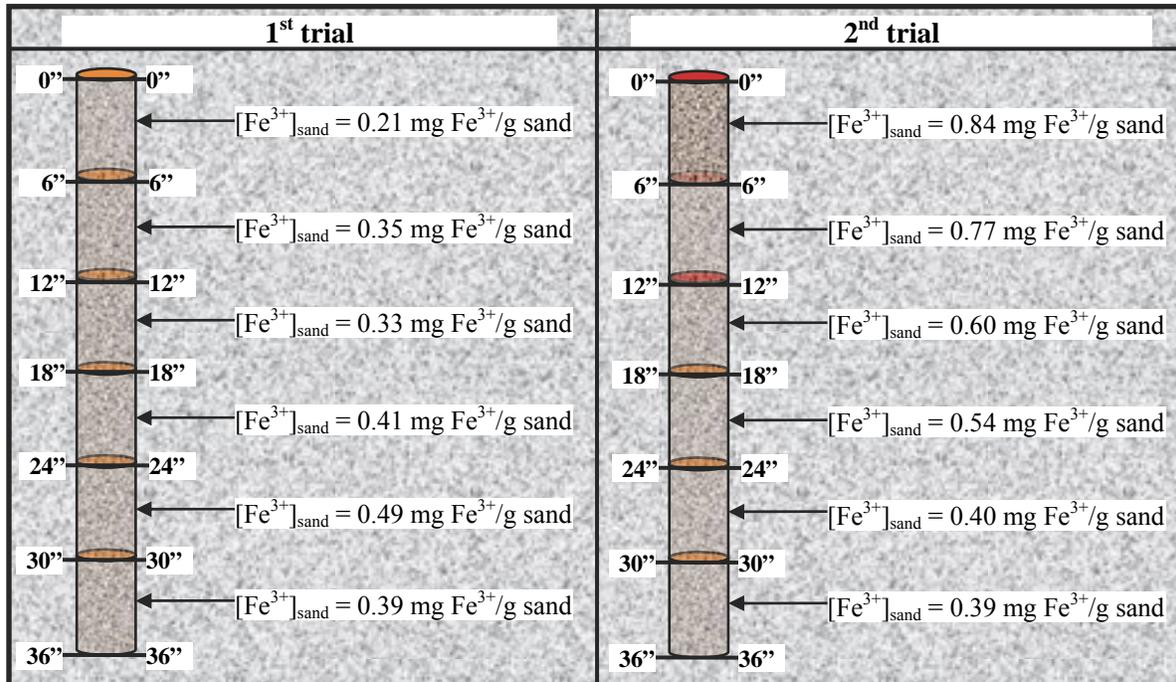


Figure 5 - Iron Oxide Accumulation Profiles

10. Intentions of the Research

- 1) Establish a sustainable and inexpensive *in situ* emplacement of iron oxides onto sand matrices with dissolved metal treatment and re-usability capabilities that can be employed for large-scale groundwater applications. This study has immense potential to be an applicable removal technology for arsenic and other metals in rural groundwater treatment.
- 2) Evaluate and re-use the devised research approach to develop reactive barriers for mercury (Hg), cadmium (Cd), chromium (Cr), and cobalt (Co) removal as mandated by the USEPA priority industrial pollutants (USEPA, 2009).
- 3) Expand the research to devise a large-scale IOCS manufacturing process that will accommodate the demand for industrial water treatment. The design of this research can be retrofitted to produce an IOCS sub-surface reactive barrier (as described in Phase 3) for a variety of applications; making this product a highly versatile technology.

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Ecohydrology of Forested Wetlands on the Texas Gulf Coast

Basic Information

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Principal Investigators:	Dex Dean, Bradford Wilcox

Publications

There are no publications.

Ecohydrology of Forested Wetlands on the Texas Gulf Coast

Project Number

2009TX330B

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Abstract

Wetlands provide critical ecological services, including flood control, water quality improvement, wildlife habitat, and enhancement of biodiversity. In the Texas Gulf Coast region, as in many areas of the country, industrialization and developmental pressures have led to a dramatic decline in wetland area over the past fifty years. Ironically, because many are considered to be isolated and not hydrologically connected to adjacent streams, they are not regulated. However, very little work has been done to examine the connectivity of these wetlands to nearby streams. As a means of investigating this issue, the intent of this study was to develop a better baseline understanding of hydrological processes of forested wetlands on the Texas Gulf Coast. An important first step in understanding hydrological processes on these wetlands is to develop quantified water budgets including rainfall, surface flow, soil water, and transpiration. We anticipate that this research will play an important role in determining the regulatory status of these wetland landscapes in the future by providing information to support policy decisions.

Problem and Research Objectives

Two of the most important water issues facing Houston and the Greater Houston area are flooding and water quality. High annual rainfall, widespread urban development, an extensive network of streams and floodplains, tidal surges, and generally flat terrain combine to make flooding a prevalent and expensive problem in and around the city of Houston. In addition, the quality of water in local watersheds and in the Galveston Bay Estuary is extremely important for

regional fisheries, wildlife, and recreational use of the bay. The estuary is a nursery for many regionally important species of fish and shellfish, and serves as a migrational stop for waterfowl and other migratory birds. Between 1990 and 2008, four seafood safety advisories were issued for Galveston Bay because of chemical contamination. In addition, biological contaminants (primarily bacteria) are a concern, especially with respect to recreational use of the bay and some bay tributaries.

The Clean Water Act was developed to protect the integrity of waters of the United States—our nation's navigable and interstate water resources and waters that are important to the integrity of navigable and interstate waters. Wetlands that are adjacent to navigable waters or abut relatively permanent non-navigable tributaries of navigable waters are within the regulatory authority of the Clean Water Act (USEPA, 2007). However, wetlands exist that do not meet the above criteria but do possess the potential to affect downstream waters for significant portions of the year. Currently, most forested wetlands on the Texas Gulf Coast are assumed to be hydrologically isolated from waters of the United States because they discharge water intermittently and therefore probably do not contribute significant volumes of flow to influence downstream waters. However, there is very little quantified hydrologic data to substantiate this assumption.

Forested wetlands, though easily overlooked, are potentially very important for detention of floodwaters and for early removal of water and sediment borne contaminants in stormflow. Since 1955, over 97,000 acres of coastal forested wetlands in Texas have been lost to development (TPWD, 1996). Development has affected forested wetland systems in two ways. They have either been drained and filled for conversion to residential, industrial, or agricultural use or they have been converted to deepwater aquatic systems—as a result of subsidence from groundwater pumping—such that they no longer provide the same ecological functions. It is important that we promptly develop an understanding of the nature of water fluxes through these wetland systems to determine their hydrologic capacity to perform critical ecological functions.

Objectives

The hydrology of forested wetlands on the Texas Gulf Coast is not well documented. In particular, only limited work has been done to define water budgets and to evaluate the hydrological connectivity of these wetlands to other systems. As noted by Rodriguez-Iturbe et al. (2007), the study of wetland ecohydrology is a fairly recent endeavor, and quantified information including soil water profiles and plant transpiration is needed for the development of new scientific frameworks. The objective of the proposed study is to develop a better understanding of wetland ecohydrology by (1) quantifying components of a water budget for a forested wetland watershed in southern Harris County and (2) determining whether or not the wetland is hydrologically connected to adjacent waterways.

Materials/Methodology

The study watershed (Figure 1) was located southeast of Houston, Texas at the Armand Bayou Nature Center. Any water discharged from the watershed flows into a channel that is directly connected to Armand Bayou, which is navigable. Armand Bayou in turn flows into Clear Lake, which ultimately flows into Galveston Bay and then the Gulf of Mexico. The watershed boundary encompasses 8 hectares (20 acres), approximately 25% of which is covered by wetland depressions. Much of the remainder of the watershed also meets the technical criteria for wetlands—evidence of reducing soil conditions, hydrophytic, vegetation, and/or wetland hydrology (Mitsch and Gosselink, 2007). Average annual rainfall in the watershed is approximately 1330 mm/yr. Some of the more prevalent tree species in the watershed include willow oak (*Quercus phellos*), swamp red oak (*Quercus pagodafolia*), water oak (*Quercus nigra*), and Chinese tallow (*Triadica sebifera*).

The size of the watershed was determined using a handheld GPS unit while the watershed was saturated and runoff was occurring. Most of the watershed had a clearly discernible boundary (peak), but in some locations, the direction of runoff flow was used to determine the boundary. An elevated trail was identified as the southern boundary of the watershed, and equipment for monitoring discharge was located at the outflow culvert. Daily rainfall data was obtained from a set of the nearest available rain gauge within the watershed operated by the Harris County Office of Homeland Security and Emergency Management (Armand Bayou at Pasadena Lake). Where data from this rain gauge was unavailable, data from the Horespen Bayou at Bay area Boulevard was used in its place. Long-term average rainfall was determined using the nearest available official rain gauge maintained by the National Climactic Data Center (Hobby Airport, 1921 to present). Wetland surface discharge (runoff) was measured using a wier instrumented with a sonic water level recorder (Infinities USA, Inc.). Near-surface soil moisture was measured in situ at depths 0 mm, 100 mm, and 150 mm depths using soil moisture probes (Hydra Probe II, Stevens Water Monitoring). Finally, transpiration through trees in the watershed was measured using the heat dissipation sap flux method (see Granier, 1987).



Figure 1 - Location of the study watershed and outlet (green dot) in relation to Armand Bayou, Bay Area Blvd., and Clear Lake (see inset).

Principal Findings

Here, results are reported from 3/1/2009 to 4/23/2010 in order to show some of the interesting results of this study that were not available prior to trees coming out of dormancy in during March 2010. Additionally, soil moisture sensors were not available for use until the later part of November 2009, and were subsequently installed during December of 2009. Instrumentation for monitoring rainfall and runoff were operational for the nearly all of the reporting period.

The 1,117 mm of rainfall received by the watershed during the study period was below-average compared to long-term average rainfall of approximately 1,330 mm/yr. Even so, it is clear that surface discharge to Armand Bayou (runoff) occurred during the study period. The first occurrence of runoff was 10/2/2009, and significant runoff was generated between 10/10/2009 and 1/27/2009 (Figure 2a). A total of 176 mm of surface runoff was measured, and surface runoff accounted for 14.9% of rainfall inputs.

Soil moisture (Figure 2b) was measured in two different soils. Surface soils in the wetland depressions are predominantly deep, heavy clays. Soils on the adjacent flats are typically loamy, and underlain by clay at 150-450 mm depth. The porosity of the soils in the depression was 0.45, whereas the average porosity of the surface soils on the adjacent flats was 0.41. If extrapolated over the entire watershed, it is capable of storing approximately 1400 m³ within the upper 150 mm of soil for the depressions and approximately 3700 m³ within the upper 150 mm of soil for the adjacent flats. This means that the upper 150 mm of soil in the watershed is capable of containing a maximum of 63 mm of rainfall at any given time. Perhaps the most interesting observation with regard to soil moisture is that the soils were essentially saturated from December up through late March or Early April, after which the soils began to rapidly depart from saturation.

Interestingly, transpiration began to increase around the same time (see *T. sebufera* and *Q. phellos*, Figure 2c: other trends are similar but less detectable at the given scale). Measured average sap flux density ranged from 2.13×10^{-5} m/s (*Q. pagodafolia*) to 3.52×10^{-4} m/s (*Q. phellos*). The lower end of the range falls in line with published values (Granier 1987), however, values in the upper range do not; this suggests that data for *Q. pellos* and *T. sebufera* may require more sophisticated data treatment to produce reliable results.

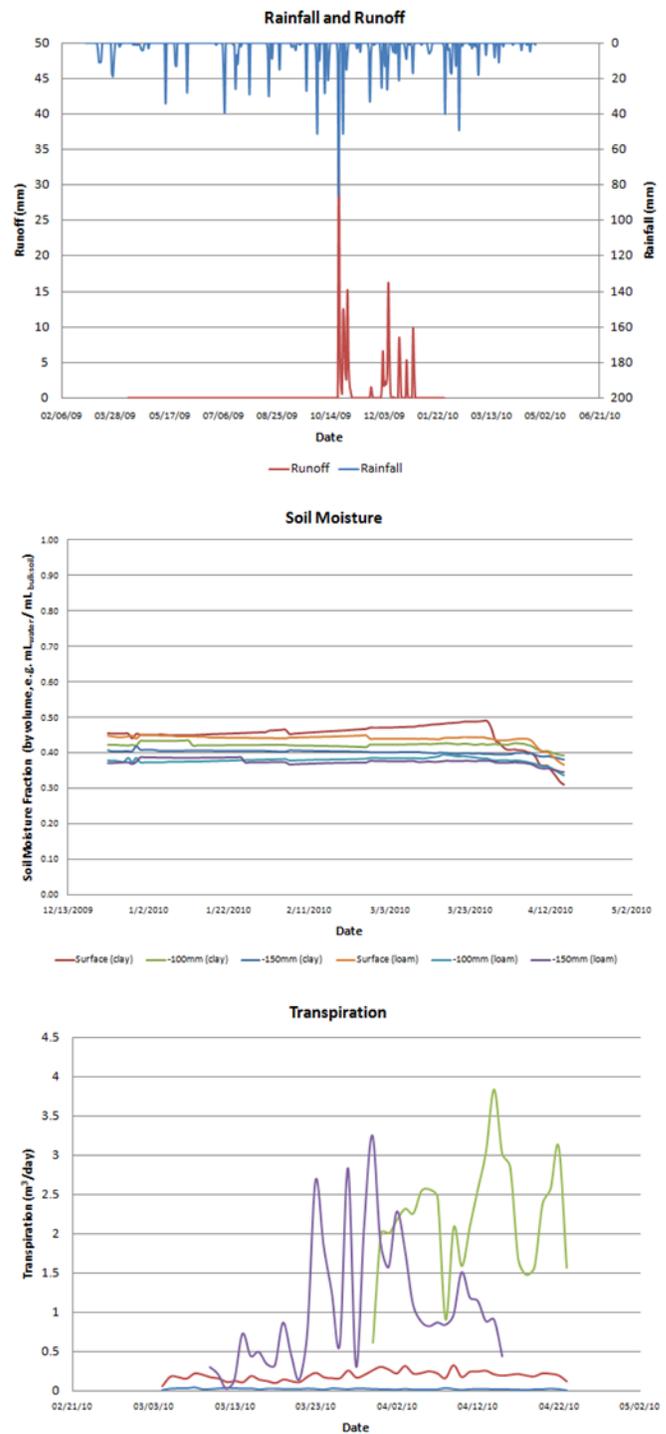


Figure 2 - Hydrologic fluxes for the wetland watershed, including (a) daily rainfall and runoff in mm (b) soil moisture in two surface soils, given as a volume fraction, and (c) measured transpiration from trees of four species given in m³/day. Please note that x-axis (date) scales vary between plots.

Significance

The principle significance of these results is that they provide baseline data that will be useful for developing frameworks that will help regulators and policy makers make decisions based upon the best available data. These data show that wetlands on the Texas Gulf Coast are not hydrologically isolated, as assumed. Instead, they are capable of discharging substantial amounts of water downstream (14.9% of rainfall in this study, with below-average rainfall). Additionally soil moisture data indicated that wetland soils were at or near saturation from the time the sensors came online until late March-early April, when the forest regained its leaves and transpiration began to contribute significantly to water fluxes leaving the watershed.

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Hydrological Drought Characterization for Texas under Climate Change, with Implications for Water Resources Planning and Management

Basic Information

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Project Number:	2009TX334G
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Principal Investigators:	Vijay P Singh, Ashok Kumar Mishra

Publications

1. Singh, V. P., 2010, Entropy theory for derivation of infiltration equations, *Water Resources Research*, 46, W03527, doi:10.1029/2009WR008193.
2. Singh, V. P., 2010, Entropy theory for movement of moisture in soils, *Water Resources Research*, 46, W03516, doi:10.1029/2009WR008288.
3. Mishra, A. K., and V. P., Singh, 2010, Changes in extreme precipitations in Texas, *J. Geophysical Research*, American Geophysical Union, (In Press). Manuscript no: 2009JD013398.
4. Mishra, A. K., M., Özger, and V. P., Singh, 2010, Association between uncertainty in meteorological variables and water resources planning for Texas, *Journal of Hydrologic Engineering*, ASCE, (in press).
5. Ozger, M., A. K., Mishra, and V. P., Singh, 2010, Scaling characteristics of wet and dry spells of precipitation data, *Journal of Hydrologic Engineering*, ASCE, (In press).
6. Ozger, M., A. K., Mishra, and V. P., Singh, 2010, Long lead time drought forecasting using a wavelet and fuzzy logic combination model, *Water Resources Research* (Submitted after first review), American Geophysical Union, Manuscript no:2009WR008794.
7. Mishra, A. K., and V. P., Singh, 2010, A review on drought concepts, *Journal of Hydrology*, (Submitted after first review), Manuscript no: HYDROL 8529.
8. Mishra, A. K., and V. P., Singh, 2010, Drought modeling: A review, *Reviews of Geophysics*, (Submitted).
9. Mishra, A. K., M., Özger, and V. P., Singh, 2010, Seasonal streamflow extremes in Texas River basins: Uncertainty, trends and teleconnections under climate change scenarios, *Journal of Geophysical Research*, (Submitted).

**Hydrological drought characterization for Texas under climate change, with
implications for water resources planning**

Project number: 2009TX334G

Progress report (Sep 2009 to May 2010)

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Hydrological drought characterization for Texas under climate change, with implications for water resources planning

1. Basic information

Title:	Hydrological drought characterization for Texas under climate change, with implications for water resources planning
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Principal investigator(s):	Vijay P. Singh and Ashok K. Mishra

2. Problem and Research objectives

Droughts in the United States result in an estimated average annual damage of \$6 to 8 billion (Wilhite, 2000). The estimated loss from the 1988 drought was \$40 billion (American Meteorological Society, 1997) and the estimated loss for the state of Texas alone from the 1996 drought was \$6 billion (Wilhite, 2000). Like other western states, Texas is a water deficient state and is highly vulnerable to droughts, and its vulnerability is being compounded by rapidly growing population. According to the Water Plan (*Water for Texas 2007*) developed by Texas Water development Board, water shortages during droughts could cost businesses and workers in the state about \$9.1 billion by 2010 and \$98.4 billion by 2060 and about 85 percent of the state's projected population would not have enough water by 2060 in drought conditions), if an additional 8.8 million acre-feet of water supplies are not developed. Further complicating the Texas water shortage is climate change, which is being much debated these days. The major concern arising from climate change is its effect on water resources in terms of droughts and the resultant impact on different sectors. The objective of the project is therefore threefold:

(i) Analysis of multivariate hydrologic droughts: Drought is characterized by severity, areal extent, and duration. Multivariate distributions of these characteristics are needed and they will be derived using copulas. Then, droughts will be characterized by constructing: (a) Severity – Duration – Frequency curves (SDF), (b) Severity – Area – Frequency (SAF) curves, and (c) Severity-Interarrival time Frequency (SIF) curves. These curves are important for water resources planning.

(ii) Assessment of drought risk under climate change: Climate change impact studies have been conducted using a top-down approach. First, outputs from Global Circulation Models (GCMs) are considered which are downscaled in a second step to the river basin scale using either a

statistical/empirical or a dynamic approach. The local weather scenarios are then statistically linked to possible large-scale climate conditions that are available from GCMs. Finally the downscaled meteorological variables are used as input to a macro scale land surface hydrologic model (i.e., VIC model) for investigating future hydrological drought scenarios. Several questions will be addressed: (a) How much percentage of a basin will undergo a drought in year 2050? (b) What will be the severity of the 2050 drought? (c) Will the drought of 2050 be more severe than the 2020 or 2080 drought? (d) What will be the duration of the drought in 2050 or 2080? (e) How much will be the water deficit in a river in 2050, considering it as a hydrological drought? (f) How will drought properties vary, when compared to the past 50 years? This objective will also attempt to quantify uncertainties in drought characterization, considering primarily climate change and different water management strategies.

(iii) Understanding of low frequency climate variations in association with Southern Oscillation Index (SOI) and Nino indexes: These variations affect Texas and their understanding will help provide improved streamflow forecasting needed for reservoir operations and will aid water management decisions. The lead-time of forecasting will be annual.

3. Accomplishments of the project

The project started on September 1, 2009; however it took a semester to recruit two doctoral students (Deepthi Rajasekhar and Li Chao) and both of them joined in January 2010. One graduate student has started working on multivariate drought analysis using copulas and the other graduate student has started working on the application of the VIC model by incorporating GCM outputs to investigate the impact of climate change on hydrological droughts. The schedule of project tasks are mentioned below along with the progress being made.

1. Data collection and processing (Sep 2009 to Dec 2009)

The data required for setting up of the VIC model as well as GCM outputs for downscaling meteorological variables have been completed.

2. Downscaling of meteorological variables (Jan 2010 to Dec 2010)

Work has been carried out based on literature review, data collection, programming and its preliminary assessment. The present analysis includes downscaling using nonparametric methods for single-site precipitation simulation and this will be explored for multisite simulation as future work.

3. Setting up VIC models (Jan 2010 to Dec 2011)

The work completed so far includes literature review, data collection and pre-processing of the data before it can be used for running the VIC model. The work carried out so far based on data collection and pre-processing includes:

1. Delineating the basin of interest: Arc-map was used for this purpose. Brazos river basin was considered. Hydro 1k data for drainage basins in North America was downloaded.

Hydro 1k is a geographic database which provides a global coverage of topographically derived datasets including streams, drainage basins, etc. The basin of interest was delineated. This basin delineation will then be used to clip out a fine resolution DEM for the basin of interest. The source of the fine resolution DEM is GTOPO30 (USGS). The basin DEM will be required later for routing model.

2. Input parameter files: This includes the Global parameter file and the user defined files. The global parameter file specifies the path for the locations of the input files. It also specifies several run time options. The important options to be specified include simulation time step length, mode of operation (whether to compute surface temperature based on energy budget or just water budget), defining the input forcing files, soil and vegetation parameter files: their pathname, file prefix and file format. The output file options are also described in global parameter file. Similarly the user defined file defines several compile-time options like: options for controlling debugging messages, option to compute statistics of the forcing, etc.
3. Forcing data: The meteorological forcing variables selected include: windspeed, precipitation and temperature. Daily time scale was chosen for the data from 1970-2000.

For wind speed and air temperature, the source of data was NCEP/NCAR reanalysis. The resolution of this data is 2.5 degrees, whereas the resolution of the VIC model is 1/8 degrees. The format of the data file is Netcdf. First the data format was converted from Netcdf to ascii. An appropriate MATLAB interface called mexcdf was used for converting netcdf to ascii. Then, the resolution was converted to match that for the VIC model. Linear interpolation will be used for resolution conversion.

The daily precipitation data for Texas was obtained from United States Historical climatology network. Regridding program is available in the VIC website for gridding the precipitation data to required resolution. The basis of this regridding program is an interpolation algorithm known as SYMAP, developed by Shepard. The daily precipitation data is then to be scaled in terms of PRISM data, which is supposedly the highest quality spatial data set available. Long term monthly means of the PRISM precipitation data should be obtained and the monthly means of the observed precipitation data should be rescaled with respect to the ratio: prism_mean/monthly_mean. This is done, so that the monthly mean of our input data is consistent with long term PRISM means. This portion is under progress now. The program mk_monthly.c gives the monthly means of the observed data, and get_prism.c gives the long term mean of PRISM data for each month. The C-program rescale.c will be used for scaling the precipitation data.

4. Multivariate drought analysis and risk assessments (Jan 2010 to Dec 2011)

Literature review completed.

5. Drought forecasting using teleconnections (Jan 2010-Dec 2011)

It is reported in section 'Principal findings and significance', which follows in the next section.

6. Preparation of research articles (Jan 2010 – Aug 2012)

Publications related to drought research are reported in the 'publication' section. These publications are based on the changes in hydro-meteorological characteristics under climate

change scenarios for the state of Texas. These conclusions drawn from the research publications will supplement the current project.

6. Principal findings and significance

a. Drought variability associated with climate indices for the state of Texas

Abstract

The variability in the sea surface temperature (SST) in the Pacific Ocean has an influence on the variability of the continental U.S. precipitation, streamflow and drought. Analysis of the dominant oscillations of droughts and large scale climate indices shows that interannual and interdecadal variations related to climate indices are significant indicators of drought occurrences. Using wavelet transforms and cross-correlations and Kriging, spatial structure of teleconnections of both El Niño Southern Oscillation (ENSO) and Pacific Decadal Oscillation (PDO) to droughts during the twentieth century is investigated, with particular reference to the state of Texas. The specific objectives of the study therefore are: 1) to identify the dominant oscillations of drought indices and their temporal variations using continuous wavelet transforms (CWT); 2) to determine the spatial correlation structure between large scale climate and drought indices with the aim at detecting the response of regions with respect to various large scale climate anomalies, such as ENSO and PDO; 3) to relate the drought variability to large scale anomalies at annual and decadal scales; and 4) to determine the phase relations between Palmer drought severity index (PDSI) and climate anomalies for all climate divisions in Texas.

Methodology

Spatial structure of teleconnections of both ENSO and PDO to droughts along with the scale analysis was investigated using wavelet transforms, correlations and spatial analysis. For this purpose CWT, cross-correlation and Kriging approaches were used.

Continuous wavelet transform

The Continuous Wavelet Transform (CWT) is used to decompose a signal into wavelets, small waves that grow and decay over a small distance, whereas the Fourier transform decomposes a signal into infinite number of terms of sines and cosines losing most time-localization information. A continuous wavelet transform of a signal produces the coefficients at a given scale. The CWT's basis functions are scaled and shifted versions of the time-localized mother wavelet. A Morlet wavelet is one of the many wavelet functions which has a zero mean and is localized in both frequency and time. Since the Morlet wavelet provides a good balance between time and frequency localizations, it is preferred for application. It can be represented as [Torrence and Compo, 1998]:

$$\psi(\eta) = \pi^{-1/4} e^{i\omega\eta - 0.5\eta^2} \quad (1)$$

where ω is the dimensionless frequency, and η is the dimensionless time parameter. The wavelet is stretched in time (t) by varying its scale (s), so that $\eta = s/t$. When using wavelets for feature

extraction purposes, the Morlet wavelet (with $\omega = 6$) is a good choice, since it satisfies the admissibility condition (Torrence and Compo, 1998).

For a given wavelet $\psi_0(\eta)$, it was assumed that X_j is a time series of length N ($X_j, i=1, \dots, N$) with equal time spacing δt . The continuous wavelet transform of a discrete sequence X_j is defined as convolution of X_j with the scaled and translated wavelet, $\psi_0(\eta)$:

$$W_n^X(s) = \sum_{j=1}^N X_j \psi^* \left[\frac{(j-n)\delta t}{s} \right] \quad (2)$$

where the asterisk indicates the complex conjugate. CWT decomposes time series into time-frequency space, enabling the identification of both the dominant modes of variability and how those modes vary with time.

Cross wavelet transform

Torrence and Compo (1998) defined the cross-wavelet spectrum of two time series X and Y with wavelet transform W_n^X and W_n^Y as

$$\left| W_n^{XY}(s) \right| = \left| W_n^X(s) \cdot W_n^{*Y}(s) \right| \quad (3)$$

where W_n^{*Y} is the complex conjugate of W_n^Y . The complex argument of W_n^{XY} can be interpreted as the local relative phase between time series X_j and Y_j . Statistical significance is estimated against a red noise model, thus Cross Wavelet Transform (XWT) can be constructed from two CWTs. XWT denotes their common power and relative phase in time-frequency space.

Results and Discussion

Oscillations in PDSI and climate indices by wavelet analysis

ENSO plays an important role in the variations of droughts and wet spells over Texas. The main characteristic of ENSO is the periodic occurrence of the warm phase (El Niño) and cold phase (La Niña) of ENSO. First, CWT was used to analyze localized intermittent oscillations in PDSI and climate indices time series. In general, one can examine two time series together that may be expected to be linked in some way. For this purpose, CWT of the average PDSI representing the entire state of Texas, NINO 3, NINO 3.4 and PDO index time series is shown in Figure 1.

The NINO 3 index exhibits interannual (16-70 month scale) oscillations of large amplitude during pre-1920 and post-1960 periods, and a reduced level of activity in between (Figure 1b) which is in agreement with previous studies (Torrence and Compo, 1998) Although it is not statistically significant, NINO 3 shows a considerable amount of power as interdecadal oscillations (180-200 months) in the 1920-1955 and 1970-1990. Also, NINO 3.4 has approximately the same resultant power map (Figure 1c). PDO shows interannual variability of 64 month scale during 1935-1960s, and post-1990s, and a few significant oscillations in between (Figure 1d). It has a strong power concentrated in the band of 200-250 month scale from 1935 to 1980.

PDSI that is the average of all climate divisions shows strong oscillations of 50 to 100 month modes during 1905 and the 1925s, and a 20-45 month oscillations pre 1910, around the mid 1920s and from 1940 to 1960 (Figure 1a). A peak exists around the 1960s at a 100 month scale. PDO does not have a significant power near the 180-250 month band between 1930 and the 1990s but still shows a considerable amount of power. There are clearly common features in the wavelet power of the PDSI and NINO indices, such as the significant peak in the 18-40 month band in pre 1910s and 64-100 month band in 1915-1925. Both series also have high powers in the 180-250 month band in the period from 1930-1980, although for the NINO indices power is not above the 5% significance level. A common power between PDSI and PDO is detected for the period 1940 to 1980, but the PDO power in this band also does not provide the 5% significance level.

Thus, it is possible to find localized intermittent periodicities by continuous wavelet transform which is visible with classical Fourier transforms. The results indicate that interannual and interdecadal variations should be considered for any drought risk analysis study. Visual comparison of Figure 1a and Figures 1b–1d indicates that the relationship between the wavelet powers of PDSI and climate indices appears to be highly unstable. Using cross wavelet analysis, one can measure the link between regional drought signals and climate indices.

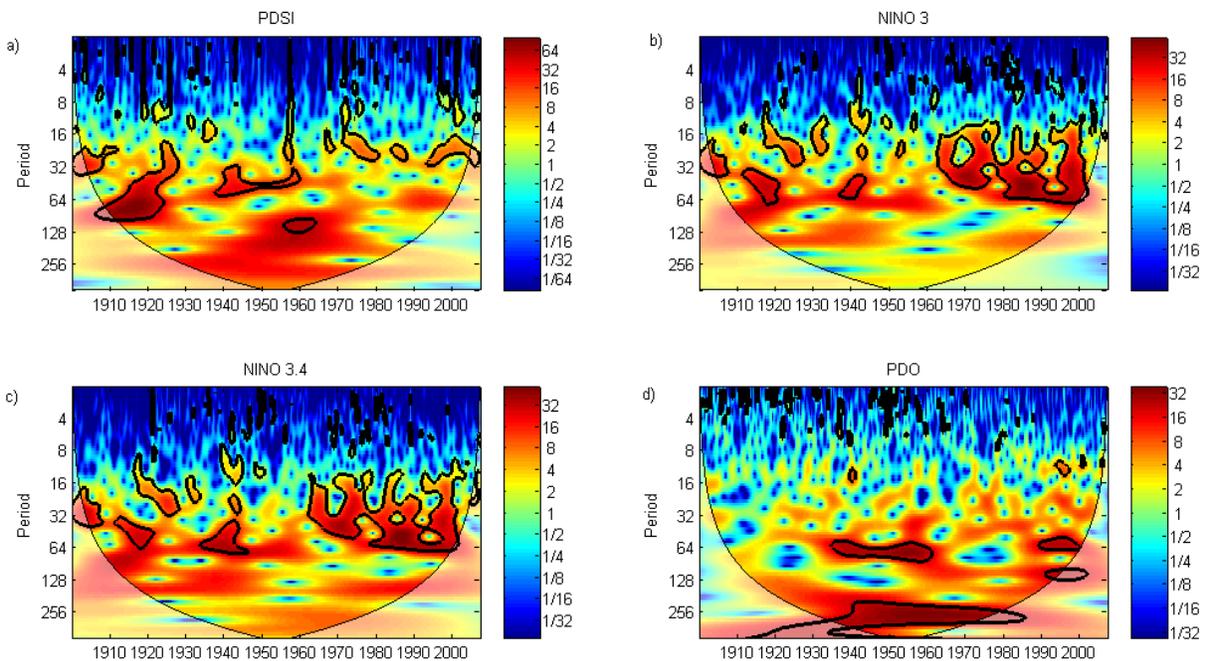


Figure 1. Continuous wavelet power spectrum of (a) Time series of average PDSI over Texas (b)NINO 3 (c) NINO 3.4 and (d) PDO. The thick black contours depict the 5% confidence level of local power relative to a red noise. The black line is the cone of influence beyond which the picture might be distorted by the effect of zeropadding.

Relationship between PDSI and climate indices by cross wavelet analysis

The XWT of PDSI and NINO 3 is shown in Figure 2a. Here it is noticed that the common features visually found from individual wavelet transforms stand out as being significant at the 5% level. There also is a significant common power in the 180–250 year band from 1930–1980. This suggests that there are large multi-year to decadal variations in droughts over Texas and the variations are closely related to strong El Niño events. In other words, when one strong El Niño event happens, there is possibly a large variability in droughts over Texas on a multi-year or decadal scale. Also, XWT of PDSI and NINO 3.4 were calculated but are not shown here. Nearly the same results were obtained.

A significant positive correlation was found between PDSI and PDO during 1960–1970 in the 80-100 month band. Common power between PDSI and PDO was detected for the period 1940 to 1965 in the 180-250 month band for which the correlation is above the 5% significance level (Figure 2b). Although it is easy to detect common properties of the time series with CWT and XWT, it is not possible to obtain a lag time relationship and quantify the correlation between two variables of concern. However, in the proposed approach one can determine lag times and between drought characteristics and climate indices along with significant correlations. Long-range drought forecasting strategies for this region should thus incorporate information from the large-scale climate anomalies.

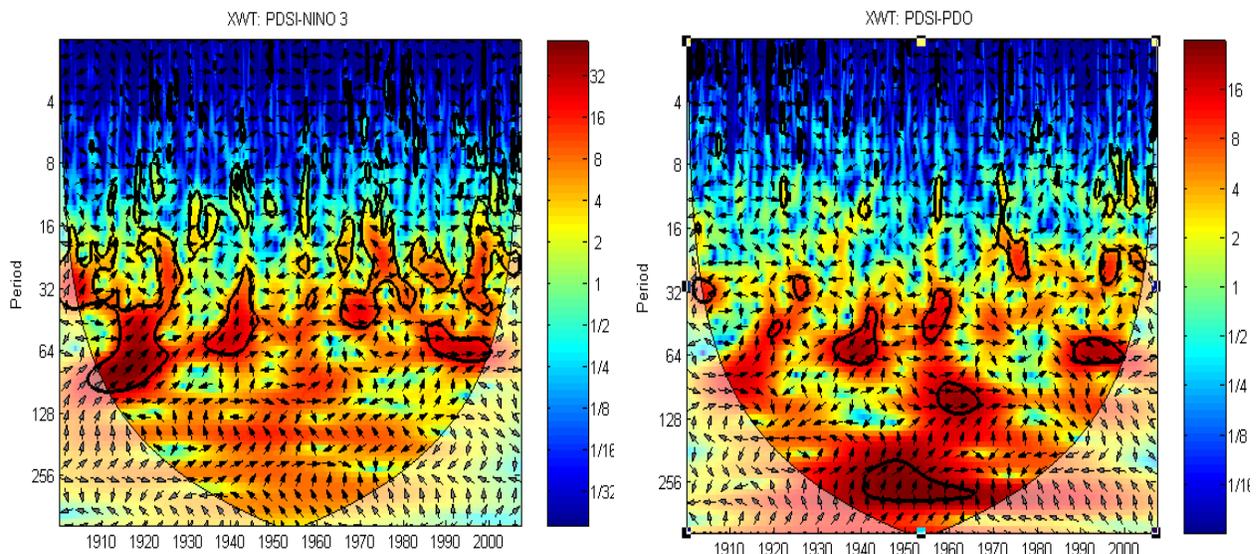


Figure 2 Cross wavelet transform of the (a) PDSI and NINO 3 and (b) PDSI and PDO time series. The thick black contours depict the 5% confidence level of local power relative to a red noise, and the black line is the cone of influence. Right-pointing arrows indicate that the two signals are in phase while left-pointing arrows are for antiphase signals.

Correlation and lag time for PDSI and NINO 3 teleconnections

From the analysis explained above it is detected that there are two apparent peaks at 60-85 months and ~200 months which represent the annual and decadal scales, respectively. These peaks are approximately common for the climate divisions. The spatial variation of lag time and correlation coefficient are shown on Kriging maps in Figure 3. On an interannual basis, lag times

decrease from north to south of the state. The minimum lag times are seen in the coastal region. On the other hand, semi-arid and continental climate regions are strongly correlated at a level of around 0.80 with NINO 3 region SSTs. This suggests that spatial response of PDSI is indeed due to ENSO. Weaker correlations were obtained for the sub-tropic humid region. Different lag time and correlation patterns were detected for annual and decadal scales. On an interdecadal basis, while the climate divisions 6 and 10 had less lag times, bigger lag times were observed in the Panhandle and far west. The sub-tropic humid region shows weaker correlations with NINO 3 as in the annual scale. Higher correlation coefficients generally concentrate in the sub-tropic semi-humid and continental climatic zones.

Because the dominant mode of variability of NINO 3 is at interannual and interdecadal time scales, these results confirm that interannual and interdecadal variability in droughts in several climate divisions is teleconnected to ENSO. The positive correlation means that El Nino years generally cause droughts, especially in the above-mentioned divisions. On the other hand, La Nina conditions do not have significant effects on drought occurrences.

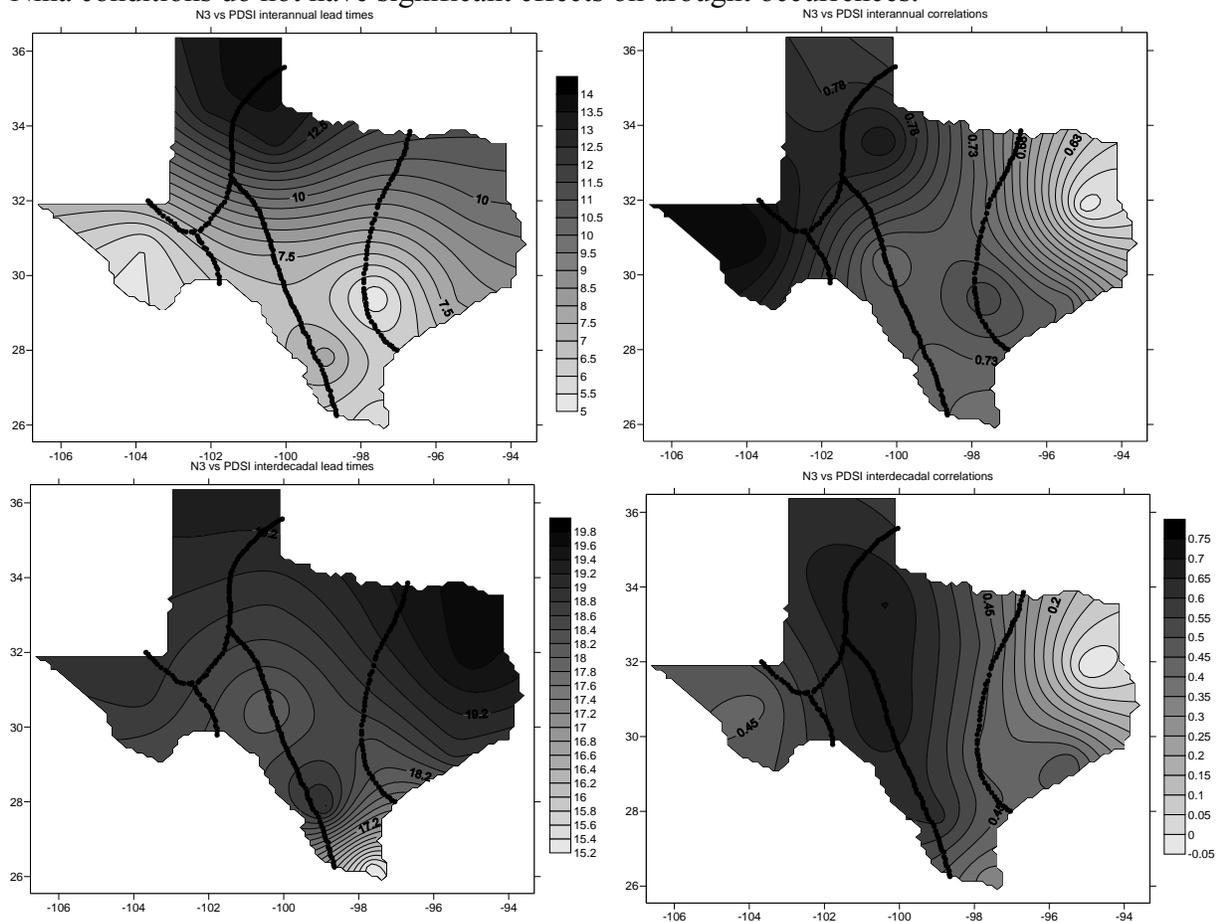


Figure 3. Spatial variation of lag-times and correlation coefficients for NINO 3 and PDSI at (a-b) annual and (c-d) decadal scales.

Correlations and lag time for PDSI and NINO 34 teleconnections

Figure 4 shows maps for the spatial response of PDSI to NINO 3.4 region SSTs. Approximately, the same results were obtained with the PDSI and NINO 3 relation that interannual and interdecadal oscillations generally concentrated around 6 year and 16.5 years, respectively, and lag times varied between 6 and 13 months for the annual scale and 15-19 months for the decadal scale. The lag time pattern decreases from north to south as in the previous relationship. Also, PDSI exhibited a strong correlation covering the arid and semi-arid regions. Weak correlations were seen in the eastern part. The fact that ENSO is weaker in this part could be another climate forcing element. For the decadal scale, while a long lag time of 18-19 months existed in the eastern part, it gradually decreased down to 7-8 months towards the western part of the state. But the correlations were still very low in the east.

Climate divisions located in the western part typically experience wet (dry) conditions following La Nina (El Nino) events. Divisions in the east showed above average conditions to La Nina events but their response to El Nino events could not be clearly detected.

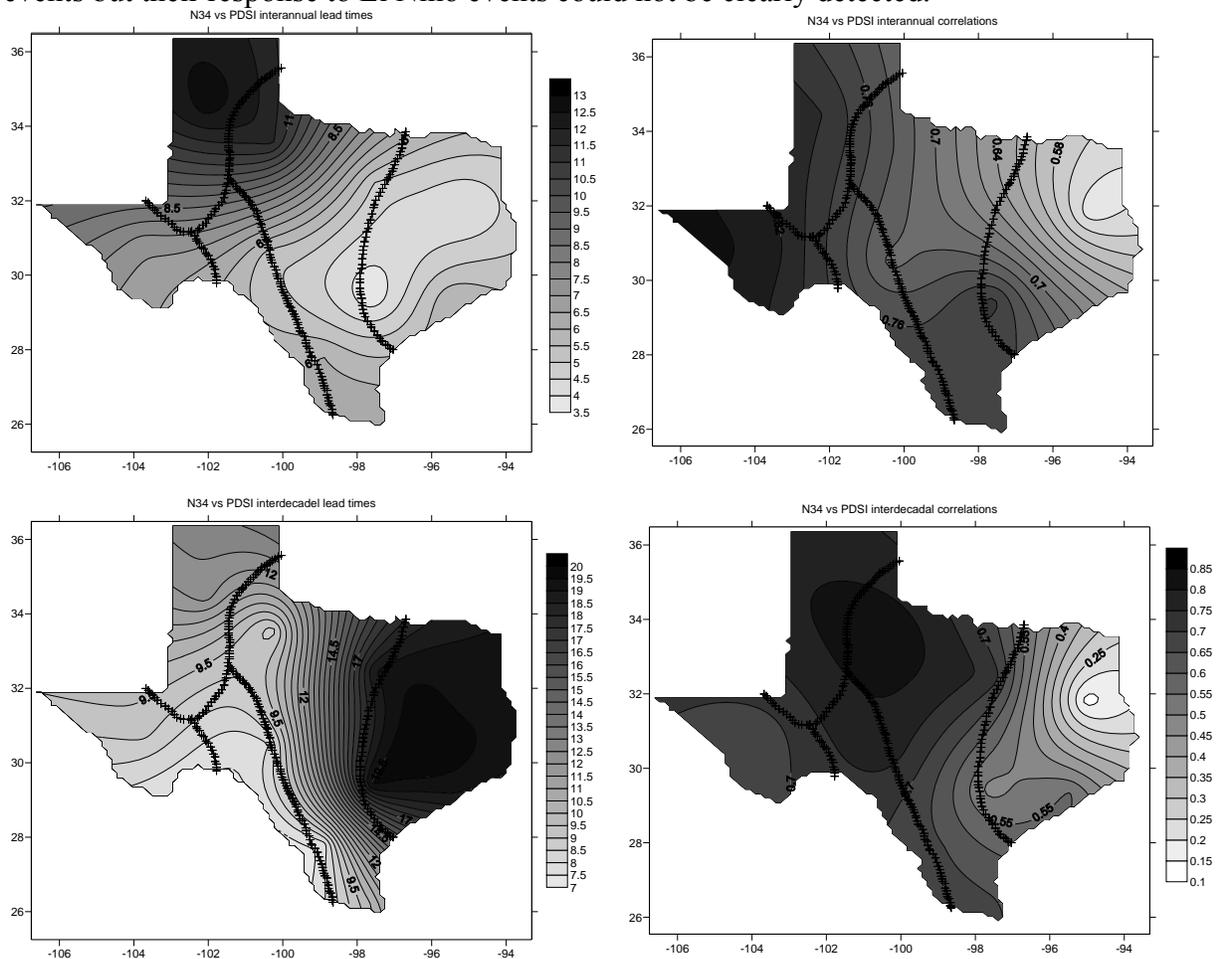


Figure 4. Spatial variation of lag-times and correlation coefficients for NINO 3.4 and PDSI at (a-b) annual and (c-d) decadal scales.

Correlations and lag time for PDSI and PDO teleconnections

In this case, for the annual scale regions in the southern parts of Texas were strongly correlated with PDO (Figure 5). However for other parts correlations were not significant. Lag times decreased from East to West. All of those suggested that the spatial response of PDSI was not as significant as in the previous cases and lag times were less reasonable. Also for decadal scale, only the Panhandle exhibited a high correlation.

There are also some differences in the spatial structure of the PDSI-PDO correlation pattern in this case. The differences in the spatial patterns for the ENSO and PDO modes in the three cases provide some insights. Hoerling et al. (1997) proposed that SST anomalies placed at different locations in the equatorial and tropical Pacific can lead to rather different spatial signatures and strengths for the continental precipitation and temperature teleconnections. In fact, the location of the primary tropical convection centers in the ENSO region affects the atmospheric moisture flow and tropical– extratropical teleconnection. Weak correlations between PDSI and PDO reveal that there is a need for investigation on the role of other internal modes of variability which warrants further research. The analysis suggests that the PDSI-PDO relationships are likely to be nonlinear.

To summarize, SST-PDSI correlation analysis for three cases was performed. The proposed approach not only performs correlation analysis using wavelet decomposition series, but also determines lag times between drought characteristics and climate indices along with significant correlations. The resulting maps exhibit differences from each other. While the ENSO SST indices and PDSI relationships were spatially similar in the first two cases, they differed in their detail. The common feature of these two cases is that sub-tropical humid region shows a weaker correlation with NINO indices. On the other hand, spatial patterns of lag time and correlation coefficients for PDO and PDSI did not coincide with the other two cases and correlations were very low as well.

Conclusions

The relationships between low-frequency climate indicators and droughts in Texas have been investigated. Relatively robust teleconnections between ENSO and drought indices in northern and western Texas are found. The approach proposed here paves a way to calculate correlations and lag times between wavelet transformed PDSI and climate indices time series. The advantage of this approach is that one can determine the spatial variation of correlation coefficients at the same time with lag time. The following conclusions can be drawn from this study:

1. It is found that two particular scales, namely multiyear (6-8 years) and decadal (16-20 years), are effective for drought occurrences associated with large scale climate indices.
2. Continuous and cross-wavelet transforms indicate that there is a strong relationship between drought and climate indices in the 80-100 month and 180-250 month bands. These results are also consistent with correlation analysis that multiyear (6-8 years) and decadal (16-20 years) play a significant role in shaping drought characteristics.
3. ENSO indices exhibit better correlations with drought indices than PDO. For interannual (interdecadal) variation, the average correlation coefficient values between PDSI and NINO 3.4 and PDSI and PDO are 0.73 (0.63) and 0.55 (0.54), respectively. Also it is revealed that NINO 3.4 has better correlations than NINO 3 at decadal scales.

4. The Kriging maps reveal that arid and continental climate zones are highly correlated with climate indices as compared with humid regions in the east part of the state.
5. The lag time between NINO 3.4 and PDSI decreases from north (~12 months) to south (~7 months). This indicates the effect of different climatic features.

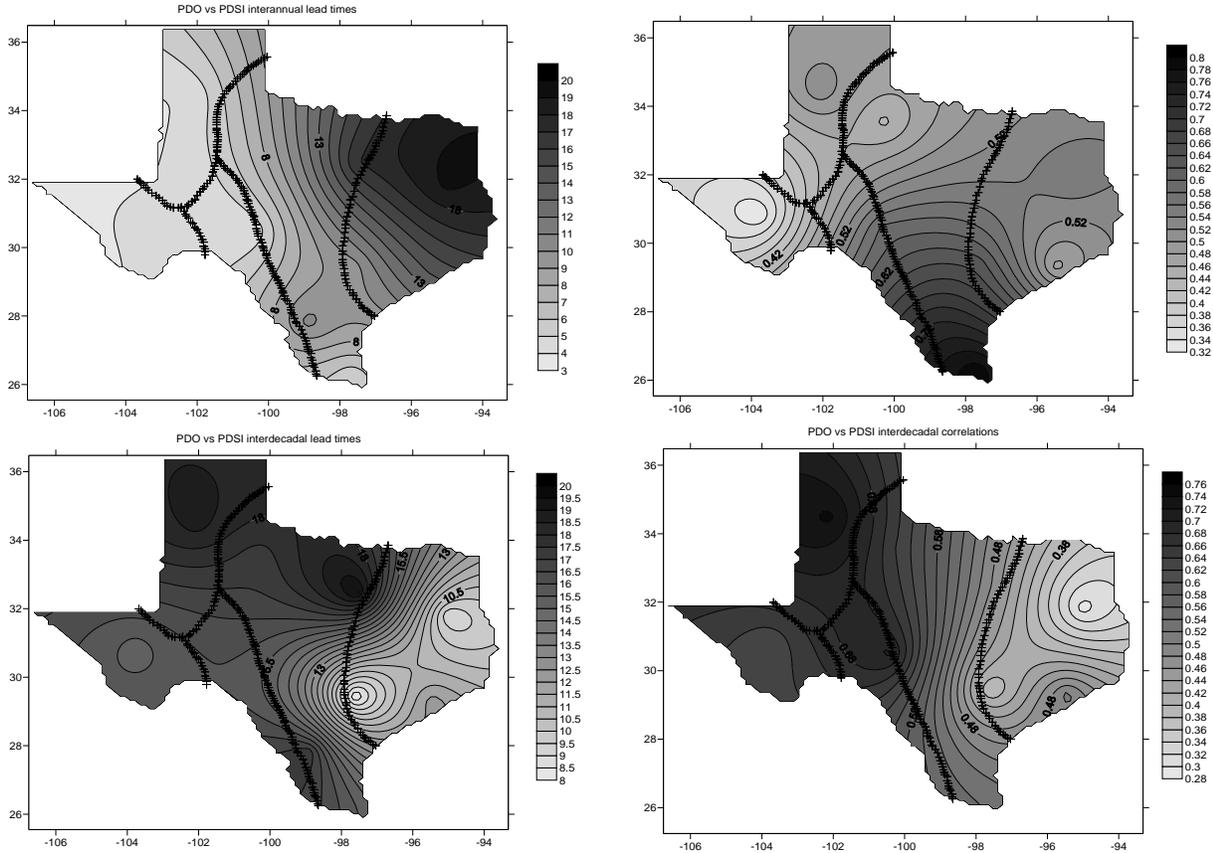


Figure 5. Spatial variation of lag-times and correlation coefficients for PDO and PDSI at (a-b) annual and (c-d) decadal scales.

The relatively high correlations with ENSO conditions and modest correlations with PDO suggest that the ENSO forcing may have an impact on shifting the distribution of drought anomalies. Apparently, successful long-range forecasting of drought requires information about ENSO, even though predictions of ENSO have been achieved at lead times of several months. The need to better understand the spatial structure of the tropical Pacific fields in predicting PDSI is highlighted. Details of both fields and their timescales of evolution are likely to be important for successful forecasting schemes. As a further work, this study can be expanded across the U.S. and the other hydro-meteorological variables such as rainfall, temperature, evaporation and streamflow can be used.

b. Long lead time drought forecasting using a wavelet and fuzzy logic combination model

Abstract

El Nino Southern Oscillation (ENSO) caused by the sea surface temperature (SST) variability in the Pacific Ocean influences the continental U.S. drought characteristics. Considering the ENSO variability this study developed a wavelet and fuzzy logic (WFL) combination model for long lead-time drought forecasting. Wavelet transform and cross wavelet transform were applied for analyzing the time series of ENSO variables and drought index to identify the intraseasonal variability and common significant parts in time and frequency domains. Most models forecast droughts for short lead times (less than 6 months), and those forecasting drought for 6 to 12 months do not yield satisfactory forecasts. This discussion focuses on long-term drought forecasting. Extending the forecasting of monthly drought indices to a 3-to 12-month lead time is the main objective of this study. This is accomplished by employing a wavelet-fuzzy logic combination model. Long range seasonal drought forecasting considers persistence in drought along with Southern Oscillation Index (SOI) and sea surface temperatures (SSTs) which denote anomalies in sea level pressure and sea surface temperatures, respectively. NINO 3.4 index representing the SSTs of a specific region in the Pacific is used frequently for forecasting. NINO 3.4 and SOI are used as ENSO indicators.

Methodology

Determination of significant bands from wavelet transform

A measured time series consists of several frequencies. The prediction sometimes can be difficult if the whole time series is taken into account without separation into frequency bands and elimination of noises. The approach may be that one can use only significant frequencies in the prediction scheme to obtain more accurate results. *Webster and Hoyos* [2004] suggested the use of significant variances in the wavelet spectra for the separation of frequency bands. The PMDI time series (Figure 6a) which is considered as predictand and its corresponding continuous wavelet transform along with the wavelet spectra are shown in Figures 6b and 6c, respectively. It is evident from the figure that there are six distinct frequency bands which are 8-13, 14-17, 18-20, 21-23, 24-28, and >29 months. The time series of wavelet bands are obtained by inverse wavelet filtering (Figure 7). The Morlet wavelet is employed for wavelet analysis. The frequency bands obtained from the wavelet transform of predictand are used for other predictors. There are six bands that should be predicted from their corresponding predictors. As a final step, these predicted bands are reconstructed to establish the desired PMDI time series.

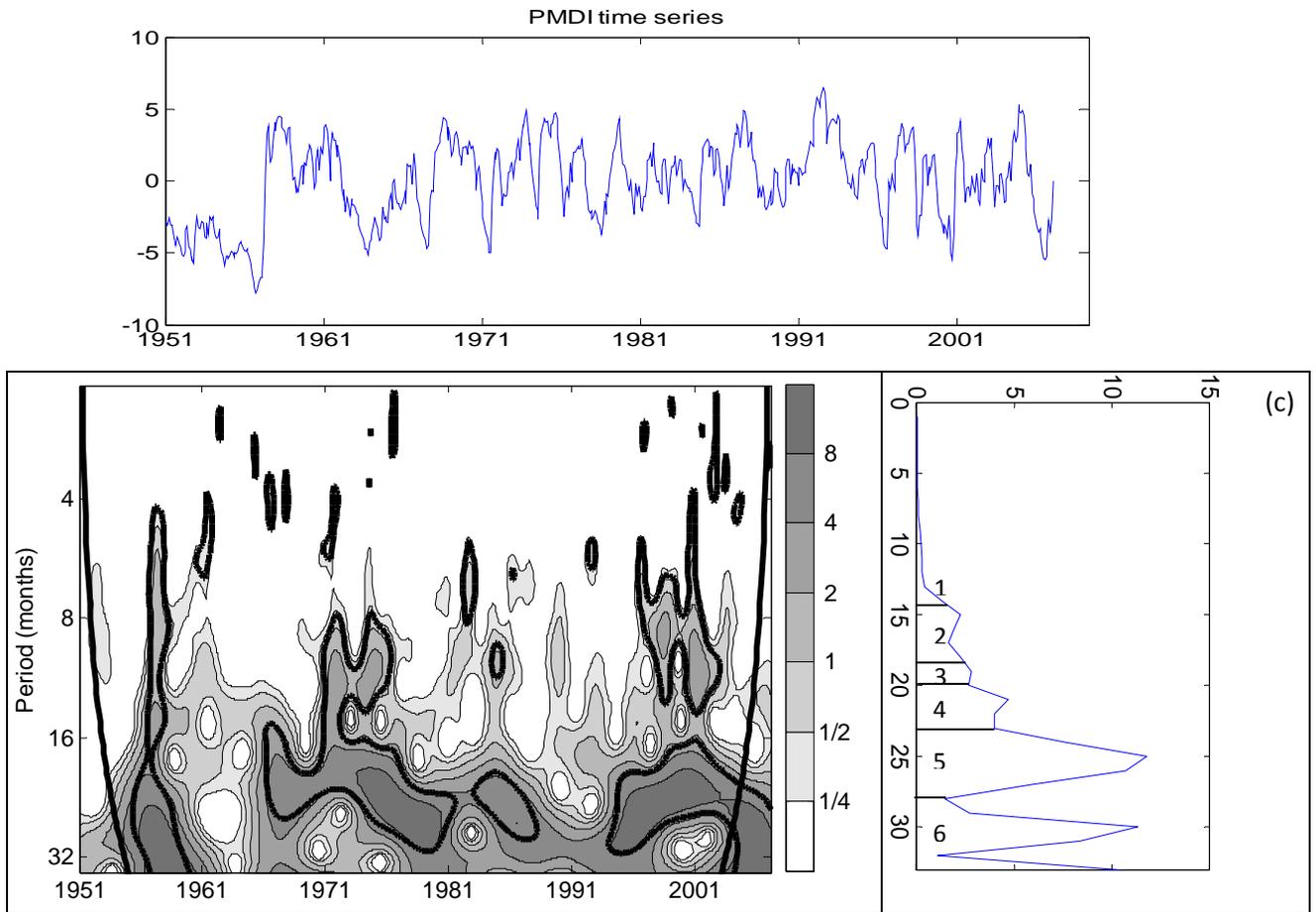


Figure 6. a) PMDI time series, b) continuous wavelet transform of PMDI, and c) its average wavelet spectra.

Fuzzy Logic approach

An FL model (FLM) consists of fuzzy rules and fuzzy sets that produce weightings for rules. Fuzzy rules appear in the form of IF-THEN statements, where the parts before and after THEN are called antecedent and consequent, respectively. In this study the antecedent part consists of ENSO indicators (e.g., NINO 3.4 or SOI) and previous PMDI values and the future PMDI values are used in the consequent part. For example, a simple fuzzy rule can be shown as “IF NINO 3.4(t) is high and PMDI(t) is high THEN PMDI (t+n) is high”. Here, n denotes the lead time in the resolution of months. There are mainly two approaches in the implementation of FL, namely, Mamdani and Takagi-Sugeno (TS) inference systems. While Mamdani approach relies on expert knowledge, numerical data is important for TS approach. Since there is available data with long periods, here, the TS system is used for forecasting. The significant spectral bands of ENSO indicators and previous drought index were used as input variables and output was taken as future values of the drought index which is considered for forecasting. A schematic of the forecasting method is shown in Figure 8.

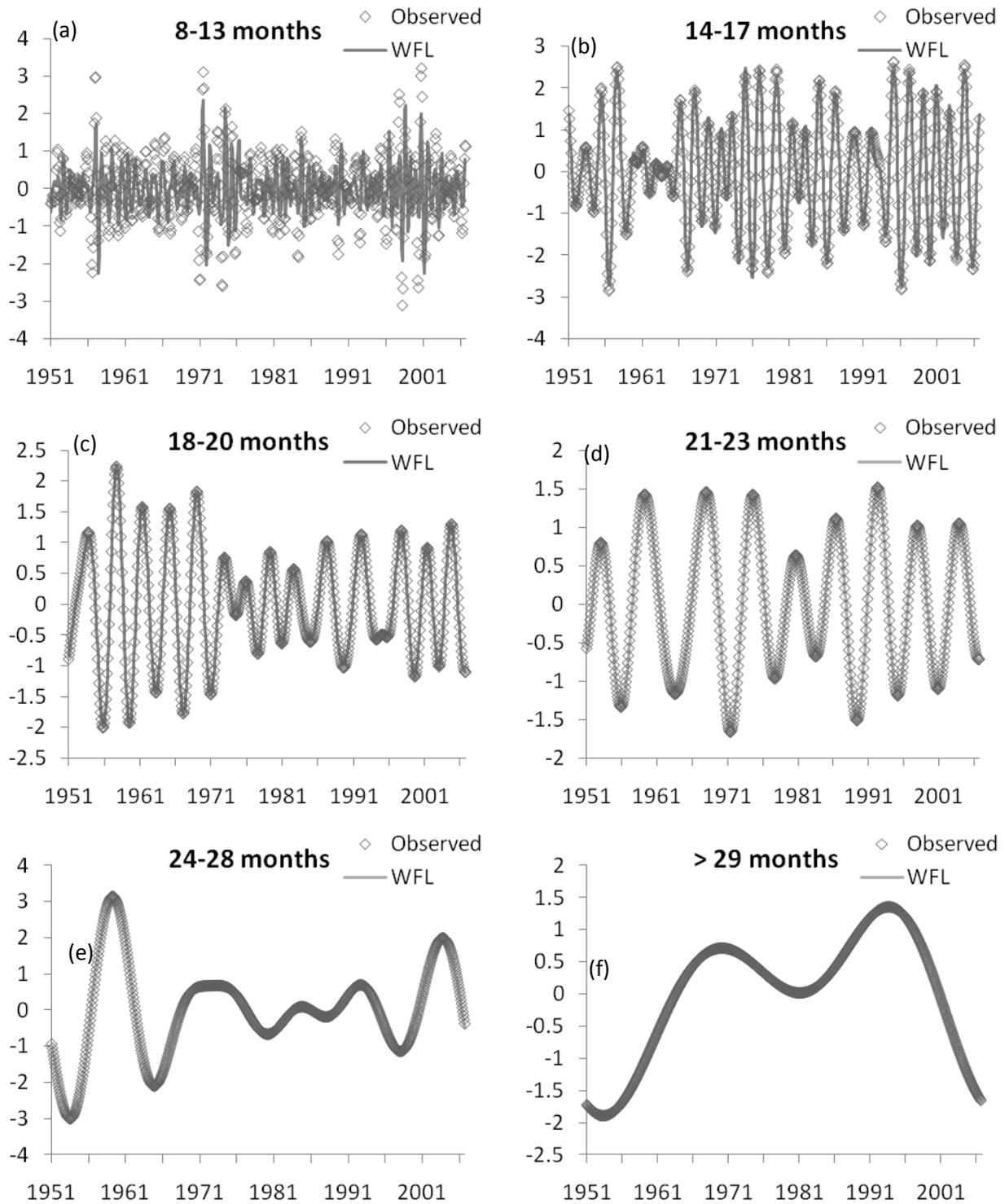


Figure 7. Significant spectral bands of observed PMDI values and their prediction by WFL. These bands are: a) 8-13 months, b) 14-17 months, c) 18-20 months, d) 21-23 months, e) 24-28 months, and f) >29 months.

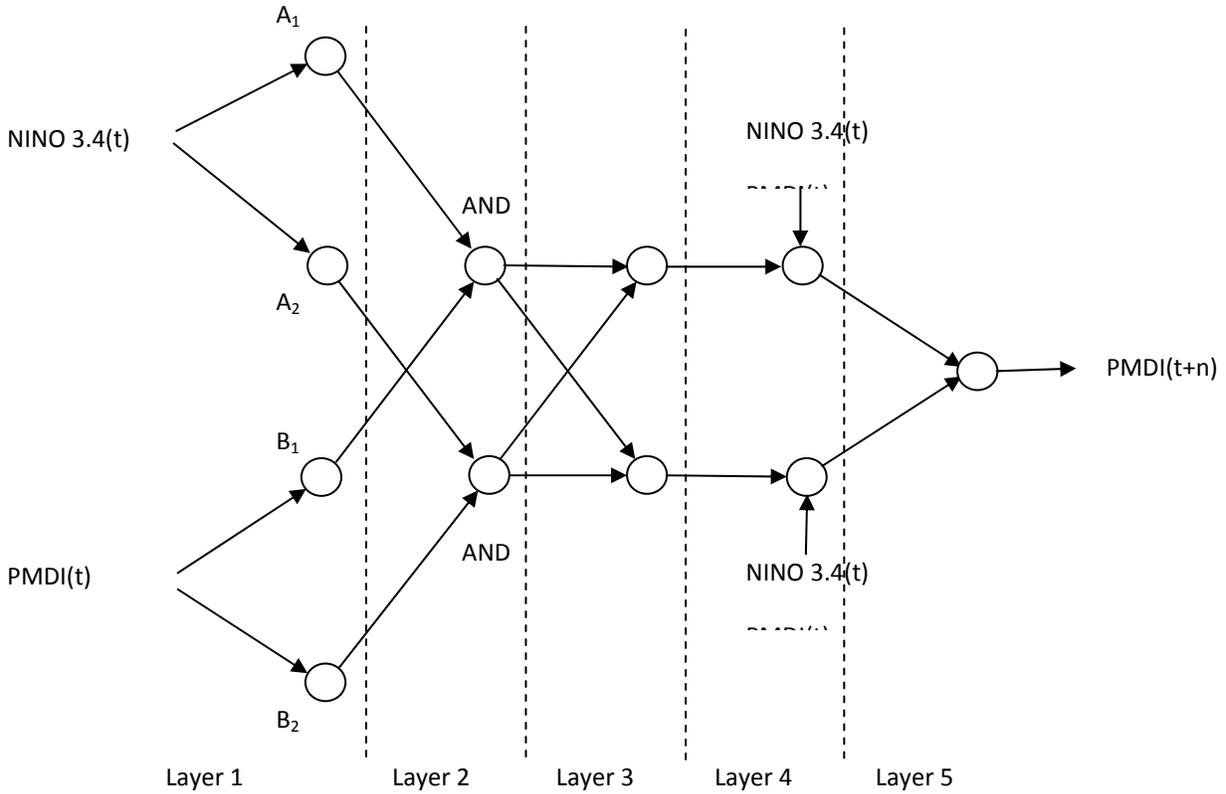


Figure 8. A schematic of the forecasting method using fuzzy logic method

For application of the FL model, one can refer to *Takagi and Sugeno*, [1985] and *Jang* [1993]. Assume that two inputs, NINO 3.4(t) and PMDI(t) and one output, PMDI (t+n) form the following two rules for a first order TS type.

IF NINO3.4(t) is A_1 and PMDI(t) is B_1 THEN $PMDI(t+n) = p_{11} * NINO\ 3.4 + p_{12} * PMDI(t) + p_{10}$
 IF NINO3.4(t) is A_2 and PMDI(t) is B_2 THEN $PMDI(t+n) = p_{21} * NINO\ 3.4 + p_{22} * PMDI(t) + p_{20}$
 where A and B form linguistic labels, such as “low” or “high”, and p_{ij} s are parameters. These fuzzy rules can express the relationship between input and output variables.

A hybrid algorithm, called adaptive neural fuzzy inference system (ANFIS), tunes the consequent parameters (p_{ij}) in a forward propagation mode and premise parameters (a, b, c) in a backward propagation mode [*Jang*, 1993]. In the forward pass the network inputs propagate forward until layer 4, where the consequent parameters are identified by the least-squares method. In the backward pass, the error signals propagate backwards and the premise parameters are updated by gradient descent. Once the premise parameters are fixed, the overall output is a linear combination of the consequent parameters and input variables. MATLAB fuzzy logic toolbox is used for fuzzy logic implementations.

Wavelet and fuzzy logic combination model

The aim of the wavelet and fuzzy logic (WFL) combination model is to forecast t -months ahead Palmer modified drought index (PMDI) from ENSO indicators and persistence. The continuous wavelet transform (CWT) is used to decompose the original series into their characteristic bands. The separation into significant spectral bands is conducted by considering the average wave spectra as mentioned above.

After decomposing the time series into several bands, each band of predictand is estimated from its corresponding predictor bands. The fuzzy logic model was employed to relate the predictand and the predictors. Since the aim of this study is to make predictions for future time, past data are used in the forecasts. As a final step, spectral bands of predictand are reconstructed to produce the single time series of PMDI.

If one desires to make a forecast starting at $t=t_1$ for a future time $t=t_2$, only data measured prior to $t=t_1$ should be used. Therefore each future value can be forecasted by the fuzzy logic model independently. For instance, PMDI data are available from 1951 to current date on a monthly basis. A 3-month ahead forecast of PMDI from October 2009 should use data from January 1951 until October 2009.

Application of the WFL model consists of three steps: (1) Decomposition of ENSO indicators and PMDI into their spectral bands by using average wavelet spectra, (2) using the fuzzy logic approach to achieve the forecasting of PMDI spectral bands from the spectral bands of ENSO indicators and previous PMDI. (3) Reconstructing the predicted spectral bands of predictand to obtain forecasts.

Results and Discussion

Forecasting using fuzzy logic model

In this study, 3, 6, and 12 month lead times were considered for drought forecasting. For each of the three lead times, the TS FL model was used with and without considering wavelet spectral bands. First, the original time series was used for forecasting. For this purpose data (1951-2006) was split into two parts, namely training (calibration) and testing. The last 20 years of entire data set (56 years, 672 month), was employed for testing and the remaining part was used for training. Trial and error is used to select the predictors used in each model. Since it is well known from relevant literature that persistence plays an important role in forecasting droughts, the previous drought measurements are used as predictand. The effect of ENSO indices on the forecasting performance is also explored. Using ENSO indices alone without considering persistence produces poor results. Different scenarios were tried, as shown in Tables 1 and 2.

The number of current and previous input variables that corresponded to the number of lagged observations of NINO3.4, SOI and PMDI were used to determine the underlying pattern in a time series and forecast future values. Using input information, the TS FL model had an ability to detect the feature, capture the pattern in the data, and perform nonlinear mapping between input and output variables. For 3-month ahead forecasting, the model with input variables

NINO3.4(t), PMDI(t), yielded the best training and testing results (Table 1). Increasing the number of lags did not improve the model performance any more. Also replacing the NINO 3.4 index with SOI variable did not improve the FL model results either.

Table 1. Results of scenarios employed for FL and ANN models

Model No.	Scenarios	FL				ANN			
		train		test		train		test	
		R ²	CC	R ²	CC	R ²	CC	R ²	CC
	3-month lead time								
1	NINO(t), PMDI(t)	0.768	0.817	0.638	0.698	0.76	0.810	0.657	0.703
2	NINO(t), PMDI(t), PMDI(t-1)	0.666	0.815	0.501	0.720	0.67	0.820	0.474	0.698
3	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.679	0.823	0.460	0.687	0.667	0.816	0.494	0.712
4	PMDI(t), PMDI(t-1), PMDI(t-2)	0.667	0.816	0.491	0.705	0.672	0.820	0.411	0.662
5	SOI(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.661	0.812	0.475	0.693	0.672	0.819	0.461	0.694
6	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2), PMDI(t-3)	0.705	0.839	0.481	0.713	0.683	0.826	0.481	0.707
	6-month lead time								
7	NINO(t), PMDI(t)	0.497	0.662	0.213	0.437	0.476	0.647	0.213	0.416
8	NINO(t), PMDI(t), PMDI(t-1)	0.505	0.710	0.030	0.404	0.436	0.660	0.051	0.401
9	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.434	0.658	0.106	0.422	0.476	0.689	0.097	0.422
10	PMDI(t), PMDI(t-1), PMDI(t-2)	0.482	0.694	0.040	0.334	0.410	0.647	-0.042	0.258
11	SOI(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.411	0.640	0.096	0.404	0.479	0.691	0.004	0.329
12	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2), PMDI(t-3)	0.502	0.708	-0.031	0.407	0.414	0.642	0.133	0.421
	12-month lead time								
13	NINO(t), PMDI(t)	0.294	0.541	-0.187	0.010	0.261	0.509	-0.173	-0.113
14	NINO(t), PMDI(t), PMDI(t-1)	0.126	0.352	-0.157	-0.092	0.201	0.446	-0.265	-0.182
16	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.370	0.607	-0.209	-0.054	0.183	0.425	-0.104	-0.097
15	PMDI(t), PMDI(t-1), PMDI(t-2)	0.198	0.443	-0.189	-0.087	0.272	0.520	-0.286	-0.050
17	SOI(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.305	0.551	-0.100	0.069	0.302	0.548	-0.126	-0.075
18	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2), PMDI(t-3)	0.348	0.589	-0.194	0.063	0.189	0.433	-0.118	-0.109

Table 2. Results of scenarios employed for WFL and WANN models

Mode I No.	Scenarios	WFL				WANN			
		train		test		train		test	
		R ²	CC						
	3-month lead time								
1	NINO(t), PMDI(t)	0.613	0.794	0.555	0.761	0.764	0.874	0.555	0.758
2	NINO(t), PMDI(t), PMDI(t-1)	0.919	0.959	0.911	0.955	0.921	0.960	0.867	0.934
3	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.920	0.959	0.906	0.952	0.920	0.961	0.818	0.908
4	PMDI(t), PMDI(t-1), PMDI(t-2)	0.919	0.959	0.906	0.952	0.920	0.961	0.885	0.942
5	SOI(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.919	0.959	0.905	0.951	0.921	0.961	0.862	0.929
6	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2), PMDI(t-3)	0.845	0.921	0.814	0.905	0.840	0.919	0.785	0.888
	6-month lead time								
7	NINO(t), PMDI(t)	0.609	0.773	0.426	0.613	0.683	0.814	0.445	0.614
8	NINO(t), PMDI(t), PMDI(t-1)	0.910	0.954	0.873	0.936	0.908	0.953	0.786	0.888
9	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.929	0.964	0.896	0.947	0.928	0.964	0.871	0.933
10	PMDI(t), PMDI(t-1), PMDI(t-2)	0.928	0.963	0.903	0.951	0.936	0.968	0.773	0.883
11	SOI(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.930	0.964	0.880	0.939	0.929	0.964	0.830	0.915
12	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2), PMDI(t-3)	0.851	0.924	0.793	0.893	0.852	0.924	0.757	0.874
	12-month lead time								
13	NINO(t), PMDI(t)	0.610	0.783	0.399	0.649	0.487	0.697	0.364	0.603
14	NINO(t), PMDI(t), PMDI(t-1)	0.843	0.920	0.778	0.884	0.858	0.927	0.695	0.862
16	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.854	0.924	0.727	0.852	0.865	0.931	0.727	0.852
15	PMDI(t), PMDI(t-1), PMDI(t-2)	0.844	0.919	0.756	0.870	0.853	0.923	0.700	0.851
17	SOI(t), PMDI(t), PMDI(t-1), PMDI(t-2)	0.852	0.923	0.717	0.848	0.856	0.926	0.716	0.852
18	NINO(t), PMDI(t), PMDI(t-1), PMDI(t-2), PMDI(t-3)	0.856	0.925	0.734	0.862	0.855	0.924	0.764	0.876

Wavelet fuzzy logic (WFL) model

In the present study, input variables for the FL model corresponded to the subseries of SOI, NINO3.4 and the previous observations of PMDI. Up to 4 previous values that were tested for all PMDI series lay within this range. It was seen that the forecast accuracy decreased beyond the three previous values. In order to improve the model results, the wavelet bands of input and output variable were taken into account. The improvement was clearly seen when the results were compared with the case where wavelet bands were not used (Table 1 and 2).

The forecast performance of the WFL model for each scenario is presented in Table 2. From the results it was observed that the WFL model provided an improvement for long lead drought forecasting over the FL model. As seen from the table, Model 2 had the highest R^2 value among the WFL models for 3-month lead time when the testing period is considered. The R^2 value of 0.501 obtained by the FL model was increased to 0.911 with the aid of wavelet transform. The increment of the model results can be explained with the elimination of some noisy data. Since the ENSO-related drought occurrences develop in low frequencies, the removal of noisy and high frequency data captures the characteristics of PMDI variable more consistently.

It is also noted that SOI did not have a significant effect on the model performance compared to the NINO 3.4 index. The model with SOI yielded less accurate results; the accuracy increased when SOI was replaced by the NINO 3.4 index as can be seen in Table 2. When NINO 3.4 was removed from the forecast model, the accuracy did not decrease significantly. Among several scenarios, it is also worth noting that persistence provided a valuable tool for PMDI forecasting.

Most of the time, various models for 12-month lead time forecasting have difficulties to reach the desired accuracy. However, this problem was addressed in this study by employing the WFL model. The R^2 values with negative numbers produced by FL were improved up to 0.78 by WFL for test results. This remarkable improvement can have a significant impact on long range forecasting. Model 14 gave higher R^2 values. NINO 3.4 along with two past values of PMDI yielded better results compared to others. Related results can be seen from Figure 9. It is also worth mentioning that lagged values of PMDI provided the most of the model skill.

Comparison with ANN and Wavelet ANN models

The proposed combination model was compared with the results obtained from artificial neural network (ANN) and wavelet ANN (WANN) models. The same input configurations were used for comparison. The best ANN models, for all configurations, have a relatively simple architecture. Three layer networks and maximum of five neurons for a hidden layer are sufficient to produce results for all lead times. It is particularly important to ensure that accurate long-term forecasts with lead times of 3 to 12 months are obtained for drought preparedness. The ANN models developed in this paper resulted in the NSS values for 6-month lead time ranging from 0.414 to 0.478 for training data and -0.042 to 0.213 for testing data, indicating poor forecasting accuracy.

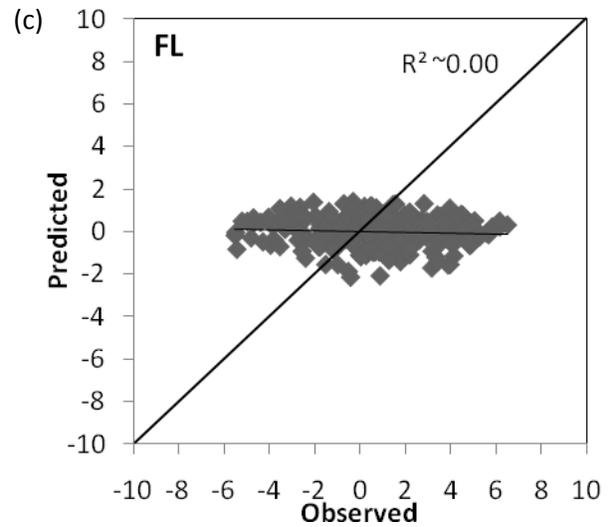
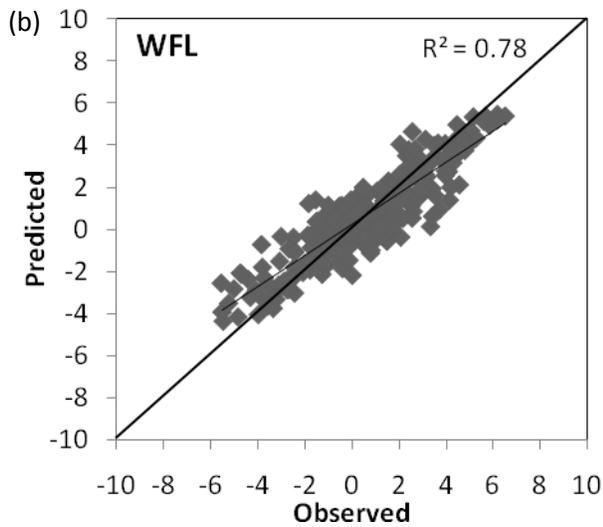
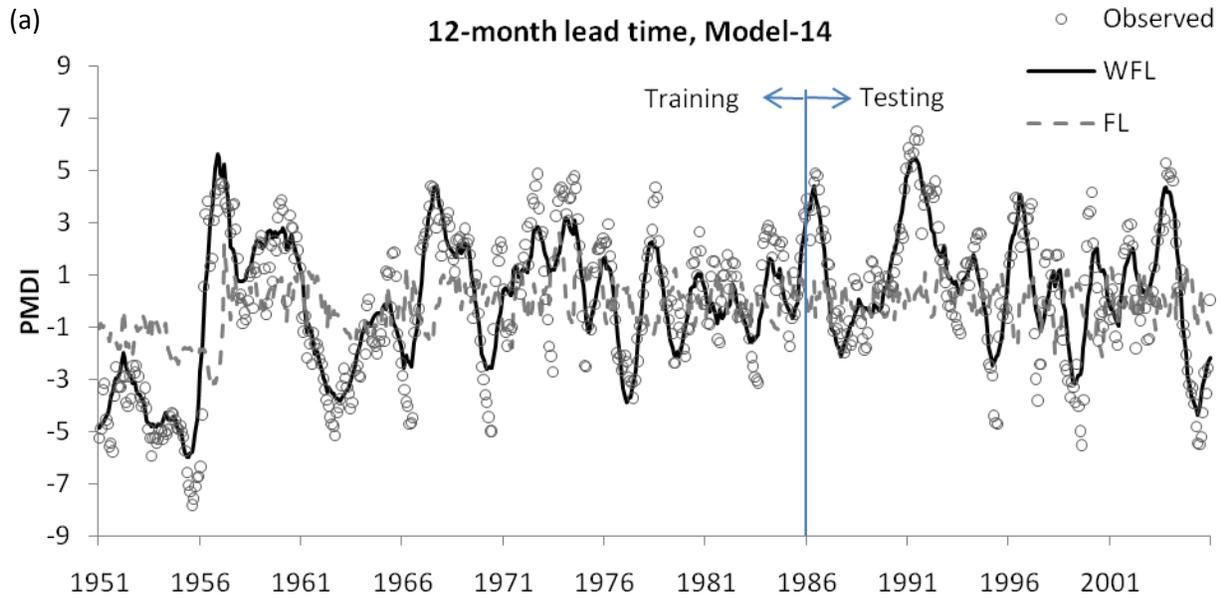


Figure 7. For 12-month lead time forecasting Model-14 is selected for comparison. (a) Time series comparison of observed series with FL and WFL, scatter of observed and predicted points around perfect model line for (b) WFL and (c) FL models.

The use of WANN allowed for generating forecasts of PMDI. For a 6-month lead time, the WANN model NSS scores ranged from 0.682 to 0.936 for training data and 0.445 to 0.870 for testing data which indicates a reasonable improvement over the ANN results. The overall results for all approaches used in this study are presented in Tables 1 and 2. The ANN model results are close to the FL model. The FL model slightly outperformed ANN in most of the cases. Also, the advantage of wavelet decomposition is seen even when the ANN and WANN results are compared with each other. For instance, for a 6-month lead time forecast by Model 9, ANN and WANN yielded the NSS values of 0.097 and 0.871 for testing data, respectively. Although the

WANN produces close results to the WFL model, there is a remarkable difference that can be seen when testing data scores is considered. The differences between them is apparent when more lead time was taken into account.

Conclusions

The wavelet fuzzy logic model is developed and applied for long lead time drought forecasting. While PMDI is chosen as a predictand, ENSO indicators, such as SOI and NINO 3.4 and previous PMDI values are used as predictors. Wavelet is used to analyze the variation of spectral power. Here continuous wavelet transform is employed to obtain the average wavelet spectra. The significant spectral bands are detected from the average wavelet spectra for predictors and predictand. 6 bands that contain significant power are determined. The Takagi-Sugeno fuzzy inference system is employed to relate predictor bands to predictand bands. 6 different scenarios are taken into consideration. For each scenario a specific fuzzy model is constructed to obtain the results.

WFL provides a remarkable improvement in the model accuracy over FL. Comparison between WFL and FL model results for three different lead times (3, 6, 12 months) shows the superiority of the WFL. It is possible to make more accurate forecasts for 12-month lead time in the level of $R^2=0.778$ with WFL. Application of wavelet fuzzy model shows that the lagged values of PMDI are important predictors for drought forecasting. NINO 3.4 index contributes to the model accuracy more than SOI does. The 12-month ahead forecasting with acceptable accuracy can be used as a tool for drought management. It is clear that the WFL model is very good agreement with observed data. Its ability to forecast extreme highs and lows especially for long lead times can be considered as its limitation. Also the proposed model results were compared with ANN and WANN. It is seen that WFL forecasts are superior to the ones yielded by FL, ANN and WANN models.

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The Role of Epikarst in Controlling Recharge, Water Quality and Biodiversity in Karst Aquifers: A Comparative Study between Virginia and Texas

Basic Information

Title:	The Role of Epikarst in Controlling Recharge, Water Quality and Biodiversity in Karst Aquifers: A Comparative Study between Virginia and Texas
Project Number:	2009TX335G
Start Date:	8/1/2009
End Date:	7/31/2011
Funding Source:	104G
Congressional District:	Texas District 25
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Water Quantity, Hydrogeochemistry
Descriptors:	None
Principal Investigators:	Benjamin F Schwartz

Publications

There are no publications.

Title: The Role of Epikarst in Controlling Recharge, Water Quality and Biodiversity in Karst Aquifers: A Comparative Study between Virginia and Texas

Project Number: 2009TX335G

Start Date: 8/1/2009

End Date: 7-31-2011

Funding Source: 104g

Congressional District: 25

Focus Category: Groundwater, Water Quantity, Hydrogeochemistry

Descriptors: Epikarst, Karst, Recharge, Water Quality, Biodiversity

Principle Investigator: Benjamin F. Schwartz, Texas State University

Co-PIs: Madeline E. Schreiber, Virginia Polytechnic Institute and State University; and Daniel H. Doctor, U.S. Geological Survey.

Annual report for March 2009 – May 2010

Progress Summary:

Progress at the Texas site has been very good. Weather data collection and precipitation sampling have been ongoing at the surface above three in-cave sites in TX, and geochemical parameters have been measured in the caves at a variety of sites, including numerous drip sites with variable precipitation response times, an in-cave stream, and a nearby well. Due to the extreme drought of 2008-2009, few water samples were collected until October 2009. Now that the drought has ended, samples are being collected on a more frequent basis and are providing valuable information.

At the Virginia site, progress has also been very good. This funding allowed us to continue monitoring and sampling activities for a third year at the James Cave site where a stream, three drip sites, and precipitation is being monitored and sampled. Additionally, lysimeters were installed in soils above the in-cave sites and water samples are routinely being collected from them. A graduate student is nearly finished with his thesis and will soon be defending and publishing his work.

Work Summary:

Over the past 9 months, numerous visits have been made to install and maintain the equipment on the surface and underground. In Texas, since the end of the drought, weekly visits are being made to maintain equipment, download data and collect samples. In Virginia, trips to the surface site and into the cave are limited to once or twice each month due to logistics.

Detailed Summary of Preliminary Results:

Texas

In Headquarters Cave, McCarty Cave, and Cave Without A Name, drip rates slowed or nearly stopped during 2009, but have recovered since the rains in the fall season of 2009.

Geochemical and drip data are currently too sparse to reach many conclusions about how the epikarst controls recharge quantity and quality. One tentative conclusion supported by some of our drip data (as well as previous studies) is that flow and storage in the epikarst at our TX sites is influenced by storage in the porous bedrock matrix. This storage component supports flow at drip sites for long periods of time and attenuates signals from precipitation events. In contrast, matrix storage appears to be much less important at the Virginia site and precipitation signals at drip sites are dominated by seasonality of ET.

Virginia

With this funding, we have extended our collection of long term records of hydrologic and geochemical data to examine the role of epikarst in controlling the quantity and geochemical evolution of recharge water as it passes through the epikarst.

Data collected from September 2007 to present are being used to identify trends in the temporal and spatial distribution of recharge to underlying aquifer. Results show that water-rock interactions and anthropogenic inputs (e.g., manure, fertilizer, and road salt) have impact on the water quality of recharge. Geochemical signatures of different water types (precipitation, soil water, epikarst drips, cave stream) are used to estimate the degree of evolution and residence time of recharge in epikarst. As is typical with karst systems, heterogeneity exists in the epikarst; however all sites share similar hydrologic and geochemical responses to recharge events. Drip rate patterns indicate that recharge primarily occurs during late winter/spring, and is almost negligible during the summer due to evapotranspiration. Analysis of water stable isotopes is being used to estimate retention time of water in epikarst.

By assessing the timing and quality of recharge, both during base flow conditions and in response to multiple recharge events of varying magnitudes, it is possible to use the results from James Cave as an analog for watershed managers to better characterize the role of epikarst in controlling recharge and water quality in similar karst aquifers.

Student involvement:

Three graduate students and three undergraduate students are involved with various aspects of the TX portion of this research, including thesis work for all three graduate students.

In Virginia, one graduate student is involved with the work and is completing his thesis this year.

Publications:

To date, one abstract has been published during this project. Several additional publications are expected to result from this work – in the form of journal articles, theses, and abstracts.

EPIKARST ROLE IN CONTROLLING THE QUALITY OF KARST AQUIFER RECHARGE

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Abstract

Epikarst, or the region of vegetation, soil, and weathered bedrock lying between the land surface and soluble bedrock, offers water retention capacity that does not exist in deeper, more mature sections of karst aquifers. Thus, the epikarst can act as a temporary reservoir for surface-applied contaminants and naturally-occurring chemical species. Long-term multi-parameter records of precipitation, soil water, epikarst drip water, and in-cave stream-water at James Cave in Dublin, VA, allow us to examine the role of epikarst in controlling the quality and geochemical evolution of recharge water as it passes through the epikarst.

Data collected since September 2007 are being used to identify trends in the temporal and spatial distribution of recharge to the karst aquifer. Drip rates indicate that recharge occurs during late winter/spring, but is minimized by evapotranspiration in summer. Precipitation over James Cave passes through the epikarst where its composition is modified by water-rock interactions. Chemical species such as Na, K, Cl, NO₃, SO₄, and DOC can serve as tracers to assess the timing and mechanisms of recharge. Geochemical differences between sites indicate that hydrologic and geochemical processes in the epikarst are spatially heterogeneous.

However, temporal variations in major ion concentrations can be correlated between sites as a function of recharge.

Specific conductance, pH, alkalinity, and major ion concentrations in epikarst drip water increase during low flow due to increased water-rock interaction. During high flow, however, younger recharge pushes older geochemically saturated water through the epikarst. High flow also inhibits the potential for natural attenuation of contaminants. The structural orientation of the epikarst, the presence of microbial activity, climate, and amount and timing of recharge are all factors in determining the extent to which epikarst controls the quality of recharge to the karst aquifer.

2009 Portland GSA Annual Meeting (18-21 October 2009)

Information Transfer Program Introduction

None.

Information Transfer

Basic Information

Title:	Information Transfer
Project Number:	2009TX332B
Start Date:	3/1/2009
End Date:	2/28/2010
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Congressional District:	17
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Focus Category:	None, None, None
Descriptors:	
Principal Investigators:	Rosemary Payton, Bill L. Harris, Leslie Jordan, Danielle Supercinski, Jaclyn Tech, Kathy Wythe

Publications

There are no publications.

**Texas Water Resources Institute
Information Transfer Activities
March 1, 2009 – February 28, 2010**

In 2009, the Texas Water Resources Institute continued its outstanding communication efforts to produce university-based water resources research and education outreach programs in Texas.

The Institute publishes a monthly e-mail newsletter, a quarterly newsletter specific for one project, a biennial newsletter for another project, and an institute magazine published three times a year.

New Waves, the e-mail newsletter, publishes timely information about water resources news, results of projects and programs, and new water-related research projects, publications and faculty at Texas universities. The newsletter has a subscription of 1,232.

RGBI Outcomes is an 8-page newsletter specifically spotlighting research and education programs of the Rio Grande Basin Initiative, a federally funded project focused on increasing available water through efficient irrigation and water conservation. RGBI Outcomes has a subscription of more than 810.

The Arroyo Colorado Watershed Partnership Newsletter is published twice a year and includes news about several projects and activities in the Arroyo Colorado watershed. The newsletter has a subscription of around 700.

txH₂O, a 30-page glossy magazine, is published three times a year and contains in-depth articles that spotlight major water resources issues in Texas, ranging from agricultural nonpoint source pollution to landscaping for water conservation. Over 2,345 individuals and entities received the magazine via subscription and approximately 1,000 more magazines are distributed.

Working to reach the general public and expand its audience, the Institute generates news releases and cooperates with Texas A&M University Agricultural Communications for them to produce news releases about projects as well. The Institute prepared numerous informational packets for Congressional contacts and other meetings. TWRI projects or participating researcher efforts had at least 64 mentions in the media.

For each of the institute's projects, TWRI published a one-page fact sheet that explains the purpose, background, objectives, and, if applicable, accomplishments of the program.

In addition to the one-page fact sheets for its projects, the institute developed 3 other publications/brochures, such as an accomplishment report for a major project and fact sheets explaining specific aspects of a project.

In cooperation with research scientists and Extension education professionals, the institute published 19 technical reports and 1 educational materials publication, which provide in-depth details of water resource issues from various locations within the state.

TWRI continues to enhance its Web presence by posting new project-specific Web sites and continually updating the information contained within the Web sites. The institute currently maintains 27 websites.

TWRI Technical Publications:

Harris, B.L. 2010, Irrigation Training Program Final Report (TR-361), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 121 pages.

Jones, C. A., 2009, Texas A&M University – Lake Granbury and Bosque River Assessment Final Scientific/Technical Report (TR-350), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 291 pages.

Karimov, Askar, Eric Leigh, and Guy Fipps, 2009, Evaluation of Canal Lining Projects in the Lower Rio Grande Valley of Texas (TR-352), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 33 pages.

Michelsen, Ari, Marissa Chavez, Ron Lacewell, James Gilley, and Zhuping Sheng, 2009, Evaluation of Irrigation Efficiency Strategies for Far West Texas: Feasibility, Water Savings and Cost Considerations (TR-360), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 70 pages.

Miyamoto, S., F. Yuan, and Shilpa Anand, 2010, A Simple Model for Estimating Water Balance and Salinity of Reservoirs and Outflow (TR-363), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 26 pages.

Mukhar, S. and L. Gregory, 2009, Demonstration and transfer of selected new technologies for animal waste pollution control (TR-349), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 22 pages.

Olivas, Dr. Alfredo Granados, 2009, The Development of a Coordinated Database for Water Resources and Flow Model in the Paso Del Norte Watershed (Phase III) Part III GIS Coverage for the Valle de Juárez Irrigation District 009 (ID-009) (Distrito de Riego 009) Chihuahua, México (TR-359 Part III), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 32 pages.

Piccinni, Giovanni., Daniel Leskovar, Wyatte Harman, Thomas Marek, and B.L. Harris, 2009, Precision Irrigators Network: On-Farm Research Demonstration to Evaluate Irrigation Scheduling Tools in the Wintergarden and Texas High Plains (TR-351), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 208 pages.

Rister, M. Edward, Callie S. Rogers, Ronald D. Lacewell, John R. C. Robinson, John R. Ellis, and Allen W. Sturdivant, 2009, Economic and Financial Methodology for South Texas Irrigation Projects –RGIDECON© (TR-203 Revised), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 40 pages.

Rogers, Callie S. Allen W. Sturdivant, M. Edward Rister, Ronald D. Lacewell, and Javier G. Santiago, 2010, Economic and Financial Life-Cycle Costs of Conventional Surface-Water

Treatment in South Texas: A Case Study of the McAllen Northwest Facility (TR-311), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 71 pages.

Seawright, Emily K., M. Edward Rister, Ronald D. Lacewell, Dean A. McCorkle, Allen W. Sturdivant, John A. Goolsby, Chenghai Yang, and B.L. Harris, 2009, Economic Implications of Biological Control of *Arundo donax* in the Texas Rio Grande Basin (TR-358), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 50 pages.

Sturdivant, Allen, M. Edward Rister, Callie S. Rogers, Ronald D. Lacewell, Joseph W. "Bill" Norris, Jesus Leal, Jose Garza, and Judy Adams, 2009, An Analysis of the Economic and Financial Life-Cycle Costs of Reverse-Osmosis Desalination in South Texas: A Case Study of the Southmost Facility (TR-295), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 66 pages.

Swanson, Charles and Guy Fipps, 2009, Evaluation of Smart Irrigation Controllers: Initial Bench Testing Results (TR-354) Texas Water Resources Institute, Texas A&M System, College Station, Texas, 30 pages.

Texas Water Resources Institute, 2009, Education of Best Management Practices in the Arroyo Colorado Watershed, (TR-355), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 47 pages.

Thompson, W. 2009, Economic impacts of salinity control measures for the upper Pecos River Basin of Texas (TR-348), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 42 pages.

Tillery, Sue, Zhuping Sheng, Phillip King, Bobby Creel, Christopher Brown, Ari Michelsen, Raghavan Srinivasan, Alfredo Granados, 2009, The Development of a Coordinated Database for Water Resources and Flow Model in the Paso Del Norte Watershed (Phase III); Part I Lower Rio Grande Flood Control Model [LRGFCM] RiverWare Model Development (TR-359 Part I), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 49 pages.

Tillery, Sue, Zhuping Sheng, Phillip King, Bobby Creel, Christopher Brown, Ari Michelsen, Raghavan Srinivasan, Alfredo Granados, 2009, The Development of a Coordinated Database for Water Resources and Flow Model in the Paso Del Norte Watershed (Phase III) Part II Availability of Flow and Water Quality Data for the Rio Grande Project Area (TR-349, Part II), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 25 pages.

Twigg, Kristina, Courtney Swyden, and Raghavan Srinivasan, Editors, 2009, International SWAT Conference; Conference Proceedings (TR-356), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 432 pages.

Wurbs, Ralph and Chihun Lee, 2009, Salinity Budget and WRAP Salinity Simulation Studies of the Brazos River/Reservoir System (TR-352), Texas Water Resources Institute, Texas A&M System, College Station, Texas, 327 pages.

TWRI Educational Materials:

Leigh, Eric, Martin Barroso, Guy Fipps, 2009, Expansion of Urban Area in Irrigation Districts of the Rio Grande River Basin, 1996 - 2006: A Map Series (EM-105), Texas Water Resources Institute, Texas A&M University System, College Station, Texas.

AgriLife Extension Service Publications:

The following new publications are available from the Texas AgriLife Extension Service bookstore at <http://tcebookstore.org/>

Web sites:

TWRI web sites

Arroyo Colorado Project	http://arroyocolorado.org/
Bacteria Fate and Transport	http://bft.tamu.edu/
The Bosque River Project (Environmental Infrastructures)	http://bosque-river.tamu.edu/
Buck Creek Water Quality Project	http://twri.tamu.edu/buckcreek/
Caddo Lake Institute Data Sever	http://caddolakedata.us/
Consortium for Irrigation Research & Education	http://cire.tamu.edu/
Copano Bay Water Quality Education	http://copanobay-wq.tamu.edu/
Dairy Compost Utilization	http://compost.tamu.edu/
Efficient Nitrogen Fertilization	http://n-fertilization.tamu.edu/
Fort Hood Range Revegetation Project	http://forthoodreveg.tamu.edu/
Improving Water Quality of Grazing Lands	http://grazinglands-wq.tamu.edu/
Lake Granbury Water Quality	http://lakegranbury.tamu.edu/
Little Brazos River Bacteria Assessment	http://lbr.tamu.edu/
North Central Texas Water Quality	http://nctx-water.tamu.edu/
Pecos River Basin Assessment Program	http://pecosbasin.tamu.edu/
Proper Organic Management	http://twri.tamu.edu/ipofm/
Rio Grande Basin Initiative	http://riogrande.tamu.edu/
Rio Grande Basin Initiative Conference	http://riogrande-conference.tamu.edu/
Texas Water Resources Institute	http://twri.tamu.edu/
Trinity River Basin Environmental Restoration	http://trinitybasin.tamu.edu
USGS Graduate Research Program	http://twri.tamu.edu/usgs.php
Watershed Planning Short Course	http://watershedplanning.tamu.edu/

Other websites

C-Map (Catastrophe Mgmt & Assessment Prgm)	http://c-map.tamu.edu/
Save Texas Water	http://savetexaswater.tamu.edu/
Texas Congressional District GIS	http://congdistdata.tamu.edu/
Texas Spatial Information System	http://tsis.tamu.edu/
Texas Water Centers	http://txwatercenters.tamu.edu/

USGS Summer Intern Program

None.

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	0	0	0	0	0
Masters	5	0	0	0	5
Ph.D.	5	0	0	0	5
Post-Doc.	0	0	0	0	0
Total	10	0	0	0	10

Notable Awards and Achievements

Thomas Abia: In addition to the Texas Water Resources Institute (TWRI) Grant, a Research and Presentation Grant (RPG) from the Texas A&M Office of Graduate Studies (OGS) has been awarded in the amount of \$400 for additional equipment and supplies. The timeline to use this grant ends on May 31, 2010. No additional awards or achievements have been reported. The project is currently awaiting decisions on funding applications submitted to the American Water Works Association (AWWA) and National Water Research Institute (NWRI) for \$5,000 and \$15,000, respectively. The announcements are expected to be made between June and September 2010.

Deborah Carr: First Place Award Student Poster Presentation at SC-SETAC Annual Spring Meeting, 2009
Travel Award to National SETAC meeting November, 2009.

Dex Dean: a fellowship from Hispanic Leaders in Agriculture and the Environment (Texas A&M) has provided up to \$5,000 to support travel, lodging, and other research needs from Sept. 2008 to Aug. 2010. To date, this research has received no notable awards, although we do have a manuscript in review.

A. Karnjanapiboonwong: American Chemical Society, Environmental Chemistry Graduate Student Award, 2010; American Chemical Society, AGRO Division Education Award, 2010; Texas Tech University, Study Abroad Competitive Scholarship, Spring 2010.

Yujin Wen: Third place, Graduate Student Poster Competition, 2010 Beltwide Cotton Conference, New Orleans, LA, Jan. 2010.