Texas Water Resources Institute Annual Technical Report FY 2004

Introduction

The Mission of the Texas Water Resources Institute is to:

(1) Serve as the designated Water Resources Research Institute for the State of Texas, as part of the National Institutes for Water Resources Research Program and established by the Texas Legislature. (2) Help faculty obtain and manage external funds for research, academic programs, outreach, and education projects. (3) Serve as the focal point for water research and outreach efforts within the Texas A&M University System. (4) Develop mutually supportive relationships with policymakers, elected officials and water resources leaders throughout Texas. (5) Identify emerging water resources issues and communicate them to researchers, stakeholders, and the public. (6) Communicate TWRI projects, research opportunities, research results, resource materials, and water resources news to the public. (7) Administer water related academic programs and administer scholarship programs for students involved in water related studies. (8) Establish relationships with water resources institutes and universities in other states to facilitate collaborative projects and enhance funding opportunities. (9) Work with the Texas A&M University Office of International Programs and develop direct relationships with agencies, individuals and other entities in other countries to foster collaborative projects and programs.

Research Program

RESEARCH PROGRAMS

During 2004-05, the Texas Water Resources Institute funded 10 research projects of graduate students at universities throughout Texas. Students were supported at Texas A&M University (6 projects), the University of Texas at Austin (1), Southern Methodist University (1), Rice University (1) and Texas A&M University Kingsville (1).

These studies covered several broad subjects, including the following: brush control to improve water yields (1 project); the development and application of computer models (3); hydrology (2); groundwater (2); surface water (3); water use (3); water policies (1); economics of water use (1); water treatment (1) and water quality (5). Note that several projects include more than one topic.

Timothy Goebel of Texas A&M Universitys Soil and Crop Sciences Department focus was to develop advanced polymers that can adsorb Atrazine and other pesticides and flocculate clays to facilitate the removal of pollutants from contaminated waters. Adrian Dongell of Southern Methodist University project focused on investigating the extent that four endocrine-disrupting chemicals or EDCs-- two types of estradiol, progesterone, and testosteroneare present in the City of Dallas wastewater treatment system. Vivekanand Honnungar of Texas A&M University-Kingsville worked to develop a practical and easy to use methodology to assess groundwater availability in South Texas groundwater systems near Refugio County. Greg Landreth of the University of Texas at Austin compared various aspects of the performance of four distinct types of water utilities now commonly used throughout Texas to serve small communitiesprivate for-profit systems, non-profit systems, municipal utilities, and special purpose water districts. The project focused on seeking to understand the complex reasons that water supplied by the private sector seems to be much more expensive than drinking water provided by non-profit water supply corporations and other entities. Eva Lovelady of the Chemical Engineering Department at Texas A&M University worked to develop integrated strategies to manage water resources, non-process elements or NPEs (byproducts from industrial processes), pollutants, and other elements associated with industrial operations. Hector Olmos of the Texas A&M Universitys Civil Engineering Department worked to refine and expand the capabilities of the WAM and WRAP models to address conditional reliability modeling (used to estimate the likelihood that projected amounts of water might really be available). Additionally, Olmos worked to increase the capability of WAM and WRAP to manage extremely large data sets (including thousands of control points within watersheds), and developed interfaces between WAM, WRAP and geographic information systems so that modeling results can be spatially displayed on maps. Bakkiyalakshmi Palanisamy of the Spatial Sciences Laboratory at Texas A&M Universities Department of Forest Science investigated how to better predict and display runoff on an hourly basis through the use of advanced weather data and state-of-the-art computer models. Itza Mendoza Sanchez of the Texas A&M University Civil Engineering Department worked to determine the extent to which the velocity of groundwater flows might affect the biological degradation of two toxic compounds--perchlorethene (PCE) and trichloroethene (TCE). Philip Taucer of the Biological and Agricultural Engineering Department at Texas A&M University investigated the extent to which the removal of juniper and other nuisance brush species may increase water yields to rivers, streams, and aquifers. However, little is currently known about the extent to which removing juniper may lead to increased groundwater recharge in the Edwards Aquifer region of South Texas. Erin Williford of Rice University worked to determine if a flood alert system developed by Rice University could be adapted for the Onion Creek watershed, an urbanized watershed prone to sever floods.

Removal of Hormones through a Conventional Wastewater Treatment System

Basic Information

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Principal Investigators:	Adrian Dongell, John Easton

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Steroid Hormone Levels and Biological Removal Strategies.

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ABSTRACT

Endocrine disrupting compounds (EDCs) are chemicals that interfere with normal hormone function, often at extremely small doses. This disruption can be through synthetic chemicals that act or block normal hormonal activity or through the exposure to high doses of naturally produced body hormones, such as those in this study. These compounds are important because of increasing evidence that excess doses affect the endocrine system in humans and wildlife. Any effect on this system could cause reproductive and/or health effects. A potential sources of EDCs in the aquatic environment is wastewater treatment plant (WWTP) discharges. The discharges from WWTPs that contain EDCs can have an effect on the receiving wildlife, such as vitellogenin production in male or juvenile fish

The steroid hormones included in this study are 17β-estradiol (E2), Progesterone (P), and Testosterone (T). This study examined the biological treatability of these compounds, using conventional suspended growth methodologies. In this study, the operating parameter of food-to-microbe ratio (F/M) was varied, ranging from 0.05-0.5 in four bench-scale biological reactors, with a constant biosolids concentration. This achieved varying solids residence times (SRT)—range 3 to 25 days—to test the degradation of hormones. Typical SRTs are 3-15 days, for conventional processes, to 20-40 days, for extended aeration. Twelve samples, taken at 12 hour intervals from each reactor, were used to assess the impact of varying F/M on removal. The mean influent hormone levels were 20.24 ng/L E2, 50.94 ng/L P, and 32.22 ng/L T. Hormone removals ranged from 60-93% with removal increasing with decreasing F/M. The removal of the steroid hormones using conventional biological treatment may not be adequate to meet future regulations.

INTRODUCTION

Endocrine disrupting compounds (EDCs)—chemicals that interfere with normal hormone activity—are emerging environmental concerns. Endocrine disruption can be through synthetic chemicals that act or block normal hormonal activity or through the exposure to high doses of naturally produced body hormones. These compounds may cause adverse reproductive and health effects in humans and wildlife.

The endocrine system controls metabolism, reproduction, behavior, growth, and development by secreting hormones which travel via the bloodstream to affect other cells of the body. Hormones circulate in the body at very low concentrations, ranging from as little as 1 picogram per milliliter of blood to a few micrograms per milliliter

of blood (Guyton 1991). The available receptors in target cells also vary; receptors on the cell must be occupied for a response to occur. The level of circulating hormones and amount of receptors available dictate cellular responses to endocrine stimuli. Endocrine disruptors can alter this natural control and lead to detrimental effects.

The steroid hormones included in this study are 17β -estradiol (E2), Progesterone (P), and Testosterone (T). These hormones are primarily produced in the gonads. Females predominately produce estrogen and progesterone, while males predominately produce testosterone. All three hormones are in each sex but at different ratios. Estrogen and testosterone are produced to regulate the reproductive functions, behavior, and development of secondary sexual characteristics. Progesterone is produced in females to prepare the body for pregnancy. E2 in the plasma circulates at 25 to 300 pg/mL in females and 20 to 90 pg/mL in males (Harvey et al. 1988). Also, between 10 to 100 µg of estrogens are excreted by cycling women daily, while pregnant women can excrete up to 30 mg of estrogen a day and 100 mg progesterone per day in late pregnancy (Baronti et al. 2000; Huang and Sedlak 2001). P levels in plasma range 237-2425 ng/dl (luteal) in females and 25-45 ng/dl in males (Harvey et al. 1988). T is produced primarily in the testes and levels in plasma range 15-95 ng/dl in females and 260-1120 ng/dl in males (Harvey et al. 1988).

Some researchers propose links between endocrine disruptors and human health, but the results are not definitive. Exposure to EDCs at key stages of pregnancy may lead to abnormal genitalia in children and lowered IQs (Guo et al. 1995; Mendes 2002). Presumably healthy babies may have lowered infertility as adults due to reproductive tract malformations (Mendes 2002). In females, exposure to endocrine disruptors has been theorized to lead to breast cancer and endometriosis (Mendes 2002). In males, exposure may be associated with prostate cancer, lower sperm count, and testicular cancer (Giwercman et al. 1993; Mendes 2002; Toppari et al. 1996).

In contrast, studies in wildlife are much more persuasive. It has been reported that fish exposed to waters receiving wastewater treatment plant (WWTP) effluents have induced vitellogenin (VTG) synthesis. VTG is an egg yolk precursor that is produced in adult females in response to estrogen. Adult males and juveniles do not normally produce VTG due to their low levels of E2; therefore, VTG has been used as a biomarker of fish exposure to estrogenic compounds. Studies have shown VTG induction in male fish downstream of numerous WWTPs (Rodgers-Gray et al. 2000; Solé et al. 2001).

EDCs enter surface waters through a variety of pathways such as WWTP effluents. Human hormone excretions enter WWTPs, are treated, and the remaining hormones are discharged into the receiving water. Studies addressing fate and transport of EDCs through the WWTP, specifically sex hormones, are limited.

Research has been conducted to examine EDC removal in WWTPs. In addition, studies have been conducted to determine the concentrations of endocrine disruptors in the effluents of various WWTPs. These studies have been conducted on both sex hormones and a variety of synthetic compounds. Estrogen removal rates from 50-95%

have been reported in conventional activated sludge plants (Baronti et al. 2000; Fujii et al. 2002; Williams et al. 2003). Other studies, on conventional process plants, have provided average discharge levels of estrogens as 0.2-4.1 ng/L. Application of the advanced reverse osmosis process at one plant produced discharges of less than 0.4 ng/L (Huang and Sedlak 2001).

Research on the fate of hormones through the activated sludge process has speculated that removal occurs from sorption onto the biofloc particles and degradation by microorganisms (Birkett and Lester 2003; Fujii et al. 2002; Sedlak et al. 2000). Most research indicates sorption onto suspended biofloc in the mixed liquor is the primary removal mechanism. Biological degradation contributes, but to a lesser extent. Biodegradation can be influenced in the activated sludge reactor by Solids Residence Times (SRT). With low SRT, biodegradation is minimal since there is little time for interaction between the target compounds and the microbes—high wasting rates and loss of specific degraders (Jacobsen et al. 1993). In contrast, high SRTs can allow for more influence by biodegradation—little wasting and an accumulation of specific degraders (Birkett and Lester 2003). Overall, perhaps up to 10% of hormones will be biodegraded, while the remainder will be removed by adsorption to sludge (Sedlak et al. 2000; Shäfer and Waite 2002).

Regarding municipal sewage discharges, this study evaluates the potential for optimizing conventional AS treatment for hormone removal by evaluating the performance of bench-scale biological reactors under different operating conditions.

MATERIALS AND METHODS

Assay

Samples were filtered through glass fiber discs and 0.2 μ m pore size cellulose acetate and cellulose nitrate (MCE) filters, then extracted using C18 discs and eluted with methanol. The methanol was dried down under filtered air and the extracts were resuspended in Enzyme Immunoassay (EIA) buffer. The samples are diluted with EIA buffer until within the standard curve. Then 5-50 microliter samples were used to detect hormones via EIA kit and method (Cayman Chemical, Ann Arbor, MI). Figure 1 shows a sketch of the basic method theory.



Figure 1. Cayman Enzyme Immunoassay (EIA) method.

Hormone Sample Collection

Hormone samples were collected in glass beakers every 12 hours at approximately 7:00 am and 7:00 pm from influent and effluent sample points. Approximately 50 mL of influent samples were collected from the influent pump discharge tube before entering into the reactors and approximately 100 mL of effluent samples were collected from the clarifier overflow weir discharge tubes. Samples were filtered through glass fiber discs and filtered with a 0.2 μ m pore size cellulose acetate and cellulose nitrate (MCE) general filter using a Millipore filtration apparatus . Samples possible containing hormones were stored in a refrigerator at 4°C until hormone extraction.

Statistics

Normality tests were conducted on the data sets collected in each reactor for each hormone to test if they fit normal distributions. For each of the three hormones, the effluent data sets passed normality with the exception of P data in reactor 1 T data in reactor 4. Because of small sample sizes, normality can not be determined with full confidence. One way ANOVAs were conducted assuming normality and repeated using one way ANOVAs on ranks , a nonparametric test in case the normality assumption was violated (as it was in two cases). Both techniques were used to

compare the reactors effluent concentrations and to determine if each effluent data set was statistically different from the other. The statistical procedure is outlined in **Error! Reference source not found.** Mean standard deviations and coefficients of variance (COV) were calculated to describe the variation in the data. All statistical analyses were performed using SigmaStat (3.10)(Systat Software Inc., Richmond, CA), SigmaPlot (9.0)(Systat Software Inc., Richmond, CA and Excel (10.0)(Microsoft Corporation, Redmond, WA).

Bench-Scale Biological Treatment Process

Four identical reactors were installed, each with a total volume of approximately 8 L. The AS reactors were constructed from a typical design (Eckenfelder et al. 1969; Qasim 2004) and were custom fabricated by a local Dallas plastics company as shown in Figure 2. The reactors were seeded with mixed liquor from the Dallas Southside WWTP. The organic substrate, containing hormones, was effluent collected from the primary clarifier at the City of Dallas Central WWTP. The reactors were operated at different Food-to-Microbe (F/M) ratios, ranging from 0.05-0.5 with a constant biosolids concentration.



Figure 2. Activated sludge reactor.

The F/M ratios were used to achieve a typical range of solids residence times (SRT) to study the degradation of hormones. Typical SRTs are 3-15 days for conventional completely mixed processes to 20-40 days for extended aeration. The influent pump rates were adjusted to achieve the four different F/M ratios and aeration was used for mixing. The partition wall was adjusted in each reactor to allow for biosolids settling and recirculation back into the aeration chamber to occur. The units were operated

for 10 days to achieve steady-state operation followed by six days of hormone data collection.

Constant influent flowed into each reactor where the biosolids degraded the waste, and then treated effluent discharged from an overflow weir in the clarifier. The supernatant then flowed down a tube to the effluent sampling location. The influent pumps were continuously monitored and adjusted to maintain a constant flow rate. The temperature was also kept at room temperature (constant 23°C) via submersible heating units.

The primary clarifier effluent, from the Central WWTP, was collected every Monday, Tuesday, and Wednesday into two 55-gallon drums and transported back to the research laboratory. The sample was then transferred using a self-priming jet pump with a garden hose to two plastic 55-gallon drums placed in a chromatography refrigerator set at 4°C. The wastewater was rapidly cooled using dry ice placed into large 13-gallon plastic bags suspended from the lids of the drums down into the sample to not allow for the dry ice to come in contact with the sewage, thus minimizing any characteristic changes that could be caused by the dry ice, eg., lowering the pH. The rapid cooling was conducted to minimize the biodegradation of the organic waste by microbes already present in the sample, to maintain a relatively constant and high substrate concentration to pump into the reactors.

The wastewater stored in two 55 gallon drums was constantly re-circulated, at a turnover rate of approximately 10 times an hour, using two Beckett submersible pumps purchased at a local home improvement store. A pump was placed in each 55 gallon drum which pumped the wastewater from each drum into the 5 gallon bucket sitting on top. The 5 gallon bucket had two overflow weirs of 1.5 inch plastic PVC pipe that emptied back into the 55 gallon drums. Each drum was connected by a 5/8 inch rubber tube to a stopcock with a hose barb at the bottom to allow for a steady volume in each. This apparatus is shown in Figure 3



Figure 3. Bench-scale biological treatment process.

Two different pump types were used for the operation of the AS reactors. Air pumps, from a local aquarium supply store, were used with 6 inch air diffuser stones to supply the oxygen for the AS reactors. One pump was used for each reactor to allow for enough oxygen transfer for microbe metabolism as well as for proper mixing. LMI electronic chemical metering pumps (series AA) were purchased from a local distributor to supply the steady flow of influent wastewater from the two 55-gallon drum holding tanks into each reactor. Each reactor had a pump that was set at a different cycle rate to allow for different flow rates entering into the reactors. This allowed for different F/M ratios in each reactor to be maintained.

Total Suspended Solids (TSS), Biochemical Oxidation Demand (BOD), and Chemical Oxidation Demand (COD) tests (**Error! Reference source not found.**-I) were conducted daily in order to make adjustments and maintain steady-state operation. Once the biosolids concentration was determined from the TSS data, appropriate daily wasting at approximately 5:00 pm would be applied in each reactor to maintain a constant level of biosolids.

Kinetic Constants

The microbial kinetics for the treatment of the domestic sewage was determined from steady-state data gathered prior to hormone sampling. This data set has BOD data that is inline with results seen previous based on the COD data. The results during the sampling week were unreliable possibly due to a faulty dissolved oxygen (DO) meter. The BOD/COD ratio is not similar to that seen in previous reactor studies prior to hormone sample collection. Hence, COD data, rather than BOD, was used to adjust operation of the reactors during the period of hormone data collection.

Results

The AS reactors were operated in Fall 2004. Table 1 is a summary of the operations data acquired from each of the four reactors. Prior to hormone sampling, the reactors were operated until steady-state conditions were present. At steady-state, reactors 1 and 2 have operational values seen in extended aeration AS reactors while reactors 3 and 4 have values seen in completely mixed AS (CMAS) reactors. Extended aeration reactors have F/M ratios of .04-.10 and SRTs of 20-40 days. Typical design parameters for CMAS reactors have F/M rations of 0.2-0.6 and SRTs of 3-15 days (Tchobanoglous et al. 2003).

				BOD					
Reactor	F ₀	S_0	S_s	Removal	X_B	W_{T}	F/M	SRT	HRT
1	9	56.4	1.38	97.6%	1200	49	0.05	24.48	22.67
2	18	56.4	1.94	96.6%	1500	69	0.08	21.89	11.18
3	36	56.4	4.80	91.5%	1200	152	0.19	7.91	5.48
4	71	56.4	7.61	86.5%	1200	373	0.35	3.22	2.83

Table 1. Operational results for bench-scale CMAS reactors.

 F_0 = Influent flow rate (L/day), S_0 = Influent substrate concentration (mg/L BOD), S_s = Effluent substrate concentration (mg/L BOD), X_B = Biosolids concentration maintained (mg/L MLSS), W_T = Biosolids wasting (mg/day TSS), F/M = Food-to-microbe ratio, SRT = Solids retention time (days), HRT = Hydraulic retention time (hours).

Table 2 shows a summary of the hormone concentration data acquired in the study. The mean influent levels were 20.24 ng/L E2, 50.98 ng/L P, and 32.22 ng/L T. The removal rates presented in the last column in Table 2 are given for the three hormones in each reactor running at different F/M ratios. The removal rates are based on the mean hormone concentrations (column 3, Table 2). The removal range was 60-93%

across the F/M range of 0.05-.035. Reactors 1 and 2—running at the lower F/M achieved the highest removal rates, up to 93%. For E2 and T, significant increases in removal occurred when the F/M ratio decreased from 0.19 to 0.08. For P, the significant differences were seen between the extreme F/Ms of 0.35 and 0.05. In general, hormone removal increased with decreasing F/M.

Table 2. Reactor mean influent and effluent hormone levels (ng/L).

Reactor III			nuent no			nograms	per mer ($(\Pi g/L)$.
Hormone	Sample	Mean	SD	COV	Min	Max	F/M	REM
	Influent	20.24	5.20	26%	12.29	28.27		
	1	4.09	1.02	25%	2.43	6.47	0.05	79.8%
E2	2	5.10	1.22	24%	3.12	7.38	0.08	74.8%
	3	8.05	2.10	26%	5.37	13.04	0.19	60.2%
	4	7.79	1.96	25%	4.14	11.01	0.35	61.5%
	Influent	50.98	23.45	46%	13.78	75.72		
	1	9.25	4.67	50%	4.32	18.30	0.05	81.9%
Р	2	12.39	5.18	42%	6.03	23.56	0.08	75.7%
	3	13.15	4.75	36%	6.40	22.63	0.19	74.2%
	4	16.83	5.50	33%	9.34	26.77	0.35	67.0%
	Influent	32.22	20.50	64%	6.94	68.22		
	1	2.19	1.19	54%	0.65	4.84	0.05	93.2%
Т	2	2.26	0.84	37%	0.92	3.33	0.08	93.0%
	3	4.75	1.92	40%	2.08	8.16	0.19	85.3%
	4	6.69	3.23	48%	3.48	14.81	0.35	79.2%

Reactor mean influent and effluent hormone levels in nanograms per liter (ng/L).

SD = Standard deviation.

COV = Coefficient of variation.

REM = Percent hormone removal

ANOVA compares whether there is a statistically significant difference (p-value <0.05) in the mean values among different groups. One way ANOVA and ANOVA on ranks were conducted on the effluent concentrations to quantify the differences, if any, among the reactors. These results are presented in Table 3. For E2, there is no significant difference in the effluent concentrations measured in reactors 1 and 2, and also 3 and 4. For T, effluent concentrations in 1 & 2 are not statistically different, whereas 3 & 4 was found to be statistically different using one way ANOVA and not different using ANOVA on ranks. All other groups are statistically different, i.e., 1 & 3, 1 & 4, 2 & 3, and 2 & 4. For P, only reactors 1 and 4 showed statistically significant differences in the mean effluent concentrations.

Comparison	E2	Р	Т
1 vs. 4	0.000^*	0.001*	0.000^{*}
2 vs. 4	0.000^{*}	0.036	0.000^{*}
1 vs. 3	0.000^*	0.065	0.003*
2 vs. 3	0.000^{*}	0.714	0.004^*
3 vs. 4	0.697	0.080	0.023
1 vs. 2	0.139	0.134	0.935

Table 3. ANOVA reactor comparison summary.

*Statistically significant difference when P < critical level

The microbial kinetics for the treatment of the waste was determined on steady-state conditions observed the week before hormone collection data are presented in Table 4. The kinetic constants calculated from the reactors were transformed from 23° C to 20° C using typical theta (θ) values. These values are compared with typical kinetic coefficients for the degradation of domestic sewage (Tchobanoglous and Burton 1991).

Table 4. Kinetic constants summary.

		Experimental		
Coefficient	Notation	Reactors ^a	Typical Range ^a	θ^{b}
Y	mg TSS/mg BOD ₅	1.0	$0.4-0.8^{\circ}$	1
b	d^{-1}	0.011	0.025-0.075	1.04
Ks	mg/L BOD $_5$	29	25-100	1
k	d^{-1}	2	2-10	N/A

Y = True Growth Yield.

b = Endogenous Decay Coefficient.

Ks = Half-Saturation Constant.

k = Maximum Specific Substrate Removal Rate.

^aValues reported for 20^o C.

^bθ Typical Temperature Correction Values.

^cTypical Range is reported in mg VSS/mg BOD_{5.}

The true growth yield (Y) is above the typical range. This could result from the reporting the coefficient Y using TSS data while the typical range is reported using volatile suspended solids (VSS) data. Typical MLVSS/MLSS ratios range from 50-

90%. Therefore, the small inorganic portion could be pushing the value above the typical range. The endogenous decay coefficient (b) is also outside typical range, while the remaining coefficients are within range. The higher value of Y and lower value of b indicates a higher observed yield of biosolids is typically observed.

Conclusions

Conclusions

The hormone levels found in the effluent may be sufficient to cause detectable toxicological effect, e.g., vitellogenin production in male or juvenile fish. Other studies have shown a response to similar hormone levels using long exposure periods (months) in several aquatic species (Cheek et al. 2001; Rodgers-Gray et al. 2000). In addition to the concern regarding ecological risks to aquatic species, there is some concern regarding possible human health risk to downstream users, e.g., drinking water consumers. However, it is likely that the risk to human health is small considering dilution in the river, detention time, and treatment at drinking water plants prior to consumption.

Activated sludge biological treatment operating at the F/M ratios of 0.05-0.35 was used to look at the removal of hormones. The microbial kinetics calculated were approximately within the typical ranges, which indicates the reactors performed characteristically for the degradation of domestic wastewater. Hormone removal rates range from 60%-80% (E2), 67%-82% (P), and 79%-93% (T). In general, removal increased with decreasing F/M. ANOVAs using parametric and nonparametric techniques applied to the treatment study indicate a significant improvement in hormone removal, perhaps up to an additional 15-20% gain, across the range of typical F/M ratios and SRTs. However, operation at the limits for activated sludge processes is unlikely to provide enough additional removal to comply with future regulations designed to protect sensitive aquatic species. If the EPA were to regulate the release of hormones, biological treatment may not be the answer. Municipal WWTP operators would likely have to employ additional advanced treatment prior to discharge.

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Novel Polymeric Water Treatment for In Situ Removal of Organic Contaminants from Water Bodies

Basic Information

Title:	Novel Polymeric Water Treatment for In Situ Removal of Organic Contaminants from Water Bodies			
Project Number:	2004TX149B			
Start Date:	3/1/2004			
End Date:	2/28/2005			
Funding Source:	104B			
Congressional District:	31st			
Research Category:	Water Quality			
Focus Category:	Agriculture, Non Point Pollution, Treatment			
Descriptors:	Water treatment, Organic contaminants			
Principal Investigators:	Timothy Goebel, Kevin McInnes			

Publication

1. No publication.

<u>Novel Polymeric Water Treatment for in Site Removal of Organic</u> <u>Contaminates from Water Bodies.</u>

Objectives:

The contamination of runoff water with pesticides such as atrazine from agricultural fields can be considerable. This contamination exists both as aqueous and sorbed phases. Sorbed phases are associated with colloids suspended in the water. Temporary detention ponds could be used to collect runoff water. The water in these detention ponds could then be treated to reduce the concentration of the contaminants prior to release into streams. Under this grant we proposed to develop a polymer flocculent which would sequester the widely used herbicide atrazine from the solution as well as flocculate and remove suspended colloids. This process could be used to reduce the amount of atrazine present in contaminated water bodies, which would then be allowed to flow into streams and rivers.

The interaction between a cyclic secondary amine and atrazine (Figure 1) has recently been shown to be a reaction involving nucleophilic aromatic substitution (1). This finding, suggested that a polymer flocculent could be modified by the addition of a cyclic secondary amine to the polymer unit which would function to trap



atrazine onto the polymer. Specifically, Poly(allylamine), an off the shelf polymer flocculent, will be modified with Isonipecotic acid (INP) as shown in Figure 2. This new polymer would allow for the irreversible binding of atrazine to the polymer which would then function to flocculate the suspended clay as well as remove atrazine from contaminated water.

One problem which exists with modifying a polymer flocculent is that the more active sites on the polymer which are modified, the less likely it will function well as a flocculent. Alternately, the less modified it is, the less atrazine will be sequestered. To this end, several polymers will be developed based on percent modification per mer of the original polymer. For these experiments the percents which will be developed will be: 100, 70, 50, 30, and 10. From these, the optimum percent modification will be determined.

Once the best polymer is determined, the synthesis will be scaled up to provide enough for biodegradation studies. The biodegradation studies will determine if the polymer-atrazine complex will degrade and if it does what byproducts are produced.

Progress To Date:

To begin the synthesis, a Di-tert-butyl dicarbonate (BOC) protected form of INP was created following the procedure discussed by Alexopoulos (2) and shown in Figure 2. This was made to prevent the coupled acid from reacting with itself. The next step was to modify the polymer with the BOC-INP. This was done by allowing the BOC-INP to react with the coupling agent (EDCI) first and then adding the polymer to the reaction

vessel (Figure 2). The following step was to remove the BOC group using 3 M HCL to hydrolyze the BOC to butanol which was removed by distillation leaving the polymer-INP in solution (Figure 2).

The first polymer to be made was the 100% modified polymer. This was not soluble in water, which is a requirement for success for these experiments since the contamination is in an aqueous environment. The next polymer that was made was the 30% modified polymer. This polymer is water soluble but has not been tested for flocculation or atrazine sequestration.

Future Experiments:

In the next quarter the 10, 50, and 70 percent modified polymers will be made and characterized. For the rest of the year these polymers will be tested for flocculation and atrazine sequestration. The polymer that shows the most atrazine sequestered while still maintaining flocculation ability will then be tested for biodegradation. The biodegradation studies will show both possibly toxic byproducts from the polymer as well as byproducts from atrazine degradation.



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Estimating Water Availability and Sustainable Yield in a Coastal Semi-Arid Region of South Texas

Basic Information

Title:	Estimating Water Availability and Sustainable Yield in a Coastal Semi-Arid Region of South Texas			
Project Number:	2004TX150B			
Start Date:	3/1/2004			
End Date:	2/28/2005			
Funding Source:	104B			
Congressional District:	15th			
Research Category:	Engineering			
Focus Category:	Groundwater, Models, Water Supply			
Descriptors:	Groundwater management, Computer modeling			
Principal Investigators:	Vivekanand Honnungar, Venkatesh Uddameri			

Publication

- 1. A manuscript describing the application of fuzzy regression and single-county mass balance model has been prepared and is being finalized for submission to Environmental Geology by April 1, 2005.
- 2. A Manuscript detailing the application of fuzzy optimization and Watershed Scale model will be prepared for possible submission to a peer-reviewed journal by June 1, 2005.

Estimating Water Availability and Sustainable Yield in Coastal Semi-arid Region of South Texas

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Estimating Water Availability and Sustainable Yield in Coastal Semi-arid Region of South Texas

Introduction

Groundwater is a precious resource that critically affects the growth and development of a region as well as nourishes the aquatic environment (Glennon, 2001) and must therefore be managed effectively. From a sustainability viewpoint, groundwater resources must be available to the future generations as they are now. Therefore, decision makers entrusted with managing groundwater resources must effectively reconcile between the competing objectives of economic development and environmental protection. Approaches to quantify, how much water can be safely extracted without causing damage to the environment are necessary to develop pertinent aquifer management policies. Therefore, there is a need for tools and technologies that enable a holistic assessment of groundwater availability and sustainable yield. From a practical standpoint, these methodologies must be scientifically credible and yet transparent and easily understood by a wide range of audiences. In addition, these approaches should account for imprecision in available data and theories and be easy to implement with available or readily measurable data.

A methodology to assess water availability by accounting for anthropogenic and ecological withdrawals was developed by coupling the fundamental concept of mass balance (water budget) and fuzzy-optimization schemes. The approach is easy to implement and incorporates the decision makers' confidence in the water budget assessment. The utility of the approach in developing groundwater management rules is illustrated and discussed by using the model to assess groundwater availability in Refugio county and Mission river watershed in Texas.

Study area

Refugio County, Texas, is located in the coastal bend of Texas between Corpus Christi and San Antonio cities. Several large-scale water supply projects are being planned in this region. Mission river watershed covers an area of approximately 690



Figure 1. Study Area - Mission river watershed

square miles covering Bee, Goliad, Karnes, and Refugio counties. The underlying Gulfcoast aquifer is characterized by Chicot, Evangeline, Burkeville, Jasper and Catahoula formations. Figure 1 shows the study area.

Methodology

The methodology was developed in a two-stage approach of increasing complexity. As a first-step, a water budget was developed for Refugio County, assuming the Chicot and Evangeline formations to be a homogeneous entity described using effective hydraulic properties. In the second-step, the water budget was carried out for the Mission river watershed, by explicitly modeling Chicot and Evangeline formations of the Gulf coast aquifer. The Burkeville formation was used as the bottom no-flow boundary in both the cases, as it is characterized by low hydraulic conductivity. Groundwater divide along the watershed boundary was used to delineate Chicot formation, while inflows and outflows across the Evangeline were also considered. Cross-formational flow between Chicot and Evangeline aquifer was also incorporated Anthropogenic water demands such as domestic, agricultural and industrial demands cause water levels in the aquifer to drop, while injection of treated wastewater will cause the water levels to rise were incorporated into the modeling methodology as well. Historical water level data and baseflow separation techniques were used to characterize stream-aquifer interactions in both models. The basic mass balance expressions pertinent to each model is presented next.

Single-layer County-scale model

For Refugio County (Figure 2), the following mass balance expression was established.

(1)

Accumulation = $In - Out \pm Source/Sinks$

$$S\frac{\partial h}{\partial t}A_{s} = \sum_{i=1,..n} Q_{i} + (I - ET)A_{s} - (L - B) + (R - W)$$
⁽²⁾

Where, **S**: aquifer storage term (specific yield),

A_s: area of cross-section parallel to the groundwater table (Ac),

h: hydraulic head measured above a pre-specified datum (ft),

 \mathbf{Q}_i : volumetric flowrate of water entering or exiting along the i^{th} face of the aquifer (Ac-ft/yr),

I: infiltration rate (ft/yr) caused due to precipitation,

ET: rate of evapotranspiration (ft/yr) from below the water-table,

L: percolation of water from surface water bodies (Ac-ft/yr),

B: baseflow (or flow of groundwater into the surface water bodies) (ft/yr),

R: direct recharge of groundwater due to direct injection (Ac-ft/yr) and

W: total withdrawal of water due to anthropogenic demands (Ac-ft/yr).



Figure 2. Study area- Single-layer County Model

The unknown parameters, S (storage coefficient) and excess water availability, were estimated by plotting the Water level fluctuations Vs. Water budget as shown in Figure 3.



Water Level Fluctuations, dh/dt (ft/yr) Figure 3. Water level fluctuations Vs. Water budget

A fuzzy regression approach (Peters, 1994) employed to develop the necessary relationship to incorporate the uncertainties arising from limited data and simplistic model conceptualization.



Water level fluctuations (ft/yr)

Figure 4. Fuzzy regression

The data on groundwater fluxes, baseflows, water accumulation and withdrawals were utilized with the parameter estimation method to develop estimates for sustainable yields. The regression-based parameter estimation scheme indicated that on an average 20000 Ac-ft of water (Figure 4) could be safely withdrawn from Refugio County without altering the aquifer water levels and maintaining requisite baseflows to Mission River. Also, the average storage coefficient of the aquifer was estimated to be 0.008 and is within the ranges presented in the literature (Freeze and Cherry, 1979).

Two-layer Watershed scale Model

For the control volume depicted in Figure 1, the fluctuations in the water-levels and the various natural and anthropogenic processes affecting them can be related using the fundamental concept of mass-balance as follows:

For Chicot,

$$S_1 \frac{\partial h_1}{\partial t} A_C = R_C - W_C - B_F + Q_F - ET$$
(3)

For Evangeline,

$$S_2 \frac{\partial h_2}{\partial t} A_E = Q_E + R_E - W_E - Q_F \tag{4}$$



Figure 5. Gulf-coast aquifer



Figure 6. Conceptual Two-layer Watershed scale Model

Combining equations (3) and (4) we obtain,

$$S_1 \frac{\partial h_1}{\partial t} A_C - S_2 \frac{\partial h_2}{\partial t} A_E = (R_C - R_E) + (W_E - W_C) - B_F + 2Q_F - ET$$
(5)

Where S_1 and S_2 are the aquifer storage terms (specific yield) for Chicot and Evangeline aquifer, defined as the volume of water released per unit surface area of the aquifer per unit decline in the water table (Freeze and Cherry, 1979). A_C and A_E are areas of crosssection parallel to the groundwater table, h is the hydraulic head measured above a prespecified datum (ft). Q_E is the volumetric flowrate of water entering or exiting along the north and south faces of the aquifer (Ac-ft/yr). R_C and R_E are the recharge (Ac-ft/yr) caused due to precipitation in Chicot and Evangeline formations, and W is the total withdrawal of water due to anthropogenic demands (Ac-ft/yr). B_F is the baseflow (or flow of groundwater into the surface water bodies) (ft/yr). Q_F is the cross-formational flow of water between Chicot and Evangeline formations. The subscripts C and E denote Chicot and Evangeline formations. The volumetric flowrate of water entering or exiting along the north and south faces of Evangeline aquifer (Q_E) can be computed from Darcy's law as:

$$Q_i = K_r \frac{\partial h}{\partial s} A_i \tag{5}$$

Where K_r is the hydraulic conductivity (ft/yr) along the direction of flow s, the derivative term is the hydraulic gradient (ft/ft) and A_i is the area of cross-section normal to the direction of flow along the face. For unconfined aquifers, the area of cross-section is also a function of the water level (h) measured along each face.

Inflows and Outflows Across the Aquifer Boundaries

Two sets of three well clusters that fall on the Evangeline formation in and around the Mission river watershed were identified to quantify the inflows and outflows of water into the Evangeline formation. Water levels measured on an annual basis between the periods of 1985 – 1994 were obtained from the Groundwater Database developed by Texas Water Development Board (TWDB, 2003). The water level fluctuations were then used to compute gradient using the procedure suggested by Pinder et al., (1982). The hydraulic conductivity of the aquifer was assumed to be uniform, and an average value of 10^{-4} ft/day was used based (Mason, 1963). The annual volumetric fluxes in and out of the aquifer were then computed via the application of Darcy's law. The flow into the watershed (control volume) was assumed to be positive while outward flows were assumed to be negative.

Aquifer Recharge due to precipitation

To estimate the amount of precipitation actually recharging the aquifer, we have used the Power law equation developed by Bureau of Economic Geology at University of Texas at Austin (Scanlon et al., 2004). Power law equation is,

$$y = ax^t$$

Where, x is the average yearly precipitation in mm, a and b are the coefficients for four different modeling scenarios; (i) non-vegetated, monolithic sand, (ii) vegetated, monolithic sand, (iii) non-vegetated, layered soil profiles, and (iv) vegetated, layered soil profiles. In this case, we have considered vegetated, layered soil profiles ($a = 3.24 \times 10^{-9}$; b = 3.407). Precipitation data is from National Oceanographic and Atmospheric Administration (NOAA). The precipitation data was interpolated for each formation in ArcInfo 9.0 and the average annual recharge was calculated using raster calculator in ArcInfo. The reasonableness of the power law expression was evaluated using double-ring infiltrometer measurements carried out at various locations in the study area.

Surface water - Groundwater interactions (Baseflows)

Mission river is a perennial river and the groundwater levels in the areas adjoining Mission river tends to be slightly higher than the average river stage, indicating potential groundwater discharges (baseflows) to the streams. The surface water-groundwater interactions in other creeks were not considered. The annual baseflow contribution to Mission river from underlying aquifer for the period of 1985-1994 was estimated using a hydrograph separation technique. Streamflow data from USGS gaging station (Station ID: 08189500) were used in conjunction with the computer program HYSEP (Pettijohn, 1979) to obtain necessary estimates.

Accumulation within the Aquifer Control Volume

Accumulation represents, the left hand side of Equation (2). A total of 4 wells within the Chicot formation, and 7 wells within the Evangeline formation were selected to estimate water accumulation. Annual accumulation over the period of 1985-1994 was estimated using measured water-table elevations and first-difference approximation using the equation,

$$\frac{\partial h}{\partial t} \approx \frac{h_t - h_{t-1}}{\Delta t}$$

Where Δt is the measurement time-step (years) and h is the water-level elevation measured from a pre-specified datum at times t and t-1 respectively.

Anthropogenic withdrawals

Based on the 2002 Water Use Survey Summary Estimates by County developed by TWDB (www.twdb.state.tx.us), water demand due to municipal, manufacturing, mining, steam electric, irrigation, and livestock was calculated per square mile area. And from this data, the anthropogenic withdrawal (W) was estimated for both Chicot and Evangeline formations.

Initial Results for Two -Layer Regional Scale Model

Results of the water-balance is as shown below. Coupling of fuzzy optimization with mass-balance in currently in progress.

Year	dh/dt (ft/yr)	R _C (Ac/ft/yr)	W _C (Ac/ft/yr)	B _F (Ac/ft/yr)	WB (Ac-ft/yr)
1985	0.05	6200.16	566.03	11886.99062	-6252.86
1986	1.48			1047.15288	4586.98
1987	0.67			0	5634.13
1988	2.63			527.187312	5106.94
1989	4.23			86.660928	5547.47
1990	0.46			15707.2932	-10073.16
1991	9.07			7460.061552	-1825.93
1992	0.25			9388.2672	-3754.14
1993	0.25			0	5634.13
1994	8.65			0	5634.13

Area of Chicot, $A_C = 54707.26$ acres

Table 1. V	Vater	budget	for	Chicot	formation
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Year	dh/dt (ft/yr)	Q _E (In/Out)	R _E (Ac/ft/yr)	W _E (Ac/ft/yr)	WB (Ac-ft/yr)
1985	15.74	10441.96	26038.83	4172.831084	32307.96
1986	3.44	10216.32			32082.32
1987	44.55	6897.35			28763.34
1988	6.50	13353.93			35219.93
1989	6.99	11383.86			33249.86
1990	2.49	18153.61			40019.61
1991	0.80	17901.93			39767.92
1992	1.71	14242.30			36108.29
1993	1.71	11127.54			32993.54
1994	1.47	14111.02			35977.02

Area of Evangeline, $A_E = 390582.38$ acres

Table 2. Water budget for Evangeline formation

Parameter Estimation

In the two-layer watershed scale model, the model requires 3 unknowns to be estimated, the storage coefficients S_1 and S_2 , and cross-formational flow Q_F . A fuzzy regression based parameter estimation procedure is being utilized to estimate these unknown coefficients (Simões, 2001).

Dissemination of Results

A manuscript describing the application of fuzzy regression and single-county mass balance model has been prepared and is being finalized for submission to Environmental Geology by April 1, 2005

Another Manuscript detailing the application of fuzzy optimization and Watershed Scale model will be prepared for possible submission to a peer-reviewed journal by June 1, 2005.

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Assessment of Four Economic and Managerial Models for Operation of Public Water Systems in Texas

Basic Information

Title:	Assessment of Four Economic and Managerial Models for Operation of Public Water Systems in Texas		
Project Number:	2004TX151B		
Start Date:	3/1/2004		
End Date:	2/28/2005		
Funding Source:	104B		
Congressional District:	19th		
Research Category:	Social Sciences		
Focus Category:	Management and Planning, Law, Institutions, and Policy, Treatment		
Descriptors:	Water system management, Water utilities, Economics		
Principal Investigators:	Greg Landreth, David J. Eaton		

Publication

1. No publication.

Assessment of Four Economic/Managerial Models for Operation of Public Water Systems in Texas Preliminary Report

This report provides an initial review of research completed to date and the preliminary results of the study entitled, "Assessment of Four Economic/Managerial Models for Operation of Public Water Systems in Texas." The project seeks to provide a comparative analysis of the four major modes in which water systems in Texas are owned and operated according to cost and quality of service. Cost is measured as the monthly cost to residential customers of standard volumes of water, 5,000 and 10,000 gallons. Quality of service is measured by three proxies: level of operator training, incidence of drinking water quality standards violations, and frequency of complaints to the state regulatory agency against providers. Because scale is such an important consideration in water service provision, systems were broken into groups for most analyses, according to the population served.

Research Completed

The bulk of the research for this project has been completed. The research has consisted of two primary methods; collection of data maintained from databases maintained by the Texas Commission on Environmental Quality (TCEQ), and case study interviews with water system managers and utility owners across the state. TCEQ data were collected in a series of visits to that agency. Data for TCEQ's various programs are managed by different individuals and with different protocols, so multiple visits were required. Specific queries were written to extract data from the Water Utilities Database (WUD). Rate data for water supply corporations and investor-owned utilities were obtained by digging through paper records on file at TCEQ. District water rates were obtained via a series of phone calls to various districts and the private companies with which districts contract for management services.

A case study methodology was selected to provide insight into the meaning of the TCEQ and independently-collected water rate data. Small and large utilities in the four ownership types (municipal, districts, investor-owned utilities, and water supply corporations) were interviewed. To date, six interviews have been performed with two municipal utilities, one district, two investor-owned utilities, and one water supply corporation.

Interviewee	Provider Type
Aqua Water Supply Corporation	non-profit
Aqua Texas	investor-owned
City of Flatonia	municipal
City of Austin	municipal
Water Management, Inc.	investor-owned
Travis County WCID #17	district

Table 0.1 Interviewees, Case Studies

Data analysis is almost complete. Data have been compiled for the cost and quality of service dimensions; some data are still being collected on water rates charged by districts. A χ^2 (chi-squared) analysis of the quality of service data is being performed to identify the significance of patterns according to ownership types.

Preliminary Findings

Findings are reported according to the various dimensions measured. Across the range of populations served and irrespective of provider type, it is clear that economies of scale are important. Those who are supplied water by larger systems pay less for the services received, can expect a lower incidence of drinking water quality standard violations, and have higher-trained professionals managing their systems.

Cost of Water

Investor-owned utilities are most expensive. Water supply corporations and districts fall in the middle, and municipal utilities are least expensive. In the smallest communities, the difference between the average price for 5,000 gallons per month in a municipal system and an investor-owned system is about \$13 (\$20 vs. \$33). In larger communities, up to 50,000 residents, the difference is similar, about \$12, but the absolute values shrink (\$16 vs. \$28).

Operator Training

Districts have more trained operators per system than water systems of the other service provider types, across population groups.

Drinking Water Quality Standards

On the surface, it appears that investor-owned utilities have a higher incidence of violations of water quality standards than other utility types. χ^2 analysis indicates that incidence of water quality standard violations in the privately owned utilities is significantly larger than the predicted incidence. When the same χ^2 analysis is performed controlling for utility size, incidence of violations in communities of less than 500 residents is especially high for privately-owned utilities. However, in the 501-5,000 population bracket, IOUs contribute minimally to the value of χ^2 , indicating that the incidence of violations in IOUs of this size is proportional to their representation in the sample set. χ^2 tests were not performed for larger population brackets because the smaller sample size in the larger population brackets renders the χ^2 analysis unreliable.

Customer Complaints

The TCEQ receives a greater number of complaints from residents who receive services from water supply corporations and investor-owned utilities than from those who receive services from districts or municipalities. The reasons why this might be are unclear.

Papers in Progress

The only paper currently in progress is the grantee's thesis. The thesis will be completed in May 2005.

Presentations Made

The grantee and his advisor have made one presentation to date. This presentation was made to faculty and students of the LBJ School of Public Affairs at the University of Texas at Austin. Presentation slides are attached.

The grantee is scheduled to make a presentation to the Texas Water Development Board in the next month, and is also slated to participate in a Texas Water Resources Institute training session for water utilities in July.

Awards Received

The grantee has not received any new awards as a match to this project. He was awarded the Walter L and Reta Mae Moore Graduate Fellowship in Water Resources in Spring 2005 by the Environmental and Water Resources Engineering Department. This \$2,000 award was in recognition of his leadership within the department.

Complementary Research/Follow-Up

While the grant funds were used in the previous semester of the project, the research continues independently. The funded research formed the basis for the grantee's thesis project, which will be complete in May 2005. No additional grants have been received, and specific follow-up research on this specific project is not currently planned.

Use of Grant Funds

Grant funds were used to pay for 1 semester of a graduate research assistantship for the grantee, in the Fall of 2004. During that semester the grantee performed much of the study design and initial field research.

Development of Optimal Water Conservation and Management Strategies for Industrial Facilities

Basic Information

Title:	Development of Optimal Water Conservation and Management Strategies for Industrial Facilities
Project Number:	2004TX152B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	32nd
Research Category:	Engineering
Focus Category:	Conservation, Water Use, Models
Descriptors:	Water conservation, Industrial water use
Principal Investigators:	Eva M. Lovelady, Mahmoud M. El-Halwagi

Publication

1. No publication.

AN INTEGRATED APPROACH TO THE OPTIMIZATION OF WATER USAGE AND DISCHARGE IN PULP AND PAPER PLANTS

Report by

Eva M. Lovelady, PhD Student and Mahmoud El-Halwagi, Advisor

Chemical Engineering Department Texas A&M University College Station, TX 77843

April 18, 2005

a] Research that has been done so far

This research has been aimed at developing a systematic methodology for the cost-effective reduction of water usage and discharge in pulp and paper plants. As the industry moves towards increased system closure, the build-up of non-process elements (NPEs) leads to serious consequences on the process equipment. In response, this research has achieved the following:

- A mathematical model to track water and primary NPEs throughout the pulping process.
- Rigorous targeting for water usage and discharge.
- A systematic framework for water reduction using mass integration strategies including no/low cost techniques as well as capital-based techniques.
- An optimization model for the optimization of allocation, recycle, and separation of aqueous streams.

These mathematical models and allocation strategies have been coded into a computer-aided tool using LINGO programming platform. The program can be readily modified to address a variety of cases. In order to demonstrate the applicability of the developed tools, a case study has been addressed. Furthermore, this research provides a generic framework that can be effectively utilized by industry to develop cost-effective water management strategies and to identify critical research needs.

b] Any preliminary insights on what the study findings suggest

- The research has yielded the following useful insights:
- Water conception in pulp and paper mills may be reduced by more than 75% while providing value-added solutions (based on the savings in water usage, reduction in wastewater treatment, reduction in chemical usage, and debottlenecking).
- As the extent of water recycle increases, small quantities of impurities begin to accumulate. If gone un-resolved, those impurities can lead to the total failure of the process.
- There are multiple technologies to remove impurities but they have vastly different economics. Process integration provides a unique and systematic approach to screenings these alternatives and determining the optimal solutions.
- Optimum solution strategies involve a combination of in-process modifications and recycle/reuse alternatives.

c] Papers in progress [please attach them]

Lovelady, E. M., M. M. El-Halwagi, and G. Krishnagopalan, "An Integrated Approach to the Optimization of Water Usage and Discharge in Pulp and Paper Plants", Int. J. of Environ. and Pollution (IJEP), (2005, in press). For a copy, please see **Appendix I.**

d] Presentations made [please attach them]

N/A

e] Awards given to the student

Graduate Education for Minorities (GEM) Fellowship NASA/Texas Space Grant Consortium (TSGC) Fellowship

f] How the research has led to further grants or expanded ongoing research programs

Two research grants have been secured based on Ms. Lovelady's work: one from NASA (to apply water integration techniques to conserve resources in planetary habitation missions) and one from the EPA's Gulf Coast Hazardous Substances Research Center (GCHSRC) to develop process integration tools to reduce environmental emissions of chemical, petroleum, and petrochemical plants.

g] An overview of how much of the grant has been spent and how it was expended

The grant has provided stipend, tuition, and fees to Ms. Lovelady.

APPENDIX I

AN INTEGRATED APPROACH TO THE OPTIMIZATION OF WATER USAGE AND DISCHARGE IN PULP AND PAPER PLANTS

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Abstract- This paper is aimed at developing a systematic methodology for the cost-effective reduction of water usage and discharge in pulp and paper plants. As the industry moves towards increased system closure, the build-up of non-process elements (NPEs) leads to serious consequences on the process equipment. In response, this paper achieves the following:

- A mathematical model to track water and primary NPEs throughout the pulping process.
- Rigorous targeting for water usage and discharge.
- A systematic framework for water reduction using mass integration strategies including no/low cost techniques as well as capital-based techniques.
- An optimization model for the optimization of allocation, recycle, and separation of aqueous streams.

These mathematical models and allocation strategies have been coded into a computer-aided tool using LINGO programming platform. The program can be readily modified to address a variety of cases. In order to demonstrate the applicability of the developed tools, a case study has been addressed. Furthermore, this paper provides a generic framework that can be effectively utilized by industry to develop cost-effective water management strategies and to identify critical research needs.

INTRODUCTION

Pulp and paper mills have historically been one of the major consumers of water since large amounts are needed for washing, bleaching, and processing. Slowly, mills began to close the water loop and reduce effluent discharge by looking for ways to reduce, reuse or recycle water streams in order to comply with environmental regulations. Between 1975 and 1995, water consumption in the US pulp and paper industry decreased from 27000 gal/ton of product to 16,000 gal/ton of product (Patrick, 1994). This huge consumption along with its economic burden and environmental impact underscores the need and potential for more aggressive water reduction strategies.

Indeed, recently there has been a growing demand in the pulp and paper industry to adopt waste minimization strategies in order to create a minimum impact mill. A minimum impact mill, or MIM, does not strictly mean a zero-discharge mill, but rather one which either has no discharge or whose effluent discharge has a minimum or no impact on the environment. The MIM makes optimal use of its raw materials, reduces air emissions, water usage, waste generation, and is a net producer of electricity (Elo, 1995). The need for MIM's in the pulp and paper industry can be summarized as follows (Nguyen, 1995):

- To eliminate the discharge of undesirable compounds, such as organic halides, to receiving waters
- To reduce or eliminate the cost of waste water treatment, which is currently \$1.5 \$5/ton of pulp
- To eliminate fresh water use, as there is currently a shortage of fresh water
- To reduce the cost of water use (\$5/ton pulp) and energy use
- To meet increasing demands for environmentally friendly products

In order to achieve a minimum impact mill, it is desirable to partially or completely close the water loop of the process. System closure will result in the accumulation of non-process elements (e.g. Al, Si, K, Cl, Mg, Mn), suspended solids, dissolved solids, and other pollutants in the closed water system. This buildup will result in increased equipment corrosion, detrimental plugging, problematic scaling, and deposit formation, and can adversely affect the papermaking process.

The traditional solution to waste minimization has involved simple in-plant modifications and end-of-pipe treatment systems. However, these modifications fall short of providing cost-effective solutions to the industry. What is needed is a comprehensive, generic approach to waste minimization which is applicable to a wide variety of solid, liquid and gaseous wastes and which would incorporate economics, reliability and product quality along with maximizing the use of already available process internal resources. Over the past decade, a new methodology has been developed which is capable of systematically minimizing waste and improving overall process efficiency. This approach, known as mass integration, involves the optimal allocation of species throughout the process utilizing four main strategies: stream mixing/segregation, recycle/reuse, unit manipulation, and interception.

A typical kraft pulp and paper mill with an ODEDED bleaching sequences has been the model for this case study. The overall objective is to optimize water usage, reduce discharge, reduce solid waste and debottleneck the process to improve overall production and yield. To achieve this, a global understanding of the mass flow within the process is needed to provide insight as to how to minimize waste.

As a result of legislation, pulp and paper mills have taken steps to create a Minimum Impact Mill (MIM). A minimum impact mill is one that will meet the following objectives (Nguyen, 1995):

- To eliminate the discharge of harmful material to receiving waters
- To reduce or eliminate the cost of waste water treatment
- To meet increasing demands for environmentally-friendly products
- To reduce the cost of water and energy

Towards this end, mills have done work in applying simple modifications and good housekeeping approaches that can be quickly implemented without much cost (Mehta, 1996). Their impact, however, is quite limited. As mills strived to achieve high-levels of water recycle, a new problem arose; the build-up of non-process elements. Non process elements (referred to as NPE's from hereon) are those elements that do not take part in the delignification process of wood. In an open mill, the presence of NPEs is not important since they are purged naturally from the system in the product, bleach plant effluent, black liquor losses, recovery boiler flue gas, dregs, grits, lime kiln flue gas, and lime mud purges. In a closed mill, however, many of these outlets are no longer available. These NPEs will begin to build up and can have a number of adverse effects on process equipment such as corrosion of the recovery boiler, sticky deposits on the evaporator tubes, and scale formation in the digester. Non-process elements can be divided into two categories: those that accumulate in the sodium cycle and those that accumulate in the calcium cycle. Most NPE's will accumulate in either cycle to some degree but their accumulation factor and effect on process equipment will differ. In an open cycle, NPE accumulation is low due to chemical and liquor losses that acted as natural purges. As mills approach closure and these natural purges disappear, NPE's will build up in the sodium and calcium cycle in the following manner (from most to least) (Galloway, 1994):

Sodium Cycle: K > Cl > Al > Fe > Si > Mn > Mg > CaCalcium Cycle: Mg > Al > Fe > Mn > Si > Na > K > S > Cl

Though accumulation of most NPE's will have adverse effects on process equipment and chemical reactions, three NPEs stood out as major offenders: potassium, chloride, and sodium. As a result, the rest of this work will focus on these three NPEs.

Potassium and chloride have the greatest tendency to accumulate in the sodium cycle. Both NPE's can be found in higher concentrations in the recovery boiler fumes (Jordan, 1996). Chloride and potassium compounds, such as NaCl, KCl, and KOH, have high vapor pressures. In the recovery boiler, these compounds can volatilize from the smelt bed into the dust stream and be carried over to the upper furnaces. These particles will condense and form deposits on the cooler boiler tubes of the upper furnace, which results in tube plugging (Jordan 1996). This leads to a unit downtime since the recovery

boiler will need to be shut down for cleaning. NaCl also causes severe corrosion of the superheater tubes and black liquor evaporators. In addition, accumulation of all these compounds will accelerate equipment corrosion and cause ring formation in the lime kiln. Failure to account for the buildup of NPEs can have serious consequences. Indeed, the first major attempt at achieving a closed cycle mill in Thunder Bay, Ontario (Isbister, 1979; Pattyson, 1979; Galloway, 1994) was discontinued in 1985 with the primary reason attributed to the buildup of NPEs that caused severe corrosion, deposits, and scaling problems. This failure and other incidents underscore the need for a comprehensive, generic approach to water reduction that is based on integrating the various units, streams, and species within the process. This approach should also incorporate economics, reliability and product quality issues along with maximizing the use of already available process internal resources.

Over the past decade, a new methodology has been developed which is capable of systematically minimizing waste discharge and fresh-resource consumption while improving overall process efficiency. This holistic approach is known as mass integration. It provides a fundamental understanding of the global flow of mass within the process and employs this understanding in identifying performance targets and optimizing the allocation, separation, and generation of streams and species. Various process objectives such as pollution prevention, debottlenecking, and resource conservation can be systematically tackled through mass integration. For an overview of the subject and application, the reader is referred to review literature (e.g.; El-Halwagi 1997, 1998; El-Halwagi and Spriggs 1998, Bedard, 2001; Kuofos, 2001; Stuart, 2002; Paris, 2003).

PROCESS DESCRIPTION

Consider the Kraft pulping process shown in Figure 1. The wood chips and the white liquor (composed primarily of NaOH and Na₂S) are fed into a continuous digester. The cooked pulp undergoes brown stock washing in which the pulp is separated from the residual liquor in a series of countercurrent vacuum drum washers. Following brown stock washing, the pulp is screened and cleaned. After brown stock washing, the residual cooking liquor, also known as weak black liquor, is concentrated to strong black liquor through a series multiple effect evaporators and concentrators. This strong black liquor is burned in a recovery boiler in order to reduce oxidized sulfur compounds to sulfide, burn the organic chemicals, recover the heat of combustion as steam, and recover the inorganic chemicals (known as smelt) which will be used to regenerate the cooking liquor. The flue gas from the recovery furnace, which contains particulate matter such as Na₂SO₄ and Na₂CO₃, goes to an electrostatic precipitator, where these dust particles are removed from the flue gas and can be returned to the strong black liquor system.



Fig. 1 A Schematic Representation of the Kraft Pulping Process

The smelt from the recovery furnace is composed primarily of Na₂S, Na₂CO₃ and some Na₂SO₄. Weak wash liquor from lime mud and dregs washing is used to dissolve the smelt and form green liquor. The green liquor is clarified to remove any undissolved materials (known collectively as dregs) such as unburned carbon and inorganic impurities. The dregs are then washed to remove any sodium compounds and then discarded. The clarified green liquor and reburned lime are fed to a slaker, where the lime and water react to form slaked lime:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Any grits (unreactive lime particles and insoluble materials) are removed via a clarifier contained in the slaker. White liquor is then formed by the causticizing reaction between the slaked lime and sodium carbonate

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$$

Much of the causticizing takes place in the slaker before flowing to the causticizer. The white liquor is sent to a clarifier to remove lime mud, $CaCO_3$ formed in

the causticizing reaction, unreacted $Ca(OH)_2$, and any inert material before it is returned to the digester. The lime mud from the white liquor clarifier is washed to remove entrained alkali and sent to the lime kiln where the lime mud is converted to reburned lime for use in the slaking reaction. The filtrate from the lime mud and dregs washing is known as weak wash liquor and used to dissolve the smelt leaving the recovery furnace.

PROBLEM STATEMENT

The problem to be addressed can be stated as follows:

Given a typical Kraft pulping process, it is desired to develop cost-effective strategies for the reduction of water discharge from the mill. Any water reduction objectives will entail the use of recycle; consequently, various species will build-up, leading to operation problems. To alleviate the detrimental effect of build-up, comprehensive mass integration strategies are required to provide answers to the following questions:

- What are the rigorous targets for reduction in water usage and discharge?
- Which streams need to be recycled? To which units?
- Should these streams be mixed or should mixing be avoided?
- What load should be removed by interception devices?

APPROACH

In order to address the abovementioned problem, the following critical tasks must be undertaken:

• A simulation model should be developed to track water and the targeted NPEs throughout the process. The model should allow simulation for the modeling case as well as the process after.

DEVELOPMENT OF SPECIES TRACKING MODEL

In developing a model to track the various species of interest, it is necessary to strike the right balance in details. A too-detailed model cannot be readily incorporated into the process integration and optimization framework and will negatively impact the effectiveness of the optimization computations. On the other hand, a too-simplified model cannot describe the process with high fidelity and may not capture critical aspects of the process is the "path diagram equation" (El-Halwagi et al., 1996; Noureldin and El-Halwagi, 1999). It is a mass integration tool whose objective is to track targeted species (e.g., NPEs and water) as they propagate throughout the process and provides the right level of details to be incorporated into a mass integration analysis. A typical form of the path equations is to describe outlet flows and compositions from each critical unit as a function of inlet flow, inlet compositions, and appropriate design and operating parameters.

CASE STUDY

The base-case data and assumptions for the case study are given in the Appendix. The model development and details are also shown in the Appendix. The resulting model consists of a set of nonlinear equations which may be solved simultaneously using the software LINGO.

The LINGO program was run on a PC Pentium II with a convergence time of 3 seconds. The results are shown in Appendix I and are illustrated in Fig. 2.



Fig. 2. Solution to Nominal Case Study (all numbers are in tons per day)

TARGETING FOR OPTIMIZATION OF WATER USAGE AND DISCHARGE

Overall Water Balance

Before proceeding to determine the optimal strategies for water management, it is insightful to determine maximum targets for reduction in fresh water usage and discharge. We start with the nominal material balances shown in Figure 2. Based on these results, the overall water balance can be determined.

We now turn our attention to the water balance for streams that include fresh water usage of the discharge of recyclable water streams. Fig. 3 depicts the four fresh water streams currently used (S_2 , S_6 , S_{24} , and S_{33}). By adding up the flowrates of these streams, the total usage of fresh water is 52,197 tons per day. The figure also shows the potentially recyclable wastewater streams (S_8 , S_{10} , S_{12} , and S_{37}). Based on these streams, the total flowrate of water that may be potentially recycled is 42,365 tons per day. If all the recyclable water is intercepted and cleaned up till their contents are acceptable to be used in lieu of fresh water and if self recycle (reuse of wastewater from a unit in the same unit after cleanup), then the target for fresh water usage can be calculated as follows:

Target for minimum water consumption = 52,197 - 42,365 = 9,832 tons per day (1)

These results are schematically illustrated in Fig. 4. Also, by adding up the flowrates of the water streams leaving the process except the recyclable streams (S_8 , S_{10} , S_{12} , and S_{37}) and water in the produced pulp (W_{35}), we get a target for wastewater discharge to be 1,669 tons per day.



Fig. 3. Fresh and Recyclable Water Streams



Fig. 4. Determination of Target for Minimum Fresh Water Consumption

Water Targeting without Self-Recycle

A particularly important constraint is recycle without self-recycle. In some cases, it is forbidden to recycle effluent to the same unit to be used in lieu of fresh water. Several reasons can cause this limitation including the following:

- To prevent the accumulation of certain impurities that will build up in a flow loop.
- To avoid dynamic instabilities that may arise as a result of high interconnection between output (effluent) and input (recycled effluent replacing fresh water)
- To enhance process reliability by disengaging the dependence of input (recycled water) from output (effluent).

If self-recycle is not allowed, then the minimum water target may not be attained even if interception is used to clean up the recycled water. For practical reasons, we will consider the use of an interception device. For the case study, we also assume that the bleach plant can only accept water without any dissolved solids (e.g., same quality as the stripper water leaving the multiple effect evaporator or the concentrator). Let us calculate the new target without self recycle with one interceptor for two cases:

- Interception of bleach plant effluent (S₃₇)
- Interception of screening effluent (S₈)

In the case of intercepting S_{37} , the flow of W_{37} (30,990 tpd) is high enough to provide all the need for fresh water in the pulping process. Hence the target for fresh water in pulping is zero. As for the bleach plant, only the effluent from the multiple effect evaporator ($W_{10} = 8901$) and the concentrator ($W_{12} = 1024$) can be used to replace fresh water. Hence the target for fresh water usage in the case of no self-recycle with one interceptor applied to the bleach plant effluent is calculated through equation 2. These results are shown in Fig. 5

Water target
$$= 30,990 - 8,901 - 1,024 = 21,065$$
 tpd (2)



Fig. 5. Minimum Water Target without Self Target while Intercepting Bleach Plant Effluent

The same approach can be adopted for estimating the minimum-water target for the case of no self-recycle while intercepting the screening effluent. Assuming that the quality of the bleach plant effluent is acceptable for direct recycle to the pulping process, we can recycle 21,207 to replace all the fresh water used in pulping. We can also replace a portion of the fresh water needed for bleaching with the effluent from the multiple effect evaporator, the concentrator and intercepted screening effluent. Hence, in this case, the water target is calculated in equation 3. These results are shown in Fig. 6.

Water target = 30,990 - (1,450 + 8,901 + 1,024) = 19,615 tpd (3)



Fig. 6. Minimum Water Target without Self Target while Intercepting Screening Effluent (S_8)

Need for Detailed Strategies

The aforementioned discussion indicates that there is a significant potential for reducing fresh water usage from 53,194 tpd to 9,832 tpd. How do we determine the detailed strategies that can attain this target (Fig. 7)? Mass integration strategies should be employed to determine optimal ways of reaching this target. This will be the subject of the next section.



Fig 7 Water Impact Diagram

DEVELOPMENT OF MASS INTEGRATION STRATEGIES

Overall Approach

In order to develop solution strategies to the problem of optimizing water allocation in a pulping process, it is necessary to coordinate two important activities in tandem: process integration and process simulation. As shown in Fig. 8, process integration techniques can handle process objectives, data, and any requirements or constraints. The application of process integration provides performance targets, solution strategies, and proposed changes to the process. As a result of these changes, the process performance must be reassessed using process analysis or simulation (such as the aforementioned modeling equations, etc). The use of process simulation enables the update of flowrates and compositions throughout the process. By closing the information loop of integration and simulation, it is ensured that the developed insights and solution strategies activities are refined and validated.



Fig. 8. Coordination of Process Integration and Simulation

Since water and NPEs, mass integration techniques constitute the primary focus of the needed process integration tools. The first step in creating a mass integration model is the development of a mass allocation representation of the process from a species viewpoint. For each species there are sources and sinks. Sources can be defined as any stream that has the desired species (e.g., water) in it and sinks are any stream or unit that can accept the species. For our case, the *sources* are recyclable water streams and the *sinks* are the various units that consume fresh water. Each source, I, has a flowrate denoted by L_I and N_{ions} . The composition of each ion (NPE) is referred to as $y_{ion,I}$. The index for ions is referred to as ion and it ranges from 1 to N_{ions} where ion is Cl, K, Na, etc.

The overall objective of mass integration is to provide maximum utilization of water while satisfying all process requirements and constraints. In other words, what is the best scheme to allocate the water and deal with NPEs? As can be seen in Fig. 9., mass integration seeks to identify optimum allocation of water streams from sources to sinks. The integration strategies include segregation and mixing of streams, assignment to units, and adjustment of NPE content using interception (e.g. separation) devices that employ mass and energy separating agents. The following analysis shows how these solution strategies can be developed.

Consider a number N_{sinks} of process units (sinks) that employ fresh water which are designated by the index j, where j ranges from 1 to N_{sinks} . For the jth sink, there are two sets of constraints on flowrates and compositions:

$$W_j^{\min} \le W_j \le W_j^{\max} \qquad j=1,2,\dots, N_{\text{sinks}}$$
(4)

where W_i is the water flowrate entering the j^{th} sink.

$$Y_{ion,j}^{\min} \le Y_{ion,j} \le Y_{ion,j}^{\max} \qquad j=1,2,\dots, N_{sinks} \text{ and } ion=1,2,\dots, N_{ions} \qquad (5)$$

where Y_{ion,j} is the composition of a certain NPE (indexed ion) entering unit j.



Fig. 9. Mass Integration Framework for Water Allocation (El-Halwagi, et.al. 1996)

We now move to the source side. Each source, i, is split into N_{sink} fractions that can be assigned to the various sinks (Fig. 10). The flowrate of each split is denoted by $l_{i,j}$.



Fig. 10. Splitting of Sources

Next, we examine the opportunities for mixing these splits and assigning them to sinks. Figure 11. shows the mixing of the split fractions into a feed to the j_{th} sink.



Fig. 11. Mixing of Split Fractions and Assignment to Sinks

Direct Recycle/Reuse

It is instructive to first consider direct recycle/reuse of wastewater streams. This refers to the allocation of wastewater streams to process units without the use of new equipment to intercept and remove NPEs. This situation is important when no capital investment is to be spent on new equipment. The structural representation of this no/low cost strategy is shown in Fig. 12. Each split flowrate $l_{i,j}$ does not have to perfectly match the sink requirement. It can be mixed with other split flows or water to match the sink requirements. This mixing (represented in Fig. 12) must satisfy the sink constraints given by Eqs. (4) and (5).



Fig. 12. Direct Recycle/Reuse Source-Sink Assignment Problem (No/Low Cost Solution)

The following constraints represent the material balances associated with the splitting and mixing operations:

Splitting of the th source:

$$L_i = \sum_{j=1}^{N_{\text{sinks}}} l_{i,j}$$
 where n = 1,2, ..., N_{sources} (6)

Mixing for the jth sink:

$$W_{j} = FreshW_{j} + \sum_{i=1}^{N_{sources}} l_{i,j}$$
 where j = 1,2, ..., N_{sinks} (7)

where $FreshW_j$ is the amount of fresh water fed to the j^{th} sink.

$$W_{j} * Y_{ion, j} = \sum_{i=1}^{N_{sources}} l_{i, j} * y_{ion, i}$$

where j = 1,2, ..., N_{sinks} and ion = 1,2, ..., N_{ions} (8)

Optimization Formulation for Direct Recycle

In order to solve the above-mentioned assignment problem systematically, it is useful to formulate the task as an optimization problem. A theoretical model is formulated based on the structural representation of the problem to account for mass balances and assignment of sources to sinks. The objective function is to be fresh water used in the process. The objective function can be mathematically represented as:

Minimize flowrate of fresh water via direct recycle = $\sum_{j=1}^{N_{sinks}} FreshW_j$

This objective function can be readily modified to accommodate other objective functions.

Subject to the following constraints: Flowrate to each sink

$$W_i^{\min} \le W_i \le W_i^{\max}$$
 j=1,2,..., N_{sinks}

NPE content in feed to each sink:

$$Y_{ion,j}^{\min} \le Y_{ion,j} \le Y_{ion,j}^{\max}$$
 $j=1,2,\ldots, N_{sinks}$ and ion =1,2,..., N_{ions}

$$L_i = \sum_{j=1}^{N_{\text{sinks}}} l_{i,j}$$
 where n = 1,2, ..., N_{sources}

Mixing for the jth sink:

$$W_j = FreshW_j + \sum_{i=1}^{N_{sources}} l_{i,j}$$
 where j = 1,2, ..., N_{sinks}

Component material balances for the NPEs

$$W_j * Y_{ion, j} = \sum_{i=1}^{N_{sources}} l_{i, j} * y_{ion, i}$$
, where j = 1,2, ..., N_{sinks} and ion = 1,2, ..., N_{ions}

Non-negativity of each fraction of split sources:

$$l_{n,j} \ge 0$$
 where n = 1,2, ..., N_{sources} and j = 1,2, ..., N_{sinks}

Finally, since the various sources are interconnected and will be affected when fresh water is replaced with recycled water, it is necessary to include a simulation model to track the changes for the NPEs throughout the process. This is consistent with the philosophy summarized by Fig. 8. Hence, we include the path equations developed in Chapter Five in the mathematical formulation.

This optimization program can be solved using software LINGO to identify the minimum consumption of fresh water, the optimal allocation from each source to each sink, and the new steady state after these changes are implemented. Appendix II shows the detailed formulation for the case study along with the solution obtained from LINGO software. Again, this is a general purpose formulation that can be readily modified to address other case studies or specific mills.

In the case study, we have four recyclable sources: wastewater from screening, multiple effect evaporator, concentrator, and, bleach plant effluent. Also, fresh water can be used at minimum consumption. There are four sinks that employ fresh water: screening, brown stock washer, washers/filters and the bleach plant. Figure 13. shows the assignment representation for the case study. In our case study, no self-recycle is allowed (i.e., effluent from a unit cannot be used in the same unit to replace fresh water). This constraint (done by assigning a zero flow from sink to unit) is placed to ensure practical operation and to reduce control problems. It is further assumed that the bleach plant can only accept demineralized water.

Sources

Sinks



Fig. 13. Assignment Representation for the Case Study

Our objective is to minimize the usage of fresh water in the four sinks subject to the process constraints. The primary constraint on the buildup of NPEs is associated with the "stick temperature" for the recovery furnace. It can be related to the Cl, K, and Na through the following constraints:

$$\frac{K_{11} + K_{16} + K_{18}}{39.1} \le 0.1 \frac{N_{11} + N_{16} + N_{18}}{23}$$
(7.8)

$$\frac{C_{11} + C_{16} + C_{18}}{35} \le 0.02(\frac{N_{11} + N_{16} + N_{18}}{23} + \frac{K_{11} + K_{16} + K_{18}}{39})$$
(7.9)

where C_i, N_i, and K_i are the ionic loads of Cl, Na, and K (respectively) in the ith source.

The results are illustrated in Fig. 14.



Fig. 14. Optimum Solution for Direct Recycle/Reuse (all flows are in tons per day)

As can be seen from Fig. 14, the fresh water consumption is now reduced to 40,123 tons per day. This is a 23% reduction from the nominal fresh water usage of 52,197 tons per day. The solution is a direct recycle/reuse which requires piping and

pumping but involves no capital investment for new processing units. Another advantage of the developed mathematical program is its ability to generate alternative solutions.

Interception Problem

The minimum fresh water targets when interception is employed have been determined earlier. It is important to identify the interception tasks that can lead to such targets. Typically, the cost of an interceptor of a specific stream is monotonically increasing with the load to be removed. Hence, our objective will be to minimize the NPE load to be removed from the intercepted stream so as to reach the minimum water target. Since we are considering three NPEs, we will solve the program three times (one per ion). Therefore, we formulate an optimization program whose objective is to minimize the load of the NPE to be removed from the intercepted stream. The formulation can be described as follows:

Minimize Load of NPEs to be removed from targeted species

Subject to:

- Desired water target
- Path equations for tracking water and NPEs
- Recycle model
- Interception equations
- Constraints on units

For instance, in order to reach the water usage target of 21,065 (shown in Fig. 15), 8.997 tpd of Cl must be removed from the bleach plant effluent. The same procedure can be repeated for removing NPEs from any source. After all single-interception solutions are exhausted, the rest of water reduction strategies will have to include new technologies that enable self recycle and may involve the use of hybrid interception devices. For each intercepted stream, the same optimization model can be used to determine the task of the new technology. The specific nature of this new technology is not known yet. However, its task has been determined. This is a valuable finding that defines needed research to be carried out. Figure 16 shows the water impact diagram for the case study.



Fig. 15 Schematic Representation for Revised Flowsheet with Interception of Bleach Plant Effluent



Fig. 16. Water Impact Diagram for the Case Study

CONCLUSIONS

This work has developed a comprehensive framework for the systematic management of water and non-process elements pulp and paper plants. Specifically, this research has achieved the following:

- Process simulation: In order to track water and the NPEs throughout the process, a mathematical model has been developed to simulate the performance of a typical kraft bleached process under nominal conditions. Algebraic equations have been developed based on conservation laws, literature values, and judicious assumptions. The model has the capability of simulating the process under nominal conditions as well as after changes recommended by mass integration.
- Targets: Based on mass-integration strategies, rigorous targets have been developed for minimum feasible water usage and discharge.

Solution strategies: Based on mass integration techniques, various strategies have been recommended to attain the targets. These strategies include no/low cost techniques as well as capital-based techniques. To extend the applicability of this work, a mathematical programming code has been developed and implemented for the optimization of allocation, recycle, and separation of aqueous streams. This program has been coded into LINGO platform. The program can be readily modified to address a variety of cases. In order to illustrate the usefulness and applicability of the developed framework, a case study has been solved. The results demonstrate that for a typical kraft mill, significant reduction in water usage can be achieved. For the selected case study, 23% reduction in water usage can be achieved using simple recycle/reuse strategies. When interception is added to recycle/reuse, 62% reduction in water usage can be achieved. Finally, when new technologies are developed for removal of NPEs, 81% reduction in water usage can be accomplished. Although the work here does not specify the exact nature of these new technologies, it defines what tasks must be undertaken by these technologies and points out the research needed to reach this target.

In addition to developing specific solution strategies systematically, this work shed insightful light on the integrated nature of the task of managing water and NPEs. It also provides an easy-to-modify platform, which can be effectively utilized to address a wide variety of water-conservation objectives in pulp and paper plants.

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NOMENCLATURE

Ci	Mass Fraction of chloride ion in stream
CHIPS	Total flowrate of woodchips on a wet basis
CY	Mass Fraction of pulp in slurry leaving washing system
DF	Dilution Factor of excess wash water in brown stock washing
FreshW _j	Flowrate of fresh water to jth sink
Ki	Mass Fraction of potassium ion in stream
Li	Total flowrate of component i to jth sink
l _{i,j}	Split flowrate in stream ij
Moisture	Moisture content of chips
Ni	Mass Fraction of chloride ion in stream
Pulp	Pulp produced = Dry Chips * Yield
Si	Total stream entering or leaving unit
SSBL	Solids in Strong Black Liquor
W_j	Water flowrate entering the j th sink
Y _{ion,j}	Composition of a certain NPE (indexed ion) entering unit j
Yield	Pulp yield from dry chips

APPENDIX

DEVELOPMENT OF THE NOMINAL BALANCE MODEL

The first step in the analysis is to develop a mathematical model that provides the appropriate level of details for mass integration. In this appendix, a model for the nominal case of the process is developed to track pulp, water, and three main ions (chloride, potassium, and sodium). These ions are selected because they are among the most important species that cause buildup problems and limit the extent of mass integration. The mass flowrate of water, chloride, potassium, and sodium in stream i are referred to as W_i, C_i, K_i, and N_i, respectively. We now proceed to model development unit by unit.

Digester:

The flowrate of the wood chips (wet basis) is referred to as *Chips*, the moisture content (mass fraction) of the wood chips is referred to as *Moisture*, and pulp yield

 $(\frac{\text{Mass of pulp produced}}{\text{Mass of bone - dry chips fed to digester}})$ is designated by *Yield*.

The following equations can be written:

$$W1 = Moisture^* Chips \tag{A.1}$$

Thus, the flowrate of the bone-dry chips can be calculated as follows:

$$Dry Chips = Chips^*(1-Moisture)$$
(A.2)

The flowrate of pulp (bone-dry basis) can be related to the flowrate of dry chips through yield:

$$Pulp = Dry Chips*Yield$$
(A.3)

The ion content of the chips varies depending on the type of wood. The load of the targeted ions in the chips can be expressed as follows:

C_1 = Mass fraction of chloride ion in incoming wood chips * <i>Chips</i>	(A.4a)
K_1 = Mass fraction of potassium ion in incoming wood chips * <i>Chips</i>	(A.5a)
N_1 = Mass fraction of sodium ion in incoming wood chips * <i>Chips</i>	(A.6a)

To track the ions in the chips, we will use the data provided by Keitaanniemi and Virkola (1978)

$C_1 = 1.0$ *CHIPS/6000	(A.4b)
$K_1 = 2.50 * CHIPS/6000$	(A.5b)
N ₁ =0.973*CHIPS/6000	(A.6b)

Brown-Stock Washer

The dilution factor (DF) in the washers is expressed as pound of water per pound of dry pulp and typically ranges from 1.5 to 3.0 (Smook, 1994, p. 102, 104). Hence,

$$DF = \frac{W_2 - W_4}{Pulp}$$
(A.7)

The mass fraction of pulp in the slurry leaving the washing system is commonly referred to as the consistency (CY). Hence,

$$CY = \frac{Mass of pulp}{Mass of pulp + Mass of Water}$$
(A.8)

i.e., the water content in the slurry can be expressed as

$$W_4 = \left(\frac{1-CY}{CY}\right) * Pulp \tag{A.9}$$

The consistency typically ranges from 0.10 to 0.16 (Smook, 1994, p. 119). Equation (A.7) can be used to calculate the wash water, W_2 , after W_4 has been determined from Eq. (A.8).

The ionic content (ppm) of Cl, K and Na in the wash water can be specified based on typical values of 3.7, 1.1, and 3.6, respectively. Thus,

$$\begin{array}{ll} C_2 &= (3.7^*10^{-6})^*W_2 & (A.10) \\ K_2 &= (1.1^*10^{-6})^*W_2 & (A.11) \\ N_2 &= (3.6^*10^{-6})^*W_2 & (A.12) \end{array}$$

To calculate the flowrate of the targeted ions in the slurry stream (S_4) , we will assume ratios to the flowrate of the ions in the black liquor stream (S_5) .

$C_4 = 0.05 * C_5$	(A.13)
$K_4 = 0.02 * K_5$	(A.14)
$N_4 = 0.009 * N_5$	(A.15)

Figure A.1 illustrates the digester-washer system. Recall that it has been stated that all inlet streams values are known. Through the above ratios and equations, stream 4 is also known. Stream 5 will need to be determined. As can be seen, the number of unknowns is four (flowrates of water and the three ions in S_5). These can be obtained via the four material balances for the four species:

$W_5 = W_1 + W_2 + W_3 - W_4$	(A.16)
$C_5 = C_1 + C_2 + C_3 - C_4$	(A.17)
	(10)

$$K_5 = K_1 + K_2 + K_3 - K_4$$
(A.18)

$$N_5 = N_1 + N_2 + N_3 - N_4$$
(A.19)



Fig. A.1 A Loop around the Digester-Washer System

Multiple Effect Evaporators

The water in the evaporator condensate can be calculated using the water recovery ratio (equation 5.20). For the case study, we will assume that 80 % of the water in the weak black liquor is evaporated (i.e., water recovery ratio is 0.8). In addition, it is assumed that there are no ions in the condensate of the multiple effect evaporator.

W_{10} = water recovery in evaporator* W_5	(A.20)
$C_{10} = 0$	(A.21)
$K_{10} = 0$	(A.22)
$N_{10} = 0$	(A.23)

Then, material balances can be used to calculate the concentrated stream leaving the evaporators:

$W_9 = W_5 - W_{10}$	(A.24)
$C_9 = C_5 - C_{10}$	(A.25)
$K_9 = K_5 - K_{10}$	(A.26)
$\mathbf{N}_9 = \mathbf{N}_5 - \mathbf{N}_{10}$	(A.27)



Fig. A.2 Multiple Effect Evaporators

Concentrator

As with the multiple effect evaporator, the water in the concentrator condensate can be calculated using the water recovery ratio (eqn A.28). For the case study, we will assume that 46 % of the water in the black liquor entering the concentrator is evaporated in the (i.e., water recovery ratio is 0.46). Again, it is assumed that there are no ions in the condensate of the concentrator.

(A.28)
(A.29)
(A.30)
(A.31)

Then, material balances can be used to calculate the concentrated stream leaving the evaporators:

$W_{11} = W_9 - W_{12}$	(A.32)
$C_{11} = C_9 - C_{12}$	(A.33)
$K_{11} = K_9 - K_{12}$	(A.34)
$N_{11} = N_9 - N_{12}$	(A.35)





Recovery Furnace and Electrostatic Precipitator (ESP)

The strong black liquor leaving the concentrators is combusted in the furnace to recover the inorganic chemicals, or smelt, which are primarily Na₂S and Na₂CO₃. Smelt contains no water. Assuming that all the water in the strong black liquor leaves with the ESP off-gas, we get

$$W_{14} = 0.0$$
 (A.36)
 $W_{16} = 0.0$ (A.37)

To track the ions in the furnace exhaust (S_{13}) , we will use the data provided by Gleadow (1996):

$K_{13} = 0.278 * K_{11}$	(A.38)
$C_{13} = 0.498 * C_{11}$	(A.39)
$N_{13} = 0.154 * N_{11}$	(A.40)

We also use the data from Gleadow (1996) to relate the ions in stream 14 (ESP dust) to those in stream S_{11} (SBL):

$C_{14} = 0.048 * C_{11}$	(A.41)
$K_{14} = 0.028 * K_{11}$	(A.42)
$N_{14} = 0.002 * N_{11}$	(A.43)

Assuming that all the water in the strong black liquor leaves with the ESP off-gas and relating the entrained ions in the off-gas to the SBL stream, we get

$W_{15} = W11$	(A.44)
$C_{15} = 0.02 * C_{11}$	(A.45)
$K_{15} = 0.008 * K_{11}$	(A.46)
$N_{15} = 0.0008 * N_{11}$	(A.47)

Next, we use component material balances around the ESP,

$W_{13} - W_{14} - W_{15} - W_{16} = 0.0$	(A.48)
$C_{13} - C_{14} - C_{15} - C_{16} = 0.0$	(A.49)
$K_{13} - K_{14} - K_{15} - K_{16} = 0.0$	(A.50)
$N_{13} - N_{14} - N_{15} - N_{16} = 0.0$	(A.51)

Assuming that the salt cake has a makeup flow of 0.0375 * Pulp, we get

$$Saltcake = 0.0375*PULP \tag{A.52}$$

Using the molecular formula for salt cake (molecular weight of Na_2SO_4 is 142 with two Na atoms whose atomic weight is 23), then

$$N_{18} = 2*23/142 * Saltcake$$
 (A.53)

The content of Cl and K in Saltcake is obtained by assuming ratios to Na in the Saltcake:

$$\begin{array}{ll} C_{18} = 0.01^* N_{18} & (A.54) \\ K_{18} = 0.0014^* N_{18} & (A.55) \end{array}$$

Since there is virtually no water contained in Saltcake, then

$$W_{18} = 0.0$$
 (A.56)
 $W_{17} = 0.0$ (A.57)

For the ions in the smelt, we can use component material balances around Fig. A.4:

$C_{11} + C_{18} - C_{15} - C_{14} - C_{17} = 0.0$	(A.58)
$K_{11} + K_{18} - K_{15} - K_{14} - K_{17} = 0.0$	(A.59)
$N_{11} + N_{18} - N_{15} - N_{14} - N_{17} = 0.0$	(A.60)

Smelt Flowrate

Since the solids in the strong black liquor make up are taken as 65 % of that stream, then Solids in SBL (referred to as SSBL) = $65/35*W_{11}$ i.e., SSBL = $1.86*W_{11}$ (A.61) The solids in the electrostatic precipitator flue gas and purge stream are small. Assuming 5% of the solids in the strong black liquor leave the ESP in the flue gas and the purge stream (streams S_{14} and S_{15}) and 47% of the strong black liquor solids are volatilized in the furnace, we can use the following solids balance around Fig. A.4 to estimate the flowrate of the smelt:

Saltcake + Solids in SBL (SSBL) = Smelt + Solids lost with flue gas and the purge stream (streams S_{14} and S_{15}) + Solids volatilized in the furnace (A.61a)

Hence, Saltcake + SSBL = Smelt + 0.05*SSBL + 0.47*SSBL (A.61b)

Rearranging and simplifying, then

Smelt = Saltcake + 0.48*SSBL



Fig. A.4. Furnace-ESP System

Dissolving Tank

Next, we move to the dissolving tank (Fig. A.5). The dissolving water is typically used in a ratio of 85 to 15 to the smelt. Hence,

$$W_{19} = (85/15) * Smelt = 5.67 * Smelt$$
 (A.62)

34

(A.61c)

 $\begin{array}{ll} \mbox{The ionic content in S_{19} is obtained by assuming ratios to the ionic content of Cl and K in the smelt and Na in the white liquor (Hough, p. 243): $$C_{19} = 0.136*C_{17}$$ (A.63) $$K_{19} = 0.136*K_{17}$$ (A.64) $$N_{19} = 0.196*N_3$$ (A.65) $$ (A.65$



Fig. A.5. Dissolving Tank

Now, we can use component material balances around the dissolving tank to evaluate the ionic content in the feed to the green liquor clarifier:

$W_{20} - W_{17} - W_{19} = 0.0$	(A.66)
$C_{20} - C_{17} - C_{19} = 0.0$	(A.67)
$K_{20} - K_{17} - K_{19} = 0.0$	(A.68)
$N_{20} - N_{17} - N_{19} = 0.0$	(A.69)

Green-Liquor Clarifier

Fig. A.6. is a schematic representation of the green-liquor clarifier. In order to get the flows and ionic contents of the overflow and underflow streams, we assume the following typical ratios of overflow to feed:

$W_{21} = 0.992 * W_{20}$	(A.70)
$C_{21} = 0.863 * C_{20}$	(A.71)
$K_{21} = 0.880 * K_{20}$	(A.72)
$N_{21} = 0.968 * N_{20}$	(A.73)

Then, material balance equations can be written around the clarifier:

$W_{22} + W_{21} - W_{20} = 0.0$	(A.74)
$C_{22} + C_{21} - C_{20} = 0.0$	(A.75)
$K_{22} + K_{21} - K_{20} = 0.0$	(A.76)
$N_{22} + N_{21} - N_{20} = 0.0$	(A.77)



Fig. A.6. Green-Liquor Clarifier

Washer/Filter System

The system is shown in Fig. A.7. The dregs leaving the washer/filter system contain little water which can be estimated by relating it to the water content in the underflow from the green-liquor clarifier based on the data of Hough:

$$W_{23} = 0.075 * W_{22}$$

(A.78)

We also assume ratios of Na, Cl, and K (based on Keitaanniemi and Virkola, 1978) to water in the dregs:

N ₂₃ - 0.250*W ₂₃	(A.79)
C ₂₃ - 0.010*W ₂₃	(A.80)
K ₂₃ - 0.001*W ₂₃	(A.81)

Using the data of Hough, we can relate streams S_{32} and S_{21} :

$$W_{32} = 0.160^* W_{21} \tag{A.82}$$

$$C_{32} = 0.237 * C_{21}$$
(A.83)

$$K_{32} = 0.016 * K_{21}$$
(A.84)

$$N_{32} = 0.156 * N_{21}$$
(A.85)

The wash water (W24) is assumed to be 90% of smelt dissolution water, i.e.

$$W_{24} = 0.9^* W_{19} \tag{A.86}$$

We also specify the ionic content of Cl, K, and Na in the wash water based on typical values to be 3.7, 1.1, and 3.6 ppm, respectively. Hence,

$C_{24} = (3.7*10^{-6})*W_{24}$	(A.87)
$\mathbf{K}_{24} = (1.1^* 10^{-6})^* \mathbf{W}_{24}$	(A.88)
$N_{24} = (3.6*10^{-6})*W_{24}$	(A.89)

Component material balances around washer/filter system:

$W_{22} + W_{24} + W_{32} - W_{19} - W_{23} - W_{25} = 0.0$	(A.90)
$C_{22} + C_{24} + C_{32} - C_{19} - C_{23} - C_{25} = 0.0$	(A.91)
$K_{22} + K_{24} + K_{32}$ - K_{19} - K_{23} - $K_{25} = 0.0$	(A.92)
$N_{22} + N_{24} + N_{32} - N_{19} - N_{23} - N_{25} = 0.0$	(A.93)



Fig. A.7. Washer-Filter System
Lime Kiln

The lime leaving the kiln (Fig. A.8) is assumed to be free of water. Hence,

$$W_{27} = 0.0$$
 (A.94)
 $W_{25} = W_{26}$ (A.95)

We also assume that the ratio of Cl and K in S_{26} is 0.0001 and that 95% of sodium entering the kiln is lost in S_{26} (i.e., 5% of Na leaves in S_{27}). Hence,

$K_{26} = 0.0001 * W_{26}$	(A.96)
$C_{26} = 0.0001 * W_{26}$	(A.97)
$N_{27} = 0.05 * N_{25}$	(A.98)

Component material balances around the kiln:

$C_{25} - C_{26} - C_{27} = 0.0$	(A.99)
$K_{25} - K_{26} - K_{27} = 0.0$	(A.100)
$N_{25} - N_{26} - N_{27} = 0.0$	(A.101)





<u>Slaker</u>

Figure A.9 represents the slaker. The slaking reaction is given by:

 $CaO + H_2O = Ca(OH)_2$

(A.102)

Since the molecular weights of water and lime are 18 and 56, respectively, then the amount of water consumed is 18/56 or 0.32 of the consumed lime, i.e.

WATERSLK = 0.32*LIME

(A.103)

(A.104)

where WATERSLK is the amount of water consumed by the slaking reaction. According to Biermann (p. 117, 1996), the amount of lime fed to the slaker is 35% of the pulp, so:

LIME = 0.35*PULP

We also assume that the slaker vapor is 0.5% of the water in the green-liquor overflow (S_{21}) and is ion free. Hence,



Fig. A.9. Slaker

For the grits, we can get assumptions relating it to the green-liquor overflow by adopting data from Hough for water and Cl and from Keitaanniemi and Virkola (1978) for K and Na:

$W_{28} = 0.0013 * W_{21}$	(A.109)
C ₂₈ - 0.0015*C ₂₁	(A.110)
$K_{28} = 0.0053 * K_{21}$	(A.111)
$N_{28} = 0.001 * N_{21}$	(A.112)

Component material balances around the slaker:

$K_{21} + K_{27} - K_{28} - K_{29} - K_{30} = 0.0$	(A.115)
$N_{21} + N_{27} - N_{28} - N_{29} - N_{30} = 0.0$	(A.116)

Causticizer/White Liquor Clarifier

Figure A.10 shows the causticizer/white liquor clarifier system. Since the causticizing system provides an additional residence time for the causticizing reactions to take place, we can assume that the water and ionic content of the entering and leaving streams are the same (although their chemical forms may change). Hence,

(A.117)
(A.118)
(A.119)
(A.120)

Then, we carry out material balances around the white liquor clarifier:

$W_{31} - W_{32} - W_3 = 0.0$	(A.121)
$C_{31} - C_{32} - C_3 = 0.0$	(A.122)
$K_{31} - K_{32} - K_3 = 0.0$	(A.123)
$N_{31} - N_{32} - N_3 = 0.0$	(A.124)



Fig. A.10. Causticizer/White Liquor Clarifier

Bleaching

Figure A.11. illustrates an overall view of the bleach plant. As shown in the figure, it is assumed that the ratio of used water to bone-dry pulp is 10.33. Also, it is

assumed that the bleach plant effluent has a fixed outlet composition of Cl, K, and Na (500, 5, and 500 ppm, respectively). Furthermore, it is assumed that used water is equal to discharged water. Hence,

$W_{33} = 10.33 * PULP$	(A.125)
$\mathbf{W}_{35} = \mathbf{W}_7$	(A.126)
$W_{37} = W_{33}$	(A.127)
$C_{37} = 0.0005 * W_{37}$	(A.128)
$K_{37} = 0.000005 * W_{37}$	(A.129)
$N_{37} = 0.0005 * W_{37}$	(A.130)



Fig. A.11. Overall Bleach Plant

The foregoing equations constitute the necessary model to track the flow of water and targeted NPEs throughout the process. It is a general purpose simulation model that can be easily modified to relax or modify any assumptions.

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Improving Capabilities for Dealing with Key Complexities of Water Availability Modeling

Basic Information

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Improving capabilities for addressing key complexities of water availability modeling

FINAL REPORT

December, 2004

Hector E. Olmos Ralph A. Wurbs, Ph.D.

Texas A&M University

This research project addressed several complexities and improvements to water availability modeling (WAM), using the Water Rights Analysis Package (WRAP) and a conditional reliability model. The main tasks of this project were to:

- 1. Develop guidelines to simplify an existing WAM dataset
- 2. Perform yield-reliability analyses for alternative system management strategies and modeling premises
- 3. Evaluate the impact of beginning of simulation reservoir storage on reliabilities
- 4. Improve, test and provide methodologies to apply the conditional reliability model and develop a new modeling methodology
- 5. Develop a tool to provide a spatial display of simulation results

All the above tasks have been completed successfully and are documented by: Olmos, Hector E. "Improving Capabilities for Dealing With Key Complexities of Water Availability Modeling", Texas A&M University, College Station, Texas, 2004; available at the Texas A&M University library.

All the funds provided by this grant have been invested on tuition fees for summer 2004.

I will be graduating in December 17, 2004 with my master's degree in Civil Engineering and initiate my professional career in the water resources field.

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Hector E. Olmos

A Near Real-Time Flood Prediction Using Hourly NEXRAD Rainfall Data for the State of Texas

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A Near Real-time Flood Prediction using Hourly NEXRAD Rainfall for the State of Texas

Bakkiyalakshmi Palanisamy

Introduction

Radar derived precipitation data is becoming the driving force for hydrological modeling. Being rainfall the key input for modeling natural resources such as water, accurate measurement of rainfall in terms of spatial and temporal is very important. The potential of radar rainfall is obvious in such a way that in recent years, hydrological modeling of all spatial scales started using it for simulation of runoff. It has been very well recognized that errors in rainfall input increases error in the estimation of stream flow (Sun et al., 2000). Thus, radar estimates supersede the raingage measured rainfall in terms of its large spatial coverage, such that it can capture any small amount of rainfall where raingage usually tends to miss some of these small events. Not only the low intensity rainfall, because the raingage network is very scarce around the area being studied, there is a very high possibility that it will fail to capture some of the high intensity, short duration rainfall too.

Hence, using radar estimates for producing accurate amount of runoff is promising in the field of hydrological modeling. Even though, radar estimates are capable enough to characterize the spatial variability of rainfall in terms of space and time, there are lot of uncertainties aroused in the estimation methods of the precipitation from the reflectivity values. Rainfall-runoff modeling is very sensitive to uncertainty in radar derived rainfall values (Borga Marco, 2002). Issues related to radar rainfall uncertainties are being studied for many years and researches are being carried out to separate effect of radar rainfall errors from the modeling errors.

Hence, take into account the spatial and temporal resolution in runoff estimation and eventually in hydrological simulation, can improve the prediction very well. It has been said in the literature that runoff simulation is very sensitive to spatial and temporal scale of the input (Winchell et al., 1998). These past studies suggest that using radar estimates with the variability being represented at very large scales of measurements can improve the prediction of runoff. Thus, this study is focused on using radar derived rainfall estimates at 4 x 4 km spatial and 60 minutes temporal resolution. Soil wand Water Assessment Tool (SWAT) model (Arnold et al., 1998) is used for runoff estimation. SWAT is semi-distributed hydrological, watershed scale model and calculates runoff based on water budget method. SWAT can simulate runoff at various temporal scales which include hourly, daily, monthly and yearly basis. Daily runoff estimation is using SCS Curve Number method and hourly runoff estimation uses Green-Ampt Mein-Larson excess rainfall method (GAML) [King et al., 1999] . In this method of calculating runoff, the amount of water that does not infiltrate into the soil becomes runoff.

The objective of this study is that to examine the performance of SWAT model to simulate runoff on hourly basis. Past study by Di Luzio and Arnold, 2004 on simulating hourly runoff shows that the model performed well and was able to generate the stream flow when compared with observed hydrograph with radar derived rainfall input. This study is focusing on generating stream flow with both raingage and radar rainfall data for the watersheds in Upper Trinity River Basin of Texas. The study area selected for this study is Eagle Mountain. Although, the study was intended to predict the flow for the entire state of Texas, this watershed is selected as test study area and trying to examine the performance of the model.

Description of the study area

Big sandy creek watershed is located in the Northwest part of the upper Trinity River basin with the drainage area of 312 square miles (Fig 1). The study area is of smooth to rolling topography. It is sloping gradually from 1,200 ft above sea level at the headwaters and decreasing as it goes down. The climate of the watershed is temperate with warm summers. The variation in climate across the study area is decreasing land elevation from west to east. Annual average precipitation is 32 inches and with uniformly distributed , average temperature of less than 65° F. Though the rainfall is of greater amount , 32 inches, the average runoff is less than 4 inches. This is primarily due to the variation of climate across the study area. The watershed experiences little water surplus in any season (Ulery and Brown, 1994). Summer experiences high intensity, short duration rainfall bursts resulting in thunderstorms. This eventually, leads to flash flood in the area.

Soil and Land Use

Thin mantle of soil is covered in the northwestern part of area with increasing depth towards downstream part of the watershed. Across the watershed, very deep to moderate deep clay, sandy loam is present. The soil data was obtained from SSURGO dataset, which is available for most of the state. Range and pasture are prevalent in the watershed



Fig 1 Study area, raingages and Radar grids

The land use dataset was collected from National Land use Land cover Data (NLCD) for the year 2000 and used in the study. The resolution of both soil and land use data is 30m. The elevation dataset needed for the model was obtained from National Elevation Dataset (NED) at 30m resolution.

Climate Data processing

Hourly precipitation was collected from National Climatic Data Center (NCDC) for the five years of simulation period, from 1999 to 2003. Corresponding observed stream flow was obtained from United States Geological Survey (USGS). Temperature data used in this study was in daily basis since; the main objective of this study was to examine the effect of spatial variability of different rainfall inputs. Radar data for the study area was collected from West Gulf River Forecasting Center (WGRFC) and Stage III data is used in this study. Since, raingage measurements are collected from 12 AM to 12 AM for a day, radar data were also extracted from 12 to 12AM for a day.

All the input files required for simulation were prepared using ArcView GIS interface of SWAT model.

Precipitation comparison

Precipitation estimates for gage and radar were compared to use with the model. The rainfall events were selected for convective storm, i.e. the events in summer as it produces more runoff than any other events occur during any other season. The selected events were for the years 2002 and 2003. Since, 2002 had some higher amount of runoff (greater than 500 cubic feet per second), in the late spring, two events were selected for that season. The comparison statistics used are defined as follows:

Total difference (mm) = Radar total – Raingage total

Positive total difference represents overestimation of precipitation by radar whereas the negative difference indicates the underestimation.

Radar Bias (%) = 100*(Radar total – Raingage total) / Raingage Total

Similar to total difference, positive radar bias represents overestimation of radar and negative radar bias represents the underestimation by radar.

Table 1 presents the comparison statistics for both gage and radar rainfall for the selected events in the year 2002. As can be seen from the statistics, radar is overestimating for all the events.

	Event_1	Event_2	Event_3	Event_4
Total Difference	35.8	31.20	123.80	71.20
Radar Bias	60.76	26.78	78.95	201.70

Table 1 Comparison statistics for the selected events in the year 2002

Where,

Event_1 is from 144 to 146th days of 2002

Event_2 is from 155 to 159th days of 2002

Event_3 is from 77 to 80th days of 2002, which is in spring season

Event_4 is from 89 to 91st days.

Table 2 presents the comparison statistics for gage and radar rainfall events for the year2003.

	Event_1	Event_2	Event_3
Total Difference	-3.4	22.50	65.90
Radar Bias	-3.73	42.13	41.95

Table 2 Comparison statistics between gage and radar for selected events in 2003 Where,

Event_1 is from 156 and 157th days

Event_2 is from 145 and 146th days

Event_3 is from 162 to 165th days

For the selected events in the year 2003, from table 2, it can be explained that radar is underestimating the rainfall for event 1 and for the other two events, radar is overestimating.

These comparisons on hourly basis, shows that when the temporal and spatial resolution is increased to capture the precipitation, the better estimates can be obtained. This is obvious from the radar derived rainfall values. Also, it clearly shows that the larger events, such convective storms, which are very typical of the study area, can be represented well with the radar data than the point measured rainfall data. Another important point to be noted in regard to the overestimation of radar in all the events is that radar captured not only the high intensity rainfall but also, the low intensity rainfall too; when raingage failed to measure these events. But for event 1 in 2003, even though the statistics show that radar is underestimating, the percentage of underestimation is negligible as it is just 3%.

Model Simulations

The simulation was performed on hourly basis for the watershed for five years using both gage and radar data. All the model parameters are kept the same except the rainfall inputs for the uncalibrated run with Priestly-Taylor method for calculating Evapotranspiration. USGS stream gage was located at the downstream of the delineated watershed. Warm up period of first two years were allowed to account for unknown initial conditions of the watershed and the simulation results from these years were not included in the analysis. Calibration was performed for both simulations using gage and radar rainfall input. To compare the simulated flow values with the observed stream flow, various statistics ranging from correlation, coefficient of determination (r^2), and Nash-Sutcliffe coefficient of efficiency, E (Nash and Sutcliffe, 1970) and to Index of Agreement (d) were used. But for presentation purpose, only efficiency and index of agreement are used.

Nash-Sutcliffe is defined as.

$$E = \frac{\sum_{i=1}^{n} (O_i - O_m)^2}{\sum_{i=1}^{n} (O_i - O_m)^2}$$

Where, n =Number of observed flow = Number of simulated flow

 $O_i = Observed stream flow (I = 1 to n)$

 O_m = Mean of the observed stream flow

 S_i = Simulated stream flow (I = 1 to n)

Value of e can vary from minus infinity to 1; higher the value of E, better the efficiency of the simulated values

Index of Agreement is defined as,

$$d = \frac{\sum_{i=1}^{n} (O_i - O_m)^2}{\sum_{i=1}^{n} (|S_i - O_m| + |O_i - O_m|)^2}$$

Values of d can vary from 0 to 1 and the value closer to 1 represents the better agreement of simulated results.

Results and Discussion

Simulation results for the selected events for 2002 and 2003 are presented in Table 3 and 4 respectively with the Efficiency and Index of agreement for calibrated and uncalibrated simulated stream flows.

	Efficiency		Index of Agreement	
	Uncalibrated Calibrated		Uncalibrated	Calibrated
Event 1	-0.12	-0.1	0.32	0.25
Event 2	-0.68	-0.74	0.46	0.46
Event 3	-63.72	-53.40	0.13	0.28
Event 4	-0.41	-0.33	0.37	0.36

Table 3a. Simulation statistics for all the events in 2002 with gage rainfall

	Efficiency		Index of Agreement	
	Uncalibrated	Calibrated	Uncalibrated	Calibrated
Event 1	-20	-4.91	0.36	0.66
Event 2	-0.93	0.02	0.64	0.86
Event 3	-15.33	-53.37	0.42	0.31
Event 4	-2.36	-0.77	0.78	0.67

Table 3b. Simulation statistics for all the events in 2002 with radar rain	fall
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	Efficiency		Index of Agreement	
	Uncalibrated	Calibrated	Uncalibrated	Calibrated
Event 1	-0.96	-0.94	0.34	0.79
Event 2	-138.00	-289.00	0.15	0.013
Event 3	-133.00	-690.00	0.17	0.06

Table 4a Simulation statistics for the events in 2003 with gage rainfall data

	Efficiency		Index of Agreement	
	Uncalibrated	Calibrated	Uncalibrated	Calibrated
Event 1	-0.02	0.57	0.75	0.92
Event 2	-28.60	-52.00	0.36	0.28
Event 3	-31.86	-54.90	0.3	0.28

Table 4b Simulation statistics for the events in 2003 with radar rainfall values

Overall, for the years 2002 and 2003, simulated flow is always overestimated when compared with observed streamflow values (Fig 2a to 2g). The water was routed using Muskingum routing method incorporated in SWAT. The annual water balance for this watershed also overestimated the surface runoff and ground water flow. While the observed annual water yield for the watershed was 33mm out of which 22 mm was surface runoff and 10 mm was ground water flow, remaining being the lateral flow; the simulated values where 80mm of total yield out of which 45mm was surface runoff, 35mm was ground water flow and remaining lateral flow.

Calibration was performed with the parameters being tuned in for increasing the width of the hydrograph and for reducing the amount of surface runoff. The main contribution of the calibration to this watershed runoff simulation was that the lag to peak was drastically decreased from 12-24 hours to 3 to 6 hours. As said in the proposal, the

primary objective of this research is to calibrate the model for decreasing the lag to peak. This task was able to be achieved in very good agreement with observed values.

The volume of the hydrograph is the main concern as can be seen from the simulated values. One of the primary reasons for increased runoff volume is type of rainfall input into the model. Due to the scarcity of raingage network around the watershed (two hourly gages for 321 square miles area of the watershed), the rainfall assigned to each delineated sub watersheds are nearly uniform; which is not of the typical climatic condition of the watershed. Especially, in the upper Trinity River basin, where the topography makes the variation of climate very sensitive to elevation, assigning uniform rainfall to such a big area is not feasible. Hence, the volume produced by raingage rainfall values, after performing calibration, is very large.

Considering the simulated values using radar rainfall, since each sub watershed will be using the rainfall occurred at that particular space, the prediction was in very well agreement with the observed streamflow; including width and timing of the graph. Yet, the volume of flow was always double, in some case, triple the amount of observed flow. The solution to this problem, is to adjust or calibrate the radar rainfall in accordance with the measured raingage values. This can be done by multiply the radar values by the bias between gage and radar total at the pixel. For this purpose, the gage data has to be interpolated using different interpolation techniques such as Inverse Distance Weighted (IDW), spline.

The next step in this study is to use adjusted radar data to improve the volume prediction of hydrograph by the model. Also, this study proposed to use radar data at the resolution of 4Km² and after doing the simulation using adjusted radar data, this task will be performed.

Conclusion

The results from the simulations performed for the selected convective storms show that radar data can predict the flow better than the raingage rainfall values. This is mainly due to its ability to capture spatial variability of rainfall across the space; in this case, at every 4 km² of the study area. Problem concerning the lag to peak; which was addressed in the proposal, was solved after performing calibration for both gage and radar rainfall values. The parameters that are calibrated were flood attenuation coefficient in Muskingum routing method, Manning's roughness coefficient, saturated hydraulic conductivity and ground water evaporation coefficient.

This research is extended to study the effect of very high spatial resolution of radar data, at every 4km² of study area and test the model's ability to produce runoff at this grid scale.



Fig 2a Hourly streamflow comparison for Big sandy creek watershed using for Julian days 144 to 146 of 2002.



Fig 2b Hourly streamflow comparison for Big sandy creek watershed using for Julian days 155 to 159 of 2002.



Fig 2c Hourly flow comparison for Big sandy creek watershed in Julian days 77 to 80 of 2002.



Fig 2d Hourly flow comparison for Big sandy creek watershed in Julian days 89 to 91 of 2002.



Fig 2e Hourly flow comparison for Big sandy creek watershed in Julian days 156 and 157 of 2003.



Fig 2f Hourly flow comparison for Big sandy creek watershed in Julian days 145 and 146 of 2003.



Fig 2g Hourly flow comparison for Big sandy creek watershed in Julian days 162 to 169 of 2003.

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This section explains additional details regarding the project:

The results from the study suggest that the model has to be evaluated for simulation on hourly basis. Mainly, the overland flow routing method for hourly rainfall input should be evaluated carefully to take into account the volume of water routed through the main channel. Also, this study clearly explains the effect of spatial variability of rainfall in runoff estimation. As the spatial and temporal resolution increases, increase in runoff simulation can be achieved. The study is being continued to use bias adjusted radar values and also to evaluate overland flow routing component of the model.

Effect of Flow Velocity on Biodegradation of Trichloroethene (TCE) and Perchlorethene (PCE) During Restoration of Contaminated Groundwater Aquifers

Basic Information

Title:	Effect of Flow Velocity on Biodegradation of Trichloroethene (TCE) and Perchlorethene (PCE) During Restoration of Contaminated Groundwater Aquifers	
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- 1. Cunningham, J.A., and I. Mendoza-Sanchez, Equivalence of Two Models for Biodegradation During Contaminant Transport in Groundwater, submitted to Water Resources Research (Appendix).
- Cunningham, J.A., and I. Mendoza-Sanchez (2004), On the Equivalence of Two Models for Biodegradation during Contaminant Transport in Groundwater, Eos Trans. AGU,85(47), Fall Meet. Suppl., Abstract H21E-1069 0800h (Appendix 1).
- 3. Mendoza-Sanchez I., (2005) Modeling the Effect of Groundwater Flow Velocity on Contaminant Biodegradation, Texas A&M University Water Week, Student Poster Competition (Appendix 1).
- 4. Mendoza-Sanchez I., (2005), Modeling the Effect of Mass Transfer on Contaminant Biodegradation in Groundwater, Texas Water 2005, Texas AWWA and WEAT, Student Presentation of Papers (Appendix 1).

FINAL REPORT:

Effect of flow velocity

on biodegradation of trichloroethene (TCE) and perchloroethene (PCE) during restoration of contaminated groundwater aquifers

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1. EXECUTIVE SUMMARY

Chlorinated ethenes (CE) are widespread contaminants in groundwater. Bioremediation of chlorinated ethenes is a viable low cost technique for decontamination of CE-contaminated sites. However, bioremediation is not fully controlled due to the lack of information of the phenomena involved. The purpose of this project is to improve our ability to predict and engineer the complete dechlorination of PCE and TCE to ethene in contaminated groundwater.

A mathematical model that accounts for the transport of the contaminants and the growth and detachment of the relevant bacteria has been developed. The mechanisms included in the mathematical model to characterize the contaminant biodegradation are: mass transport in the bulk liquid by advection and dispersion, mass transfer from the bulk liquid to the biofilm (BF) by diffusion, molecular diffusion within the BF, biological reaction within the BF, growth of the active bacteria, and shearing of the biofilm under the influence of groundwater flow. A simplified version of the mathematical model (which assumes the bacterial populations are at steady-state) has been solved numerically using a finite difference method with operator splitting and an iterative solution procedure.

The most important findings of the present study are: a) the numerical solution of the mathematical model is a practical approach to solve contaminant-reactive transport in porous media, b) preliminary results suggest that chemical mass transfer rate may be a limiting factor in the rate of biodegradation, b) chemical mass transfer depends on the flow velocity, therefore flow velocity may have a significant impact on the extent and/or rate of biodegradation of PCE. The next steps are: to implement the bacterial growth and detachment mechanisms in the model; to construct the lab-scale aquifer model; to design the operation of the experimental model based on the final results of the mathematical model; and to observe if the numerical simulation is able to predict experimental results.

2. INTRODUCTION

Trichloroethene (TCE) and perchloroethene (PCE, also known as tetrachloroethene) have been widely used as solvents and degreasing agents. Due to their wide use, their historic improper disposal, and their recalcitrance to degradation, TCE and PCE are widespread contaminants in groundwater. Because of their toxicity and suspected carcinogenicity, contamination of groundwater by TCE and PCE prevents the use of groundwater for drinking, irrigation, or nearly any other beneficial use. According to the U.S. Environmental Protection Agency (EPA) web site, there are, within the state of Texas, 26 sites on the National Priority List (also known as Superfund sites) at which the groundwater is contaminated. At most of these sites, the groundwater contaminants include chlorinated volatile organic compounds (VOCs), such as PCE, TCE, or other chlorinated solvents.

Biodegradation of PCE under anaerobic conditions is conducted by bacteriallymediated sequential reductive dechlorination [1]. That is, PCE is converted sequentially to TCE, dichloroethene (DCE), vinyl chloride (VC), and finally ethene, a benign endproduct. Transformation of PCE to TCE and DCE is observed at almost all contaminated sites, but degradation of DCE to VC and ethene has been observed only at some sites. Consequently, DCE and VC often accumulate at contaminated sites. VC is the most toxic and carcinogenic of all the chlorinated ethenes.

Several factors have been identified that may affect the degree of dechlorination observed at contaminated sites. These factors include: the presence or absence of the dechlorinating bacterium *Dehalococcoides ethenogenes* [2–5]; the presence and activity of syntrophic fermentative bacteria to produce hydrogen for the dechlorinating species; a sufficient supply of electron-donating compounds [6–7]; competition among dechlorinating, sulfate-reducing, and methanogenic bacteria for nutrients and electron donors [8–9].

Finally, there is one factor that may be quite important with regard to the degree of dechlorination, but that has received relatively little attention so far: the flow velocity of the groundwater. Cabrirol et al. [10] observed that sulfate influenced the degree of dechlorination in batch reactors, but not in flow-through column reactors. This effect was attributed to two phenomena, namely, the rate of chemical mass transfer through the active biofilm and the relative ability of different bacteria to adhere to the biofilm surface.

During the period of March 1, 2004 to February 28, 2005, the effect of flow velocity on biodegradation of perchloroethylene (PCE) and trichloroethylene (TCE) during restoration of contaminated groundwater aquifers was studied.

3. PROJECT GOALS

The objective of this research is to quantify the effect of groundwater flow velocity on the biodegradation of perchloroethene (PCE) and trichloroethene (TCE).

The hypothesis is that groundwater flow velocity may be one important factor with regard to the degree of dechlorination. Flow velocity may affect two important phenomena; the rate of chemical mass transfer through the active biofilm (BF), and the relative ability of different bacteria to adhere to the biofilm surface.

4. RESEARCH APPROACH

The work proposed in the original statement is to conduct experiments in sand columns to observe and analyze the effect of groundwater flow velocity on the biodegradation of PCE and TCE. In order to properly design the experiments and interpret the results, it is first necessary to develop a relatively sophisticated conceptual and mathematical model.

4.1. Conceptual Model

The framework of the mathematical model is that the rate of transformation of the contaminant will be a function of the flux of substrate from the bulk solution to the surface of the biofilm (see figure 1). The model will account for transport processes in the bulk solution, the mass transfer from the bulk solution to the biofilm, and diffusion and degradation inside the biofilm.



Figure 1. Schematic representation of the conceptual model

4.2. Mathematical Model

The equation used to describe the flux of substrate in the bulk solution is the advection-dispersion equation (ADE). Mass transfer is described adding a mass transfer term to the ADE equation resulting in an advection-dispersion-mass transfer equation (ADMTE) (1). Definition of the terms in the equation is given in table 1 at the end of this section.

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} - v \frac{\partial C(x,t)}{\partial x} - \frac{3(1-n)}{nR_1} \mathbf{a} \left[C(x,t) - C_{BF}(x,R=R_1,t) \right]$$
(1)

Biodegradation is described inside the biofilm considering molecular diffusion and microbial transformation simultaneously. The microbial transformation is described using Monod Kinetics with a dual substrate limitation and competitive inhibition reaction (2). Hydrogen will be the limiting chemical substrate, and competition will exist between PCE, TCE, DCE, and VC for the available hydrogen to be used in the dechlorination process.

$$\frac{\partial C_{BF}(x,R,t)}{\partial t} = D_{BF} \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial C_{BF}(x,R,t)}{\partial R} \right) - \frac{qXa(x,R,t)C_{BFi}(x,R,t)}{C_{BFi}(x,R,t) + K_i \left(1 + \frac{C_{BFj}(x,R,t)}{K_j} \right)} \quad \text{for } \mathbf{R}_0 < R < R_1 \quad (2)$$

$$\left(\frac{H(x,R,t) - H^*}{H(x,R,t) - H^* + K_h} \right)$$

The ADMT equation is coupled with the biofilm equation through the boundary condition in equation 3.

$$n_{BF} D_{BF} \frac{\partial C_{BF}(x, R = R_1, t)}{\partial R} = \boldsymbol{a} \left[C(x, t) - C_{BF}(x, R = R_1, t) \right]$$
(3)

The set of equations presented were solved for a hypothetical sand column with flow of PCE-contaminated water through the porous medium. For this case the boundary conditions, related to equation 1 are as follow: a) flux into the column equals flux just inside the column (4), and b) there is no dispersive flux at the end of the column (5).

$$v\frac{\partial C(x=0,t)}{\partial x} - D\frac{\partial C(x=0,t)}{\partial x} = vC^{0}$$
(4)

$$\frac{\partial C(x=L,t)}{\partial x} = 0 \tag{5}$$

The boundary conditions for the biofilm equation (2) are the following. Mass flux to the surface of the biofilm ($R=R_1$) equals mass flux away from the surface of the biofilm (3). The boundary condition at the surface of the grain ($R=R_0$) is that there is no contaminant flux into the grain (6).

$$\frac{\partial C\left(x, R = R_0, t\right)}{\partial x} = 0$$

No contaminant is present as an initial condition.

$$C(x,t=0)=0$$

(7)

(6)

Table 1. Definition of the terms used in the equation	ons.
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Symbol	Definition	Dimen
		sions
С	Concentration of the chemical in the bulk solution	ML ⁻³
v	Flow velocity of the groundwater	LT^{-1}
D	Dispersion coefficient	L^2T^{-1}
Ν	Porosity of the column	1
RO	Radius of the grain	Т
R1	Radius of the grain + length of the biofilm thickness	L
α	Mass transfer coefficient from the bulk to the biofilm	LT^{-1}
C _{BF}	Concentration of the chemical inside the biofilm	ML ⁻³
C _{BFi}	Concentration of the competitive chemicals inside the biofilm	ML ⁻³
C _{BFj}		
Xa	Biomass concentration in the biofilm	ML ⁻³
n _{BF}	Porosity of the biofilm	1
D _{BF}	Diffusion coefficient within the biofilm	L^2T^{-1}
\hat{q}	Maximum specific dechlorination rate	$M_{s}M_{x}^{-1}$
K _i K _j	Half velocity coefficient for dechlorination	ML ⁻³
Н	H2 concentration inside the biofilm	ML ⁻³
H*	Threshold concentration of H2 for dechlorination	ML-3
K _h	Half velocity coefficient for hydrogen consumption	ML ⁻³

4.3. Solution Procedure

The equations 1 and 2 are solved using initial and boundary conditions 3 to 7. Since the biofilm equation (2) is non-linear we solve the set of equations by splitting the ADMTE (1) and the biofilm equations (2), and coupling them by the boundary condition (3). The coupled equations have been solved using finite difference methods and Runge Kutta with operator splitting and an iterative solution procedure. We use the following procedure at each time step to solve the set of equations.


This procedure allows us to use the best method to solve each operator. We split the system of equations in three operators: the advection-dispersion-mass-tranfer operator (1), the diffusion operator of the biofilm equation (2) and the reaction operator of the biofilm equation (2). Implicit finite difference method (Crank Nicolson) has been used to solve the ADMT and the biofilm diffusion operators, while fourth order Runge-Kutta was used to solve the biofilm reaction-operator.

Using the presented operator-splitting procedure it is possible to use different time steps for each operator, avoiding instabilities when using the Runge-Kutta numerical method. In addition different space steps and time steps may be used when instability problems occur when solving the implicit finite difference method. So the operatorsplitting-iterative process helps us to save time and CPU operations compared to a whole system solution.

5. RESULTS

5.1. Modeling Results

Preliminary results for PCE reactive-transport along a cylindrical column with homogeneous grains were obtained (see figure 2). Further development of the numerical modeling is necessary to obtain values of concentration of PCE, TCE, cis-DCE, VC, ethene, hydrogen, and biomass density in space and time. Results from the mathematical model will be used to design the chemical and biological analysis necessary in the experimental phase of the project.



Figure 2: Concentration at the surface of the biofilm mass transfer coefficient (a) units is cm/day

6. RECOMMENDATIONS FOR FUTURE WORK

6.1 Laboratory Experiments

The design of the soil columns as lab-scale models of contaminated aquifer has been completed. Columns consist of acetal delrin hollow rods with 0.05 m (2 inch) inside diameter, 0.06 m (2.5 inch) outside diameter, and 0.76 m (30 inch) length. This material was chosen due to its resistance to chlorinated ethenes. The hollow rods (tubing) will be sealed at the top and bottom with two 0.08 m (3 inch) diameter discs of the same material. The discs, top end, and bottom end of the tubing will be threaded and tap so the discs could be screwed and sealed to the tubing. Both discs will be drilled to allow a 0.015 m (5/8 inch) to 0.06 m (1/4 inch) stainless steel reduction union to provide inlet and outlet of water coming through the column. A stainless steel screen will be placed in the interior of each disc to prevent solid particles from exiting with the flow of water. The columns were designed to have sampling ports located at every 0.20 m along the column. The sampling ports were constructed by drilling the columns to allow 0.06 m (1/4 inch) stainless steel unions (1/4 inch NPT to 1/4 inch Swagelok). Sampling ports are equipped with 0.008 m (10/32 inch) Thermogreen GC septa in order to avoid introduction of oxygen each sampling time. Twelve identical columns will be constructed. Figure 3 shows a diagram of the column design.

Columns will be wet-packed with well-graded 0.002 m mean diameter sand. Before packing each column will be sterilized. Approximately 0.05 m section of the top and bottom of the column will be filled with 0.002 m mean diameter glass beads. Each column will be filled half full with de-ionized water. Saturated sand will be poured into the column and allowed to settle. Discs will be screwed and sealed to the top of the column. After packing each column will be placed in horizontal position.

Water flow rates through the columns were designed to span the range of realistic groundwater flow velocities. Thus columns will be fed at the following velocities: 0.01, 0.03, 0.05, 0.07, 0.09, and 0.12 m/day. So we will obtain a travel time range from 6 to 76 days. Each column will receive water at a constant rate by means of a peristaltic pump consisted of a Masterflex **(B)** L/S**(B)** variable speed economy drive, 3 L/S**(B)** 4-Channel, 8

roller pump heads equipped with Masterflex ® L/S® small cartridges. Each pump channel with a defined velocity will be connected to each column. Twelve columns will operate at six different flow rates so two columns will have the same hydraulic conditions in order to replicate the tests.



Figure 3. Column design

Contaminated water of known chemical composition will be pumped through the column continuously until equilibration. Then biodegradation will be initiated by inoculating the columns with a culture that is known to degrade PCE completely to ethene

Samples will be taken at regular intervals from the columns' sample ports. We will define the sampling size and intervals from the preliminary mathematical model results. It is likely that at early times more frequent intervals will be required, while at later times more spaced intervals will suffice. Samples will be taken by means of gas

tight syringes and will be analyzed for the concentration of chlorinated ethenes, ethene, hydrogen, and biomass concentration.

Analysis of chlorinated ethenes, ethene, and hydrogen will be performed by means of gas chromatographs equipped with flame ionization detector, thermal conductivity detector, and reduction gas detector.

Change in culture composition along space and time will be obtained in order to correlate velocity with community structure. Biomass concentration will be estimated by volatile suspended solids analysis of the samples. Analysis for biological community structure this will be accomplished by using appropriate molecular biological tools (DGCE, T-RFLP, PCR).

6.2. Additional Mathematical Modeling

Follow-up work to the mathematical and experimental modeling is to conduct a sensitivity analysis of the mathematical model. These results will allow us to determine how the dechlorination rate of TCE and PCE depends upon the groundwater flow velocity.

7. SUMMARY AND CONCLUSIONS

The mathematical model developed in this project represents a first step to improve our ability to predict and engineer complete dechlorination of PCE and TCE to ethene in contaminated groundwater.

To date, the effect of flow velocity on the extent of biodegradation of chlorinated ethenes has been only mildly explored or quantified. This project is significant because it will model the degradation potential of dechlorinating consortia based on flow velocity, chemical transport, and microbial transport in a contaminated aquifer. This, in turn, will allow us to advance the field of bioremediation. For instance, new tools or strategies that might result from this project include: determination if a particular contaminated site would be amenable to remediation by natural attenuation; optimization of the design of engineered remediation strategies that involved forced gradients (i.e., injection or extraction wells); and/or a method for determining the optimal location and rate of microorganism addition during bioaugmentation.

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Development of Smoke Tracer Instrumentation for Groundwater Recharge Investigations in the Edwards Aquifer Region

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SMOKE TRACER SYSTEM DESIGN

DEVELOPMENT OF SMOKE TRACER INSTRUMENTATION FOR GROUNDWATER RECHARGE INVESTIGATIONS IN THE EDWARDS AQUIFER REGION

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Development of Smoke Tracer Instrumentation for Groundwater Recharge Investigations in the Edwards Aquifer Region

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SMOKE TRACER SYSTEM DESIGN

INTRODUCTION

I. Project Objectives: The current project focuses on the development of instrumentation for investigations of brush control impacts on shallow subsurface flow paths in the Edwards Aquifer region. Current research at the Honey Creek State Natural Area and the Camp Bullis training area north of San Antonio, Texas has demonstrated that applied rainfall on large plot areas moves predominantly through discrete conduits and fractures in the subsurface layers. For the Honey Creek site, lateral subsurface flow is observed directly through a trench located at the downhill end of the project plot. While the subsurface flow outlets are easily identified by their discharge into the trench, the contributing zones on the plot surface that feed these outlets and the degree of interconnection between conduits remains unknown. While two dye tracer tests have been carried out in an attempt to address these questions, dyes present a number of limitations. Dyes reveal only the general area of surface inlets and cannot pinpoint exact inlet locations; additionally, they tend to persist in the soil, limiting their effectiveness for multiple tests. However, it may be possible to locate discrete inlets by using a gaseous tracer traveling from an outlet location to the plot surface to identify inlet points. As such, the objectives of this study are: (1) to develop a small, portable, non-invasive portable injection system that uses smoke as a tracer for fractured geologic material (2) determine locations of flow path inlets for the project plot, (3) identify flow path interconnections for the plot, and (4) assess the feasibility of using smoke as a tracer in the Edwards Aquifer region.

II. Use of Smoke as a Tracer: Smoke has been successfully used as a medium to trace air movement in a broad range of fields. It is an especially common tool for testing ventilation systems for domestic, industrial, and agricultural facilities, as well as for locating leaks in piping and other closed-conduit flow systems. In some situations with favorable soil conditions, buried conduits for wastewater/storm water movement can be tested in isolated sections using concentrated smoke at high airflow rates. However, natural geologic formations display a much greater deal of physical complexity than artificial conduit systems and as such must be examined from a different perspective. The size of natural preferential flow paths may span orders of magnitude, ranging from hairline fractures and root-associated soil macropores to large caverns. Even in situations where the potential range in flow path size is known, it is difficult to determine the degree of flow path interconnection with nondestructive techniques. Although smoke has seen only limited use in natural geologic studies, early work by Sasaki et al (2000) indicate the potential for smoke to be used in fractured rock settings; in their study on fracture distributions and persistence, the researchers noted visible smoke travel through fractures ranging in size from approximately one millimeter to over one meter in width, with distance of movement in some cases reaching 100 m and with travel time of approximately 25 minutes. However, the location used for the Sasaki et al study consisted primarily of fractured rock with little or no soil cover. The karst landscapes of the Edwards Aquifer region are considerably more complex, with highly heterogeneous limestone formations overlaid by soils with various textures and depths as well as complex vegetation patterns. As such, one cannot assume that the results of the earlier study will be replicated exactly in different settings, even over a relatively small distance

III. <u>Conceptual Design Review</u>: Although the research team has developed several different tracer system designs during the course of the project, all of the different systems have conformed to the conceptual design presented in the project proposal. Primary components of the system include an airflow source, smoke generation/containment chamber, a conveyance line network, an injection port, and an adjustable compression member. The injection port is placed over a fracture or conduit outlet and sealed against the rock face using some form of airtight, compressible material. Compression is provided by a hydraulic jack and transmitted to the injection head through a beam. Airflow from the blower unit moves through the conveyance lines to the generation/containment chamber where smoke enters the air stream. The smoke-laden air then travels through the conveyance line to the injection port, where it will enter the fracture outlet. All components are small and modular, simplifying assembly and disassembly in enclosed spaces.

SITE FOCUS

The smoke tracer project has focused primarily on outlets contributing to an artificial trench at the project plot in the Honey Creek State Natural Area. However, additional brush control study sites are located over caves, which allow monitoring of deep subsurface flow rather than shallow flow. If the smoke tracer concept can be adequately demonstrated at Honey Creek, it is likely that the tracer project will shift focus to more cave-based applications.

CONSTRAINTS

I. <u>Physical/Implementation</u>: As stated in the objectives, the design must be small, portable, and non-invasive. It must be able to perform under a variety of conditions and in any orientation. Additionally, it must be capable of forming an airtight seal against irregular surfaces.

II. <u>Environmental</u>: Although initial application and testing for the project are focused on exposed rock face in an artificial trench, future project stages may expand the scope of the study to incorporate testing in natural cave formations. Due to the importance of such features to aquifer recharge and the fragile nature of cave ecosystems, the study requires significant environmental consideration. Any injected smoke or particulate tracer should not reduce surface or groundwater quality or flow properties in any way, nor should it harm cave dwelling species or surface vegetation. Additionally, in accordance with standard caving practices, the equipment should not damage cave formations.

III. <u>Safety</u>: Although the study uses non-toxic smoke cartridges, any source of fine particulate matter can act as an irritant, especially in enclosed situations. To insure the safety of researchers, system components must be inspected for air tightness in the field prior to testing. Additionally, all entrances to the project trench or caves must remain clear to allow free movement of personnel out of enclosed spaces. For a more detailed list of project constraints see Appendix A.

ITERATIVE DESIGN PROCESS

I. <u>Method</u>: While the basic concepts of air conveyance are easily applied in a well-understood setting such as a ducting network, applying these concepts to field conditions presents a considerable challenge. In a natural and complex geologic setting such as the Honey Creek project site, where the hydraulic properties of individual flow paths remain largely unknown, equipment specifications cannot rely on idealized equations or standard equipment. As such, the smoke tracer project makes use of an iterative design method. While trial and error testing exhibits little technical sophistication in of itself and requires considerable time, it is the only method of translating the conceptual design into a functional system. To date there have been four major design iterations for the project, with minor variations on the iterations developed during laboratory testing. The research team is currently considering a fifth major design using somewhat larger components and a more powerful blower than earlier systems.

II. <u>Evaluation Procedure</u>: Each design iteration was evaluated under laboratory conditions before consideration for field testing. Several criteria were applied in a set order to determine the feasibility of each design.

a. *Implementation*: After the individual components of each design were constructed, the design was evaluated on ease of assembly and transport. All designs passed this criterion easily, with only minor modifications for transport (addition of handles and similar changes). Modifications for assembly were made primarily to conveyance line connections on the smoke generation / containment chamber, which proved to be more difficult than expected.

b. *Smoke Conveyance and Sealing*: All design iterations were also tested on the basis of smoke conveyance and sealing under nonrestrictive flow conditions; the injection port remained uncovered during testing to minimize flow resistance to internal friction and turbulence losses. Small cartridges were loaded into each design to test system smoke production. Tests resulting in little or no smoke production indicated high smoke particle deposition losses within the apparatus or "pooling" of smoke in isolated pockets. Modifications were made where necessary to prevent smoke loss. The small cartridges also allowed the research team to locate and seal any leaks in the generation chambers and at conveyance line connections.

c. *Media Column*: Designs which performed well in previous testing underwent porous media column testing as well. Note that selection for this testing stage was somewhat subjective, with those designs capable of conveying smoke but producing low airflow rejected for further testing. For this stage, designs were tested for the ability to convey smoke through a highly resistive column filled with various media used to simulate geologic profiles similar to those to be encountered under field testing conditions. Lower layers of the testing column consisted of a coarse medium (stone of two to five centimeter diameter) overlaid with finer rock and coarse soils. Designs capable of forcing smoke through the column were judged acceptable for further testing under field conditions.

DESIGN ITERATIONS

I. <u>Prototype Design</u>: The prototype smoke tracer equipment utilized a very basic design, with air moving directly from its source to a simple smoke generation box and then through a conveyance line to the injection apparatus. For illustrations of this design, as well as other iterations, see Appendix B.

a. *Airflow:* The prototype design utilized a Toro Model 51591 Super Blower Vac industrialgrade leaf blower as an airflow source. Alternative sources were considered in terms of peak flow rate, pressure generation, size, weight, and cost; the selected device represented the most favorable combination of the described properties. Although flow rate and pressure generation play an important role in determining system performance, size and weight considerations played a major role in component selection due to the need for easily-portable components for use in remote locations (and possibly under space-limiting conditions). The 3.3 kg leaf blower unit produces a maximum conveyance velocity of 96 m/s and maximum volumetric flow rate of 0.13 m³/s. The current draw listed for the enclosed motor is given as 12.0 amps (Toro 2005).

b. *Power Supply*: Power for the prototype unit was supplied by a Generac Model SV 2400 portable generator system with a rated power output of 2400 watts at 120 VAC. Maximum current draw for the generator is listed as 20 amps, which is adequate for the leaf blower apparatus described above. Total mass of the generator system is 37.2 kg (Generac 2005); although this component outweighs other system components, it remains light enough for transport over rough terrain by no more than two people.

c. *Containment*: The initial design made use of a simple chamber for introduction and containment of smoke. The prototype chamber consisted of a wood-framed plywood box with outer dimensions of 27 cm x 28 cm x 64 cm. Inlet and outlet ports were located on opposite ends of the box with ports centered on the ends. Smoke cartridges were loaded into the box through a 10.2 cm (4") threaded PVC sewer cleanout port mounted on the top face of the box.

d. *Conveyance*: Conveyance of smoke-laden air from the containment unit to the injection apparatus utilized a 7.6 meter section of 5.08 cm diameter swimming pool hose. The thick, smooth-sided hose offers significant material strength and minimal resistance to airflow, although limited flexibility and increased weight increase the difficulty of implementation in the field. However, testing of alternative materials (including portable irrigation hose and lightweight laundry water discharge hose) indicated poor durability and high resistance to airflow.

e. *Injection*: The injection apparatus used for the prototype design is similar to that described in the first quarterly project update, with the body of the injector consisting of two parallel metal plates with a canister connected to the top plate and a pipe leading from the conveyance system to a hole in the upper plate, centered within the ring formed by the injection canister. f. *Seal*: The primary seal for the prototype design consisted of a two-centimeter layer of closed-cell foam pipe wrap ringing the end of the injection canister. Under field conditions a layer of urethane foam was applied at the injection head/trench wall interface as a secondary seal to cover small cracks not sealed by the closed-cell foam.

g. *Smoke Source*: The initial tracer system design used small, colored-smoke cartridges (of the type commonly used on model airplanes) as a smoke source. The cartridges selected were Regin HVAC Model RC 104 cartridges, with a listed smoke production of 34 m³ and a burn time of approximately three minutes (Regin HVAC 2005). Testing carried out by the project crew indicated that the cartridges typically exhibit a shorter true burn time of roughly 2 minutes and 15 seconds, with the cartridge orientation and rate of ambient airflow having little effect on burn time. In spite of this shortcoming, the cartridges were retained for use in the project due to their small size and relatively low price.

h. *Variations*: The research team constructed several variations on the prototype design before settling on the unit described above. The earliest configuration used a hinged lid on the smoke generation chamber rather than a round port for candle loading. While the lid allowed the use of smoke cartridges of various sizes, it did not seal easily and resulted in smoke loss. In another variation, a valved tee was connected to the round loading port on the top of the chamber, enabling cartridges to be loaded without venting air from the chamber. However, this design was abandoned due to problems with smoke deposition in the tee.

i. *Laboratory Testing*: The prototype design operated well under laboratory conditions, with only minor modifications required to the initial configuration. The most significant problem with the prototype design was that of sealing, with the smoke generation chamber displaying a significant number of leaks during early testing. The unit also performed well during media column testing, with several locations of smoke emergence from the top of the media column. Note that for this design a large diameter column with coarse media was used; a taller, narrower column with a more realistic media profile was developed to test later designs.

II. <u>Combined Blower and Containment System</u>: The second major design utilized a combined blower and containment system approach in order to circumvent the sealing problems encountered for the prototype design. By placing the airflow source within the smoke generation and containment chamber, air was drawn into the box rather than forced through by the blower. As such, any leaks in the box allowed fresh air to enter the box rather than permitting smoke to escape.

a. *Airflow*: For the combined blower and containment system, a new blower unit was installed within the smoke containment and generation chamber, with the blower outlet located at the chamber outlet. The blower selected was a Jabsco Model 34744-0000 flange mounted blower. The 2.3 kg blower unit produces a maximum volumetric flow rate of approximately 0.05 m^3 /s, roughly a third of that produced by the leaf blower. The current draw listed for the attached motor is given as 0.75 amps (Jabsco 2000).

b. *Power Supply*: The second design used a permanent laboratory power supply during the testing process. Because the blower did not include any integrated speed control, power for the unit was routed through a dimmer assembly, allowing flow rates to be adjusted smoothly between a no-flow condition and full power.

c. *Containment*: The smoke generation and containment unit for the second design was very similar to that used in the prototype, with the chamber body consisting of a wood framed plywood box with dimensions 29 cm x 30.5 cm x 91 cm. The inlet and outlet openings were placed in the same manner as the openings for the prototype chamber. The flange mounting plate on the blower attached to the inside of the chamber, centered about the outlet connection. Rather than installing a loading port in the box, the research team replaced the plywood box top with a 29 cm x 91 cm sheet of clear polycarbonate; because the combination blower and containment system required no sealing, the top was simply placed on top but not fastened. This allowed the project team to observe movement of smoke through the chamber; once smoke depletion was observed, the lid was slid aside by several inches, a new cartridge was added to the chamber, and the lid was replaced.

d. *Other Components*: For this design, no changes were made to the conveyance system or the injection apparatus. No new seal materials were tested during this stage.

e. *Laboratory Testing*: This design performed poorly in laboratory testing. While the system did convey smoke to the injection apparatus under unrestrictive conditions, the ability of the blower to handle resistance to flow was minimal and flow rates were much lower than expected. Although this system clearly failed to perform in a satisfactory manner, its complete lack of smoke leakage indicated benefits of combining the blower and containment components.

III. <u>Modified Combined System</u>: The third major design iteration developed directly from the second design and could be considered a variation of this earlier design. However, because a completely new containment system was built and several variations were made on the new equipment, it is described here as a separate design.

a. *Airflow*: The modified combined system returned to the leaf blower used in the first design as its airflow source. While the actual blower mechanism did not require modification, the project team had to remove the unit's handle and inlet guard so that it would fit into a smoke chamber of similar dimensions as the previous box.

b. *Power Supply*: The modified combined system also used a permanent laboratory supply for testing. Although the blower unit included a two-position speed selection switch, including the blower in the box rendered the switch inaccessible. As such, the power supply for this design was also routed through a dimmer assembly for speed control.

c. *Containment*: The containment unit for this design was similar to that used in the earlier combined system, consisting of a 28 cm x 32 cm x 91 cm wood framed plywood box with inlet and outlet ports on opposite ends and an upper surface consisting of polycarbonate sheeting. Because the leaf blower did not have a built-in mounting plate, a wooden frame was constructed inside the containment unit to hold the blower in place and elevate the blower inlet above the floor of the chamber.

d. *Other Components*: For this design, no changes were made to the conveyance system or the injection apparatus. The project team did test a new material during this stage. Various thicknesses of fiberglass insulation were tested as potential seals due to the high compressibility of the material, but the highly porous nature of the insulation proved to be a very poor seal for surfaces of high relief.

e. *Variations*: The design team attempted to several variations on this unit with regard to the cartridge loading procedure. Several different loading tees were installed at the inlet of the smoke chamber to allow for more rapid loading of cartridges; however, all of the tee configurations tested severely limited airflow and resulted in significant smoke loss due to deposition on internal surfaces.

f. *Laboratory Testing*: The modified combined system performed quite well in most aspects of the laboratory testing process. Smoke production and airflow were comparable to that produced by the prototype, while the internal blower system eliminated the smoke leakage which had caused problems with the first design. The modified combined system also offered considerable ease of implementation, reducing total size and the overall number of components for transport and assembly. Unfortunately, the enclosed design did not permit for proper cooling of the blower and prevented the unit from operating continuously for more than ten minutes without a severe drop in performance.

IV. <u>Side Chamber System</u>: The fourth major design concept constructed for the project departed from the directly in-line component approach of earlier designs, although it is essentially a modification of the side canister configuration (in-line chamber configuration D) presented in the first project report. These changes were made to facilitate more rapid changing of smoke cartridges while improving containment during reloading. Details of the design are presented below.

a. *Airflow*: The side chamber system utilized the same leaf blower apparatus as the first and third designs. An open wooden frame elevated the blower approximately three feet from the ground, reducing unnecessary flow resistance at the blower inlet.

b. *Power Supply*: The research team used a permanent power supply for laboratory testing, while field testing utilized the same generator apparatus as the prototype. For both laboratory and field experimentation, power was routed through the dimmer assembly built for the modified blower/containment system. However, lower speed settings were only used for minor troubleshooting; all testing was carried out at the maximum speed setting.

c. *Containment*: As stated earlier, the side chamber system departed from the in-line chamber approach used in other iterations. The main body of the containment unit consisted of a 7.6 cm diameter (3") pipe with inlet and outlet connections at opposite ends. Two vertical loading chambers connected to the bottom of the main pipe through tees located along the main line. Smoke cartridges could be inserted into the loading chambers through an access port at the chamber bottom; when not in use, the ports were sealed with a threaded cap. A viewing window mounted in the main line near the outlet enabled the project crew to monitor smoke movement and determine when to load a new cartridge.

d. *Injection*: For the side chamber system, the injection apparatus used in earlier designs was retained but underwent minor modification. The injection canister was removed from the front plate of the injection apparatus to provide a greater surface area for sealing against the rock face.

e. *Seal*: Due to the long curing time of the urethane sealant used for prototype testing and the poor performance of closed-cell foam and fibrous insulation, the design team chose a malleable modeling clay as a sealant material. This clay provided an easily-removable, reusable seal which performed well in both laboratory and field testing. Additionally, implementation time for the clay seal was far less than for the urethane foam.

f. *Smoke Source*: Due to the need to increase smoke density and to decrease the frequency of reloading, the project team chose to abandon the smaller Model RC 104 smoke cartridges in favor of a large cartridge with a longer burn time. The new cartridge selected was the Model S107 cartridge, with approximate smoke yield of 510m³ and a burn time of roughly eight minutes. Results of field testing by the project crew indicate positive performance by these cartridges, with high smoke yields and burn times up to 10 minutes.

g. *Variations*: The initial configuration for the side chamber system utilized a more complex vertical loading chamber arrangement. The loading chambers were initially much longer, with valves for each chamber to allow loading without venting smoke-laden air. However, preliminary testing showed that the longer chambers trapped all of the smoke. As such, the vertical chambers were shortened until smoke trapping was reduced to an acceptable level.

h. *Laboratory Testing*: The side chamber system performed extremely well during laboratory testing, producing as much smoke as the prototype system while offering a much better loading mechanism and the ability to monitor airflow through the system. During media column testing, the system conveyed smoke through a column consisting of 60 cm of coarse stone, 30 cm of coarse gravel, 30 cm of wet sand, and 5 cm of cedar leaf litter.

FIELD TESTING PROCEDURE

I. <u>Initial Test</u>: For the initial test, the prototype system was assembled in the trench with only the generator remaining outside of the trench. The injection apparatus was centered around flow outlet A_1 on the trench face and pressed into place using a wooden beam and a bottle jack braced against the opposite wall of the trench. Urethane foam was applied around the contact of the injection head and the trench face and allowed to dry, after which the system was switched on and the seal was tested using small smoke cartridges. Additional urethane foam was applied to leak locations and the testing process was repeated until all leaks were sealed. The system was then switched on and loaded with smoke cartridges; the system was run for approximately seven minutes before being shut down due to smoke buildup in the trench from smoke emergence from flow outlets on the trench face.

II. Second Test: For the second test, the side chamber system was assembled in the trench with the generator remaining on the outside of the trench. A clay ring of two inches in thickness was built up around location A_1 and the injection apparatus was pressed against the trench face in the same manner as for the first test. The system was switched on and the seal was tested using small smoke cartridges. Additional clay was used to seal all leaks. After all leaks were eliminated, the system was loaded with the RC104 cartridges used with the prototype and allowed to run for ten minutes, during which smoke emergence from other flow outlets in the trench face was monitored. All locations producing smoke were then covered with clay and the system was restarted using large S107 cartridges. The system continued to operate for 20 minutes, after which the side chamber system failed due to warping caused by the heat generated by the large smoke cartridges. The side chamber unit was quickly replaced with the prototype chamber and the test was restarted using the large cartridges. Total test time using the prototype chamber was 20 minutes. See Appendix C for images of field testing and results.

FIELD TESTING RESULTS AND DISCUSSION

I. Flow Path Interconnection:

a. *Results*: For the first test, smoke injected into location A_1 was observed emerging from locations A_2 , A_3 , and A_5 in Region A and locations B_2 and B_3 in Region B (see Appendix D). Response time was inversely proportional to distance from the injection point, with nearby A_2 and A_3 responding within 20 seconds, A_5 responding in approximately two minutes, and B_2/B_3 responding after five minutes. Outlet size appeared to play a subordinate role in outlet smoke production as compared to injection to proximity. Although the largest outlet (A_5) produced the greatest amount of smoke, the B_2/B_3 conduits produced far less smoke than the much smaller fractures in Region A.

Results from the second test differed somewhat from those generated in the initial field test. For the second test, smoke emerged from the same three locations in Region A, with nearsimultaneous emergence of smoke from outlets A_2 and A_3 and later emergence from A_5 . Response times were much slower than for the first test, with smoke emerging from A_2 and A_3 after approximately thirty seconds and from A_5 after five minutes. Overall smoke production/density was also reduced; while A_2 and A_3 were almost unchanged in smoke production, the A_5 outlet, which dominated flow for the first test, produced only faint traces of smoke. No smoke was observed from any location in Region B.

b. *Discussion*: Give the results of the flow path interconnection tests, it is quite clear that some of the preferential flow paths which contribute lateral subsurface water flow to the trench are interconnected. This possibility had been considered likely in the past. Data from earlier dye tracer studies at the plot indicate several locations in Regions A and B which connect to similar plot surface locations; locations A₁, A₂, A₃, B₁, B₂, and B₃ all transmit water from both the forward portion of the plot and the area around the tree in the center of the plot. Several locations also displayed similarly-timed responses to rainfall application, suggesting that the flow networks had some degree of interconnection. However, the emergence of smoke from outlets in the trench face proves at least some degree of interconnection exists. Although this information is of interest to the major research projects at Honey Creek, one must note that while hydraulic interconnection has been demonstrated, air and water are very different fluids with significant differences in behavior. While water will tend to flow downward from the plot surface, the more readily apparent buoyancy effects of the warm, smoke-laden air may allow it to rise into void spaces not normally accessed by water.

While both tests demonstrated physical connection of subsurface flow paths, the differences in response times and locations also require consideration. The simplest explanation would be that the system used for the second test was itself inefficient in conveying air and smoke through the system. However, this seems unlikely since laboratory testing showed that the second system could rapidly convey smoke through a highly restrictive media column. Given the size of the smoke producing outlets and the rapid rate of water movement through the subsurface during rainfall, it is probable that these conduits themselves are less restrictive than the media column. Because antecedent moisture conditions were higher for the second test, it is possible that some portions of conduits were filled or nearly filled with

water in a ponded condition, reducing the size and number of flow paths available for air movement.

Recent observations of the trench under field conditions suggest that failure of smoke to appear from the B_2/B_3 area may represent an actual change in conduit structure rather than simply water ponding. While this area once produced the majority of the flow into the trench for simulated rainfall events, for recent events it has produced little flow, while flow from A_1 has increased dramatically. Alteration of the flow paths contributing to B_2/B_3 , possibly from sediment clogging or soil pocket collapse, may explain the lack of movement of both smoke and water through these outlets.

II. <u>Inlet Locations</u>: Smoke emergence was not detected at any location on the plot surface for either test. Because airflow was maintained through the tracer units during testing, there are three possible explanations for the lack of smoke emergence which must be considered:

a. *Smoke Loss*: The first is that air may have in fact moved from the injection point through subsurface flow paths to the plot surface but without retaining a detectable concentration of smoke particles. A number of factors could prevent the suspended particles from reaching the surface. If the transit time of the air through the conduits was greater than the suspension time of the smoke particles, the particles may have settled out of the air stream. Smoke particles may also have adhered to the sides of the conduits and soil macropores without settling.

b. *Simulation Time*: Simulation time may have been insufficient for the injected smoke to reach the surface. If the simulation duration was less than the time required for air from the blower to move to the plot surface, no smoke would be observed.

c. *Alternate Paths*: Smoke-laden air may have traveled through flow paths to a location other than the plot surface. As with any fluid, the amount of air that flows through particular pathways is proportional to resistance to flow; the majority of the air will flow through the pathways that offer the least resistance. If the injected air encountered a less restrictive flow path before reaching the plot surface, it would take the easier path and little or no air would reach the surface inside the plot. This is essentially what happened during the first field test, when the least restrictive paths led back to the trench face rather than to the plot surface. This scenario seems quite likely for the second test as well, given the highly complex nature of the subsurface flow paths.

EVALUATION AND FUTURE WORK

Given the results of field testing at the Honey Creek project site, the research team has evaluated the feasibility of small, portable smoke tracer equipment as a tool for geologic research in the Edwards Aquifer region. While the equipment performed quite well in determining flow path interconnections and coordinated well with dye tracer testing results and field observations, it failed to reveal the surface flow inlets of the plot. Although the prototype and side chamber systems were physically capable of forcing smoke through restrictive media, complex field conditions and an unpredictable moisture regime seemed to limit applicability in complex, highly fractured settings. Since the equipment did achieve some of the objectives set forth and follows a precedent set by a larger scale study, the project team intends to continue the project but will likely shift the focus to even more discrete flow paths in a less fractured setting. It is also likely that future work will utilize the more powerful blower system currently in development by the project team.

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APPENDIX A

PROJECT CONSTRAINTS

PHYSICAL/PERFORMANCE CONSTRAINTS

-Adjustable from 1.5 ft to 6 ft in height

-Device performance independent of orientation (horizontal, vertical, angled)

-Lightweight components

-Easy assembly/disassembly in confined spaces

-Capable of forming an airtight seal against uneven surfaces (up to 2-inch differences in relief).

-Equipped for regulation/monitoring of air flow, pressure, possible smoke content

-Conveys air against resistance to flow caused by narrow flow path

-Power supply and blower can be located far from injector

-Injection ports are a modular component

-Unit contains fine adjustment to compensate for minor irregularities in rock surface

-All structural components designed for durability

ENVIRONMENTAL CONSTRAINTS

-No harm caused to cave formations or surface

-No permanent staining of rock surfaces

-Surface/groundwater quality is not impacted by smoke residue

-Cave dwelling species and surface plants are not harmed

-Natural water flow properties cannot be changed

SAFETY CONSTRAINTS

-Smoke source fully contained

-No smoke released into cave volume

-Unit is capable of rapid shutoff

-Cave access is not blocked

APPENDIX B

DESIGN DRAWINGS













APPENDIX C

FIELD TESTING



Injector apparatus in the trench



Injector apparatus in the trench







Jack apparatus



Smoke chamber after test



Smoke emergence from A5



Smoke emergence from A3





Region A



Smoke emergence from B2/B3



Another view of B2



Side chamber system in trench



Cartridge loading







Seal and injection head



Seal functioning after test

APPENDIX D

OUTLET LOCATIONS



Smoke Injection and Emergence Locations (Note: Region A only)

Radar-Based Flood Alert System for Austin, Texas

Basic Information

Title:	Radar-Based Flood Alert System for Austin, Texas
Project Number:	2004TX158B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	2670
Research Category:	Social Sciences
Focus Category:	Floods, Models, Surface Water
Descriptors:	Flooding, Geographic information systems, RADAR
Principal Investigators:	Erin E. Williford, philip b. bedient

Publication

1. No publication.
TWRI Progress Report

"Radar Based Flood Alert System for Austin, Texas"

by Erin E. Williford

Rice University

December 2004

Note: Erin was funded by a TWRI USGS grant awarded in 2004. She is now working as an engineer for J.F. Thompson, Inc, in Houston, Texas.

INTRODUCTION

Overview

Flood Warning Systems have been in use for three decades and have steadily increased the ability to predict peak flows at a point of interest in a watershed while alerting city officials and residents to flooding conditions. Currently, the City of Austin has a localized Flood Early Warning System (FEWS) in place that utilizes a series of approximately 80 rain gages that report rainfall rate and amount and 40 creek and lake gages that monitor water levels and flow rates. While this system provides useful information, much like any gage based system; it has the potential to malfunction during operation giving incorrect data and also cannot provide the complete spatial coverage as that of radar based flood warning systems. For this reason, a real-time flood warning system is being developed for the Onion Creek watershed in Austin, Texas.

The rainfall events of October 1998, November 2001, and July 2002 were historically damaging storms for the City of Austin due to flooding; therefore developing a Flood Alert System for the Onion Creek watershed in South Austin is necessary. Flooding problems are prominent in areas of the watershed where tributaries intersect the main branch of Onion Creek as well as in the downstream, urbanized areas of the watershed.

The system follows the template used in the Flood Alert System (FAS-1) that has been a valuable tool in flood prediction for the Texas Medical Center in Houston, Texas. Developing a similar system for Onion Creek proves to be a challenge. The watershed spans approximately 340 square miles and varies in elevation. The Austin hill country is mostly composed of sedimentary limestone and calcitic rocks, and is underlain by the Edwards Aquifer. The Edwards Aquifer is a karst, therefore complex, aquifer that adds additional dimension to the hydrologic modeling and FAS development for Onion Creek.

The availability of Next Generation Radar (NEXRAD), hydrologic modeling tools, Geographic Information Systems (GIS), and internet capabilities has made the development of advanced, real-time flood warning systems possible. Operation of the Flood Alert System for Austin (FAS-Austin) begins with the radar data obtained from the National Weather Service's NEXRAD, KEWX, in San Marcos, Texas. This radar data is produced in terms of radar reflectivity data which then is directly converted into rainfall estimates. These rainfall estimates are transformed into flow values that are used in flood predictions and flood warnings.

The rainfall is input directly into HEC-1, a flood hydrograph package developed by the Hydrologic Engineering Center. HEC-1 converts rainfall directly into runoff in a manner that allows for fast computations using hydrologic parameters such as subbasin characteristics, loss rates, and river routing that have been computed using GIS or have been gathered from a HEC-HMS model created by the United States Army Corps of Engineers and the City of Austin for Onion Creek. Quick results are available every five to six minutes, which corresponds to the time it takes the radar to make one complete volume scan of the atmosphere. The results, therefore, give flow values in real-time. Large historical rainfall events and hypothetical storms have been calibrated for Onion Creek and its tributaries to ensure the model's prediction accuracy. In addition to FAS-Austin, a pattern recognition program called PreVieux is being used to help predict flooding. PreVieux is a product of Vieux and Associates that uses radar data to project a storm one hour into the future which provides a more precise warning for heavy rainfall to a specific area of the watershed.

Once fully operational, this state-of-the-art Flood Alert System at Onion Creek will provide an increased lead time and accurate predicted flows for the City of Austin. Lead time, is the amount of time available from the point where a prediction is made using modeling technologies to the time of a peak flow predicted. Increasing the lead time allows for more flood precautionary measures to be implemented. The increased lead time and accurate flow levels will give city officials and emergency personnel a chance to perform road closures and administer high water warnings. The accuracy of the Flood Alert System will also help prevent the loss of life in the event of a flood and raises awareness of the elevated dangers associated with severe flooding.

Motivation for Research

Since 1993, nearly 45 billion dollars in damage has occurred and at least 599 people have lost their lives due to flooding disasters (not including hurricanes) in the United States. The National Oceanic and Atmospheric Administration (NOAA) estimates that while only seven percent of U.S. land is designated as flood plains that nearly fifty percent of the communities in the United States are affected by flooding. The number of those affected by flooding continues to rise each year by a percent or two. Table 1.1 is data taken from NOAA and shows a brief list of damaging floods in recent history throughout the United States. The location of the flooding, the dates of the storm events, the amount of monetary damage, and the number of deaths in each case is listed.

Date	Location/Flood Problem	Damage	Deaths
Summer 1993	Midwest	\$21 billion	48
	Flooding		
October 1994	Texas	\$1 billion	19
	Torrential Rain		
1995	Northern California	\$3.6	unknown
	Flooding		
May 1995	Texas, Oklahoma, Louisiana,	\$5-\$6 billion	32
	Mississippi		
	Rain, Hail, Tornadoes		
January 1996	Northeast, Mid-Atlantic,	\$3 billion	187
	Appalachians		
	Blizzard Snow Melt		
Winter/Spring 1998	Southeast	\$1 billion +	132
	El Nino rainfall		
June 2001	Gulf Coast/Texas	\$5.1 billion	22
Tropical Storm Allison			

 Table 1.1 Recent Flood Related Damages and Deaths in the United States

The occurrences of damaging floods are not confined to specific regions but are capable of inundating any piece of land that receives ample rainfall. Since controlling the rainfall intensity, duration, and location is not a feasible option to protecting structures and lives from the danger flooding imposes, creating a system that is capable of warning those in harms way is a practical and viable alternative.

George Oswald of The City of Austin comments on the use of the current Flood Early Warning System (FEWS) during the November 2001 Storm as well as the improvements expected with the addition of gage-adjusted radar and FAS-Austin.

"Generally the system was operating very well during the event; a very high percentage of the rain gages and stream gages remained operational under very demanding conditions. Our manually developed warnings and suggested action plans were very accurate. We used IDF curves and historical rainfall/response records to make our calls that night. It was an all out effort of three engineers manually interpreting data and then polling the group for consensus action recommendations. The success in that storm depended on having three individuals with significant knowledge of hydrologic principles, past floods and flood hazard areas. Obviously, radar based rainfall estimations and predictive models have the potential to improve prediction accuracy while reducing the skills set required to issue flood warnings and recommended public safety actions."

The City of Austin has seen devastating floods recently as well and could therefore benefit from a real-time, radar-based flood warning system for the local creeks. Figure 1.1 and 1.2 show two recent flood events that caused major damage to the city and are courtesy of the City of Austin's website. Figure 1.1 shows the flooding associated with the November 2001 rainfall which caused damage throughout Austin and the Onion Creek Watershed. Figure 1.2 shows one home (in Williamson Creek) damaged in the October 1998 storm that caused 20 counties throughout the state of Texas to be declared disaster areas. The October 1998 event occurred when a continuous wave of moisture moved inland from the Pacific Ocean off the coast of Mexico. Almost one billion dollars in damage was reported, 31 people lost their lives, and approximately 7,000 people were evacuated from their homes.



Figure 1.1 November 2001 - Flood waters reached extreme levels causing damage to vehicles and structures.

Figure 1.2 October 1998 – Flood waters in caused extensive damage in this Williamson Creek home.

Figure 1.3 was provided by the City of Austin and is a map of Onion Creek. It shows the location of Onion Creek in relation to downtown Austin, the counties encompassed by the creek, major highways in the area, and the eight major tributaries that feed into Onion Creek. Other things to note on this map include the areas encircled with red. These indicate the flood-prone areas in Onion Creek. Special attention should be paid to Williamson because it is one of the most urbanized areas in Onion Creek and experiences more potential for loss of property and loss of life during a flood event than any other location in the watershed. Onion Creek, in general, is in need of a radar based flood alert system that will aid the city officials, emergency personnel, and local citizens in flood prediction with the goal to reduce the amount of property that sustains damage and prevent the loss of life.



Figure 1.3 – Location of Onion Creek and its tributaries in relation to Austin, Texas, areas encircled with red indicate flood prone areas of the watershed.

The channel of Onion Creek at different locations in the watershed can be seen in Figures 1.4 and 1.5. Figure 1.4 is Onion Creek as it is seen in the upper end of the watershed. Figure 1.5 shows Onion Creek as it flows through one of Texas' state parks.



Figure 1.4 Onion Creek Channel near Driftwood, Texas



Figure 1.5 Onion Creek Channel in McKinney Falls State Park

Research Objectives

- Use Geographical Information Systems and HEC Geo-HMS to delineate subareas and gather hydrologic parameters for Onion Creek to be used in a Real-Time Flood Alert system for the City of Austin, Texas.
- 2. Develop a HEC-1 model for Onion Creek within a GIS framework and calibrate the model to observed data for several storm events using radar rainfall and hypothetical events.
- Examine recharge characteristics of the Edwards Aquifer as it relates to the accurate prediction of hydrologic response in the upper portion of the Onion Creek Watershed.
- 4. Use the calibrated HEC-1 model along with Next Generation Radar (NEXRAD) data to develop a real-time model that predicts the flow at various points of interest in the watershed.
- 5. Provide guidance and up to date information regarding real-time flooding issues for city officials and emergency personnel.

CONCLUSIONS AND FUTURE RESEARCH

Conclusions

ArcView GIS along with various extensions was used to delineate the Onion Creek watershed and to gather values needed to calculate parameters that are used to hydrologically describe the watershed. The USACE HEC-HMS Model that was created by the USACE in conjunction with the City of Austin was applied to the subareas delineated in ArcView GIS. Hydrologic parameters from the HMS model were reviewed and used to the extent possible. Parameters describing each of the 61 subareas in Onion Creek and the Onion Creek channel including the basin area, loss method, transform method, and routing method, along with gage-adjusted radar rainfall data were used to create the Onion Creek HEC-1 Model.

In addition to the model calibration, recharge characteristics of the Edwards Aquifer were examined and tested in the model. The model was created as the basis for a Flood Alert System servicing Onion Creek in Austin, Texas. Three historical storm events, including the June 1997, November 2001, and the June 2004 storms, were input into the model for calibration efforts and design storm parameters were applied to the model in various instances to better understand the hydrologic response of the watershed and to provide guidance to Austin officials. Conclusions derived from this model creation and storm calibration are listed in detail.

• The Onion Creek HEC-1 Model performed with much more accuracy than the USACE HEC-HMS Model for the November 2001 storm. The success in the HEC-1 model is attributed to more accurate hydrologic parameters and to the subareas chosen for the model.

- It was originally thought by the City of Austin that the November 2001 storm was less than a 100-year event. After modeling uniform rainfall it is evident that the non-uniform November 2001 event was greater in magnitude than a 100-year event producing a peak flow of 93,200 cfs. The November 2001 storm is one of the largest events ever recorded on Onion Creek. With the model created in this study the November 2001 storm was more accurately defined.
- The radar data from Vieux and Associates, Inc (used in the HEC-1 model)
 produced outflow values that matched the measured data far more accurately than
 the NEXRAIN radar data (used in the HEC-HMS model) as seen in Figure 6.3.
 NEXRAIN data is processed differently than the data from VAI such that it
 produced a skewed rainfall product.
- The recharge zone for the Edwards Aquifer is present across approximately 75 square miles of the 340 square mile basin, although it directly affects half of the watershed. The recharge zone is a place where water enters the underground aquifer. The amount of recharge is solely dependent on the amount of rainfall the area receives. For Onion Creek, recharge becomes a more prominent issue as the intensity and duration of a storm increase. For instance, in the large rainfall event of November 2001 recharge accounted for approximately half of the volume of water in the Onion Creek channel above the Driftwood gage. However, in the smaller June 1997 and June 2004 events the model results matched the measured outflow more accurately when recharge wasn't included.
- Based on the previous conclusion regarding recharge, the Onion Creek HEC-1 Model that was used for the smaller June 1997 and June 2004 events should be

the primary model used in the Flood Alert System for Onion Creek. This is primarily due to the frequency of events that are more similar to the June events modeled. In addition, the Onion Creek HEC-1 Model that includes recharge should be run simultaneously during rainfall events for the uncommon but more devastating larger storms where recharge is a factor.

- Another recharge conclusion revolves around the issue of the stream flow in the channel prior to a storm event. If the antecedent flow is very low there is a better chance that as the next storm moves over the watershed the percentage of water lost to recharge will be high. Compare this situation to one where the flow in the channel is fairly high just before a storm. As this storm moves though, the saturated channel bed does not permit much infiltration to the aquifer. Thus, the recharge is less for events where flow in the channel is higher prior to the storm.
- Design storm data was put into the Onion Creek HEC-1 Model. The output from these various model runs shows that the location in the watershed where precipitation occurs affects the peak and the length of time for that peak to occur. Rainfall in the lower end of the watershed has the most adverse affects on the basin, and rainfall in the upper end affects the basin the least. This proves that it is important to know not only the intensity of the precipitation, but also the location where the rain is likely to fall.
- The use of radar rainfall data in the model calibration provided accurate results. The improvements in the quality of the radar data over time are obvious when comparing the results seen in the outflow hydrographs for the June 1997 event and the June 2004 event. In 1997, radar data was widely used but still lacked

accuracy. Today, there have been numerous technological advances such as the improved understanding of the Z-R relationship that enhance the quality and accuracy of the radar data that is available for input into the Onion Creek HEC-1 Model that weren't available in 1997.

Future Research

In addition to the work done in this study, there is still much more to do in relation to the project. These ideas to further the research in this area include the following list.

- Continued calibration to various rainfall events would be useful to get the Onion Creek HEC-1 Model as prepared for real-time use as possible. The results from another large event similar in magnitude would be useful if the radar data exists for such a storm.
- Program the Onion Creek HEC-1 Model to run in simulation mode for various storms to compare the real-time capabilities of the model to the existing Flood Early Warning System's response and the USGS Stream Gage data. After the real-time simulation is complete, a continual feed of radar data can be directly dropped into the calibrated model for model results in real-time and displayed on a website to make the flow data and the alert levels available to the public, emergency personnel, and city officials.
- The low water crossings that are in the process of being installed at approximately ten to 15 locations in Austin, Texas should be tied into FAS-Austin to create a more complete flood warning system.
- In addition to the actual installation of FAS-Austin other research related options include the application of Flood Alert System's to other flood prone areas in Texas and elsewhere.
- The issue of slope in the Onion Creek watershed is an important factor that makes this watershed unique. While slope was analyzed in this study in a GIS

framework it is an topic worthy of future study. Taking a closer look at slope calculations and issues would be helpful in further understanding the hydrologic response of the basin.

- To increase the accuracy of the model used, LiDAR data could be used in place of the 30 meter DEM to delineate the watershed. LiDAR maps an area on a much smaller scale on the order of ten feet between data points with 15cm of vertical accuracy (Whitko, 2004). LiDAR can be sampled every six inches, but in many cases data this detailed overloads computer systems. Detailed data of this magnitude would be useful for more accurate slope calculations in Onion Creek where slope is a concern.
- Recharge to the Edwards Aquifer is a complex and variable component of this study that poses many questions that need to be examined more closely. Different recharge modeling techniques, a more in depth study relating to the karst aquifer, or anything else that would further the knowledge of this issue would be useful.

Bridging the Gap Between Plankton Dynamics and Spatial Variability in Water Quality in the Guadalupe Estuary (Texas): The Importance of Freshwater Pulses

Basic Information

Title:	Bridging the Gap Between Plankton Dynamics and Spatial Variability in Water Quality in the Guadalupe Estuary (Texas): The Importance of Freshwater Pulses		
Project Number:	2003TX112G		
Start Date:	9/1/2003		
End Date:	8/31/2004		
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Descriptors:	Estuary, Freswater Inflows, Salinity		
Principal Investigators:	Stephen Edward Davis, Daniel L. Roelke		

Publication

- 1. Will present preliminary findings of research in Estuarine & Tidal Wetlands Session at the 2004 Annual Meeting of the Society of Wetland Scientists, Seattle WA. Abstract entitled: Determining the Importance of Freshwater Inflows to Ecological Structure and Function in the Bays and Marshes of the Guadalupe Estuary (TX).
- 2. Roelke, D., S. Davis, G. Gable, H-P. Li, C. Miller. 2005. Biological response during a >300-day period of high-inflow in San Antonio Bay, TX: Fixed station data. Estuarine Research Federation. Norfolk, VA, USA. October 16-21. (abstract accepted for presentation).
- Davis, S., D. Roelke, G. Gable, H-P. Li, C. Miller. 2005. Physical, chemical, and biological responses to inflow events in Galveston and San Antonio Bays (TX): Bay-wide characterizations. Estuarine Research Federation. Norfolk, VA, USA. October 16-21. (abstract accepted for presentation).
- Davis, S.E., B. Allison, R. Butzler, G. Gable, C. Miller, and D. Roelke. 2004. Determining the Importance of Freshwater Inflows to Bay-Marsh Structure and Function in the Guadalupe Estuary (TX). Society of Wetland Scientists. Seattle, WA, USA. July 19-23.
- 5. Davis, S.E., B. Allison, T. Assal, R. Butzler, G. Gable, C. Miller, and D. Roelke. 2004. Determining the Importance of Freshwater Inflows to Ecological Structure and Function in the Bays and marshes

of the Guadalupe Estuary (TX). Gulf Estuarine Research Society, Pensacola, FL, USA. October 8-9.

- 6. Roelke, D.L., S. Davis, C. Miller, T. Assal, G. Gable, Hsiu-Ping Li. 2004. Freshwater inflows and productivity in the Guadalupe Estuary: Use of high-resolution spatial mapping. TX Sea Grant Researcher Conference. Port Aransas, TX. September 23-24.
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BRIDGING THE GAP BETWEEN PLANKTON DYNAMICS AND SPATIAL VARIABILITY IN WATER QUALITY IN THE GUADALUPE ESTUARY (TEXAS): THE IMPORTANCE OF FRESHWATER PULSES

Research Progress Report

May 26, 2005

Submitted to:

National Institutes of Water Resources

Through:

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> USGS Project ID# 2003TX112G TAMU Account No. 57136800

INTRODUCTION

In accordance with the reporting policies established by the National Institutes of Water Resources, this report describes the activities undertaken by researchers at Texas A&M University throughout the first 20 months of funding (September 1, 2003 through May 26, 2005) for project ID # 2003TX112G. Please refer to the accompanying portable document file entitled SanAntonioBay.pdf for figures (i.e. slides) referenced throughout the report.

The San Antonio Bay system is a lagoonal estuary located along the Texas coastal bend. It is approximately 500 km² in area and is fed by the Guadalupe River, that accounts for approximately 70% of gauged, freshwater inflows to the bay system. This amounts to an average of about 2 million acre-feet of freshwater inflow each year. The region immediately around the estuary is mostly agricultural with littler residential development (**Slide 1**). Aransas National Wildlife Refuge is located within this estuary as are the wintering grounds of the only naturally migrating population of whooping cranes (Grus Americana) in the world (currently numbering 216 birds).

Recently, water managers in central Texas proposed to divert about 100,000 acre-feet of freshwater each year from the lower Guadalupe River to meet growing needs for potable water in the San Antonio metropolitan area. During an "average" year, this diversion would amount to roughly 5% of inflows. Although the diversion is not expected to start until 2011, we saw the need to study the importance of freshwater inflows in driving estuarine loadings, water quality patterns, and estuarine function. The overall goal of this project is to understand how this particular estuarine system responds to a range of inflow characteristics (pulse magnitude, pulse duration, pulse frequency, etc.) from the Guadalupe River. We hope our findings from this research will be helpful in developing future water management plans for this region that protect necessary habitat for commercially important species such as blue crabs, shrimp, and oysters in addition to protecting marsh habitat for whooping cranes.

TASKS COMPLETED

After resolving confusion over the accounting and location of funds transferred from the U.S. Geological Survey, we had access to our grant's account on October 9, 2003. At that point, we began the process of acquiring necessary field and lab equipment to initiate our study in the Guadalupe Estuary. This involved updating necessary quotes for items and submission purchase order requests. The major equipment purchases supported by this project are: 1) a **Dataflow unit** to be used for high resolution spatial sampling of water quality in the Guadalupe Estuary, 2) a **refrigerated water sampler** to sample surface water from the lower Guadalupe River. Data from these samples will be used in conjunction with USGS gage data to quantify loading of materials into the estuary, and 3) an **incubator array** to conduct experiments on the effects of water residence times and salinity on plankton community dynamics.

We currently support 3 graduate students (2 MS and 1 PhD) in part with the funds from the National Competitive Grant from USGS. These students are utilizing these cutting edge techniques, some of the data generated from this project, and infrastructure supported by the study to conduct their respective graduate projects.

Dataflow Mapping

Due to purchasing delays and bidding problems, Texas A&M University did not release a purchase order for the construction and delivery of the Dataflow unit until February 2004. We expected to have the Dataflow unit "in hand" by April 2004 and "field ready" before our anticipated first sampling in May 2004. Unfortunately, the unit did not arrive until July 2004. We conducted our first field test in San Antonio Bay on July 30, 2004, running a coarse set of transects that covered the entire bay system. The test was deemed a success, but the sampling transects needed to be refined. We ran another field test on Lake Somerville, a freshwater reservoir near College Station, TX on October 12, 2004. This reservoir sampling was also a success, and afforded us the confidence to schedule our first full complete sampling of San Antonio Bay for October 28, 2004. See **Slide 2** for pictures of the Texas A&M Dataflow system in operation.

Technical problems arose during this first sampling of San Antonio Bay, as rough weather and choppy conditions on the bay periodically disabled the Dataflow system. We were only able to sample half of the bay before the power was completely cut off to the sensors. Although the Dataflow was designed to function in a small boat, the excessive rough water conditions caused several of the power leads to sever and resulted in a redesigning of the power distribution system. By late November 2004, repairs were complete and the system was ready for another field test in Lake Somerville. This test was conducted on December 4, 2004 and was successful. As a result, the next sampling of San Antonio Bay was scheduled for January 2005. Since then, the unit has been in operation on a monthly basis (see **Table 1**). We had technical problems with the salinity/conductivity sensor in January and February 2005), but these problems have since been corrected. Also, a sensor for photosynthetically active radiation (PAR) was added in March 2005 and a depth sensor will be added soon.

Flow conditions in the Guadalupe River have varied by more than 4,000 cfs among our samplings thus far (**Slide 3**). However, we have not seen low flow values in the Guadalupe River (i.e. less than 1000 cfs) since the project began. We anticipate seeing these lower inflows as we progress into the late summer. July and August are typically the driest months of the year and are thus characterized by the lowest flows—with means of 97,868 and 78,386 acre-feet per month, respectively.

Table 1: List of Dataflow samplings and parameters measured in San Antonio Bay, TX.

Dates	Parameters
July 30, 2004	transmissivity, chl a, DOM, temperature, salinity/conductivity
October 12, 2004	transmissivity, chl a, DOM, temperature, salinity/conductivity
January 4, 2005	transmissivity, chl a, DOM, temperature
February 25, 2005	transmissivity, chl a, DOM, temperature
March 28, 2005	transmissivity, chl a, DOM, temperature, salinity/conductivity, PAR
April 25, 2005	transmissivity, chl a, DOM, temperature, salinity/conductivity, PAR

We sample approximately 160 linear miles of San Antonio Bay during each Dataflow run and collect more than 5000 rows of data (see **Slide 4** for example). At the conclusion of each run, all data are transferred from the datalogger to a PC. They are subjected to a thorough QA/QC check, are archived in Excel format, and are backed-up multiple times to prevent loss. Maps for each parameter from each sampling are generated in both Surfer and ArcGIS using standard interpolation (e.g. nearest neighbor) techniques. All maps from the sampling trips in **Table 1** are contained in the accompanying portable document file (see **Slides 5–36**) and are available in digital or high quality, hard copy format upon request.

Estuarine Loadings

This project supported the establishment of an automated water sampler based in the Lower Guadalupe River, near the saltwater barrier (**Slide 37**). Working with representatives of the Guadalupe-Blanco River Authority (GBRA), we were able to establish this sampler in August 2004. This involved GBRA installing an electrical outlet (110 volt) to power our sampler for the duration of the project (see images in **Slide 38**). This same site also houses a USGS gauging station (station # 08188800 Guadalupe River near Tivoli, TX). Flow data generated from this station are used in conjunction with nutrient data derived from analyses on the water collected by our sampler to estimate nutrient loading into the estuary.

We are currently in the process of requesting to have the power directly connected to the sampler via a junction box. The current set-up requires the use of a fault-protected receptable. Unfortunately, this set-up is very sensitive to regional storm activity and power surges that trip the fault protector, resulting in a loss of power to the sampler and refrigerator. Consequently, we have lost a large number of samples due to contamination and inability to pump water from the channel. We hope to have this problems corrected in the coming months and feel this direct connection will prevent future problems and data loss.

Since late October 2004, we have been using the sampler to collect and refrigerate water samples on a tri-daily basis. 4, 250 ml sub-samples are collected at 18-hr intervals and injected into a 1-liter bottle within the sampler's refrigerator unit. Thus, these composite, tri-daily samples represent water quality conditions over a 3-day period of time. Sub-samples are always collected at dawn (6 AM), midnight (12 AM), dusk (6 PM), and noon (12 PM) to represent diurnal variation in light and temperature conditions. Thus far, the samples we have been able to analyze from this sampling station spanned a period of record high flows in the lower Guadalupe River during November 2004 (**Slide 39**). Concentrations of total suspended solids were quite high throughout this period of high flow, but loadings to the estuary were overwhelmingly driven by flow more than by concentration. These samples have been analyzed for nutrient content, but the data are currently being analyzed and nutrient loadings will be included in a future report.

Fixed-Station Sampling

This project also supports a fixed-station sampling program across San Antonio Bay. We selected 8 sites along the estuarine salinity gradient and within the area to be sampled with the Dataflow system (**Table 2**). See **Slide 40** for sampling station ID number and approximate site location within the estuary. We have been sampling each of these sites since February 2, 2004. At each of these sites, we collect basic water quality measurements (Secchi depth, temperature, pH, salinity, dissolved oxygen, etc.) with a handheld water quality meter. We take water

samples for nutrient (inorganic N, P and Si) analyses. We take Schindler trap and plankton net tows for qualitative and quantitative measurements of the plankton community. Lastly, we collect surface water in order to conduct light/dark bottle experiments to measure primary productivity and community respiration in the water column. The latter experiments are carried out over a 2-4 hr period of time between the hours of 10 AM and 2PM. See all current fixed-station data in **Slides41–51**.

ID	Latitude	Longitude	General Location Description
1	28°19.00'	96°36.00'	Espiritu Santo Bay
2	28°16.00'	96°41.00'	San Antonio Bay
3	28°14.00'	96°44.00'	San Antonio Bay
4	28°18.00'	96°45.00'	San Antonio Bay
5	28°21.00'	96°44.00'	San Antonio Bay
6	28°23.00'	96°48.00'	Hynes Bay
7	28°26.00'	96°46.00'	Guadalupe Bay
8	28°30.20'	96°53.04'	Lower Guadalupe River

Table 2: GPS coordinates and location description for all eight fixed sampling sites in the Guadalupe Estuary.

Plankton Incubations

This project also provided funds to build a plankton incubator array. The entire array is complete and fully functional (see **Slide 52**). To date we have conducted three laboratory experiments that investigated the influence of flow magnitude and mode on dynamics of natural plankton assemblages. Experiments were conducted in the summer and autumn (2004), and winter (2005). A fourth laboratory experiment is being initiated this month (spring 2005). Preliminary results from the summer 2004 experiment indicated that mode of inflow (continuous vs. pulsed) had little effect on accumulated phytoplankton biomass or secondary (zooplankton) productivity when inflow was low, i.e., 0.5x average hydraulic residence time for San Antonio Bay. However, when inflows were at the average and 2x the average hydraulic flushing, mode of inflow had a profound impact on plankton dynamics. Pulsed inflows resulted in a doubling of the accumulated phytoplankton biomass, and a near 10-fold increase in secondary productivity (i.e. zooplankton; **Slide 53**).

SUMMARY OF PLANNED ACTIVITIES

- We just completed our May 2005 Dataflow and fixed-station sampling. We also brought "whole" water back to the lab and immediately initiated our 3rd incubation experiment.
- The June 2005 trip has not been scheduled yet, but we will continue to perform our samplings each month for the duration of the study. We also intend to repeat samplings on consecutive days during high inflow events or during an extended drought as described in our proposal.
- Both PIs (Davis and Roelke) will present preliminary findings of this research in Norfolk, VA at the 2005 Biennial Meeting of the Estuarine Research Federation. See references below in "Contributed Talks" for titles and list of co-authors.

CONTRIBUTED TALKS

Roelke, D., S. Davis, G. Gable, H-P. Li, C. Miller. 2005. Biological response during a >300-day period of high-inflow in San Antonio Bay, TX: Fixed station data. Estuarine Research Federation. Norfolk, VA, USA. October 16-21. (abstract accepted for presentation)

Davis, S., D. Roelke, G. Gable, H-P. Li, C. Miller. 2005. Physical, chemical, and biological responses to inflow events in Galveston and San Antonio Bays (TX): Bay-wide characterizations. Estuarine Research Federation. Norfolk, VA, USA. October 16-21. (abstract accepted for presentation)

Davis, S.E., B. Allison, R. Butzler, G. Gable, C. Miller, and D. Roelke. 2004. Determining the Importance of Freshwater Inflows to Bay-Marsh Structure and Function in the Guadalupe Estuary (TX). Society of Wetland Scientists. Seattle, WA, USA. July 19-23.

Davis, S.E., B. Allison, T. Assal, R. Butzler, G. Gable, C. Miller, and D. Roelke. 2004. Determining the Importance of Freshwater Inflows to Ecological Structure and Function in the Bays and marshes of the Guadalupe Estuary (TX). Gulf Estuarine Research Society, Pensacola, FL, USA. October 8-9.

Roelke, D.L., S. Davis, C. Miller, T. Assal, G. Gable, Hsiu-Ping Li. 2004. Freshwater inflows and productivity in the Guadalupe Estuary: Use of high-resolution spatial mapping. TX Sea Grant Researcher Conference. Port Aransas, TX. September 23-24.

Roelke, D.L., S. Davis, J. Pinckney, Y. Buyukates, C. Miller, T. Assal, G. Gable. 2004. Use of high-resolution spatial mapping to estimate plankton response to freshwater inflows entering the San Antonio Bay System. Meeting of the Texas Parks and Wildlife Freshwater Inflow Research Group. McKinney Roughs, TX. September 8.

Roelke, D.L., S. Davis, J. Pinckney, C. Miller, T. Assal, G. Gable. 2004. Use of high-resolution spatial mapping to estimate plankton response to freshwater inflows entering Galveston Bay: Importance to watershed development and ecosystem health. Meeting of the Research Coordination Board of the Galveston Bay Council Galveston Bay Estuary Program. Webster, TX. August 19.

Davis, S., D.L. Roelke, D.L., R.D. Slack, W. Grant, B. Allison, T. Assal, R. Butzler, G. Gable, K. Gil de Weir, H. Li, K. Millenbach, C. Miller, D. Rutka. 2004. Determining the Importance of Freshwater Inflows to Ecological Structure and Function in the Bays and Marshes of the Guadalupe Estuary. Meeting of the Texas Parks and Wildlife Freshwater Inflow Research Group. McKinney Roughs, TX. September 8.

Land-Use and Wetland Area Around the San Antonio Bay System



Dataflow in Action

bringing the water on-board

sensor array and datalogger



Measures GPS coordinates, Temperature, Salinity/Conductivity, Beam Transmittance, Chlorophyll *a*, CDOM, Depth, and PAR at approximately 8 second intervals from a vessel running at 20 kts.

Mean Daily Discharge (August 2004–May 2005) in Lower Guadalupe River (at Victoria)



Provisional Data Subject to Revision

Example of Transects Followed in Sampling San Antonio Bay with Dataflow



4

July 30, 2004 Temperature (°C)













Salinity in San Antonio Bay

July 30, 2004 Salinity (PSU)



11

Salinity in San Antonio Bay



Salinity in San Antonio Bay


Salinity in San Antonio Bay



Conductivity in San Antonio Bay



Conductivity in San Antonio Bay



July 30, 2004 Transparency



* higher value indicates water of higher clarity











July 30, 2004 Chl *a* (µg l⁻¹)













July 30, 2004 CDOM (µg l⁻¹)













PAR* striking San Antonio Bay



PAR* striking San Antonio Bay



Fixed Sampling Station at the Saltwater Barrier of the Lower Guadalupe River



Sampling Station at the Saltwater Barrier of the Lower Guadalupe River

refrigerated water sampler Guadalupe River

TSS concentrations and 3-day fluxes* from the Guadalupe River to San Antonio Bay



* Discharge data from USGS gauges 08177500, 08188800, 08165700, and 08188500 used to calculate 3-da**gg**uxes (http://tx.usgs.gov/basins.html)

Fixed Sampling Stations in San Antonio Bay and along the Lower Guadalupe River



Secchi Depth at Fixed Sampling Stations in San Antonio Bay



1° Productivity and Community Respiration at Fixed Sampling Stations in San Antonio Bay



Salinity at Fixed Sampling Stations in San Antonio Bay



[SiO₃] at Fixed Sampling Stations in San Antonio Bay

Day of Year

Day of Year

Station 8: SiO₃ Station 7: SiO₃ . S 150 **1**50 Day of Year Day of Year Station 6: SiO₃ Station 5: SiO₃ 28.50 <u>o</u> 150 Sio 28.45-28.40 Construction (00) 28.35 28.35 28.30 Day of Year Day of Year San Antonio Bay Station 1: Station 4: SiO₃ SiO₃ 28.20-Gulf of Mexico . 150 S Sio 28.15 -96.7 -96.5 Longitude (^OW) Day of Year Day of Year Station 2: Station 3: SiO₃ SiO₃ <mark>ິອ</mark> 150 . 90 150 S

Chlorophyll a at Fixed Sampling Stations in San Antonio Bay



[TP] and [SRP] at Fixed Sampling Stations in San Antonio Bay



[DIN] at Fixed Sampling Stations in San Antonio Bay



Copepod Biovolume at Fixed Sampling Stations in San Antonio Bay



Biovolume of Protozoans and Barnacle Nauplii at Fixed Sampling Stations in San Antonio Bay


Biovolume of Rotifers, Polychaetes, and Cladocerans at Fixed Sampling Stations in San Antonio Bay



Zooplankton Biovolume at Fixed Sampling Stations in San Antonio Bay



Plankton Incubation Chamber Set-up



flow-through phytoplankton reaction chambers



light box with 3 chambers

temperature control bath

Zooplankton and Phytoplankton (fluorescence) Response to Continuous vs. Pulsed Mode of Delivery Under Different Hydrologic Flushing Rates







53

Information Transfer Program

Information Transfer (IT) Plan

The TWRI information transfer plan will consist of the following elements.

1. Newsletter Production. TWRI will publish three quarterly newsletter series, with all newsletters available both in print and on the Institutes website. The newsletters reach a combined circulation of 8,000 readers, and continues to be a popular and effective means to communicate with a variety of targeted audiences

Texas Water Resources is a 12-page newsletter examining Texas water resources-related topics.

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Publicity brochures related to on-going research in irrigation efficiency in the Lower Rio Grande Valley, proper use and benefits of composted dairy manure, watershed protection and water quality issues and land revegetation/restoration practices through the use of composted dairy manure.

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Dairy Compost Utilization: Up to date research data, available resources, and links to publications concerning utilization of dairy compost manure.

North Central Texas Water Quality: Keeps up-to-date activities of on-going research and Extension programs on the North Central Texas Water Quality Project, USDA-NRCA and EPA funded research and Extension Initiatives.

Fort Hood Revegetation: Keeps up-to-date activities of on-going research programs on Fort Hoods Training Facilities, USDA-NRCA funded research Initiatives.

4. Video teleconferences. TWRI will continue to sponsor video teleconferences to publicize results of Institute-funded research projects. Video teleconferences are transmitted to universities statewide.

5. Other Efforts. The TWRI Director, Associate Director, and other TWRI staff will respond proactively to emerging issues and opportunities related to water resources research and educational programs. In consultation with its Advisory Committees, TWRI continually seeks partnership opportunities with other institutions, as well as the water management community, and regulatory and private sectors. TWRI will continue to develop, sponsor, and support special events and publications on an as-needed basis. Additionally, TWRI staff will actively represent the Institute and The Agriculture Program at state water-related organization meetings, conferences, and committees.

Information Transfer

Basic Information

Title:	Information Transfer
Project Number:	2004TX159B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	8th
Research Category:	Not Applicable
Focus Category:	Law, Institutions, and Policy, Management and Planning, Water Use
Descriptors:	Newsletters, Publications, Web site
Principal Investigators:	Bill L. Harris, Clint D. Wolfe

Publication

- TR-248 Economic and Conservation Evaluation of Capital Renovation Projects: Maverick County Water Control and Improvement District No. 1 (Eagle Pass) - Lining Main Canal - Preliminary M. Edward Rister, Ronald D. Lacewell, Allen W. Sturdivant, John R. C. Robinson, Michael C. Popp.
- 2. TR-255 The Water Rights Analysis Package Reference Manual, Version 2.0. Ralph A. Wurbs.
- 3. TR-256 The Water Rights Analysis Package Users Manual, Version 2.0. Ralph A. Wurbs.
- 4. TR-262 Paso del Norte Watershed Council Coordinated Water Resources Database Project. Christopher Brown, Zhuping Sheng, Matt Rich.
- TR-264 Economic and Conservation Evaluation of Capital Renovation Projects: Maverick County Water Control and Improvement District No. 1 (Eagle Pass) - Lining Main Canal Final. M. Edward Rister, Ronald D. Lacewell, Allen W. Sturdivant, John R. C. Robinson, Michael C. Popp.
- 6. TR-266 SWAT 2003: 2nd International SWAT Conference Proceedings. Raghavan Srinivasan, Jennifer H. Jacobs, Ric Jensen.
- 7. TR-269 Urban Water Conservation along the Rio Grande. Valeen Silvy, Ronald Kaiser, Bruce Lesikar, Craig Runyan.
- 8. TR-271 How Much Water is Enough? Using PET to Develop Water Budgets for Residential Landscapes. R. White, R. Havalak, J. Nations, J. Thomas, D. Chalmers and D. Dewey.
- 9. TR-273 Pecos River Ecosystem Monitoring Project. Charles R. Hart, Alyson McDonald.
- TR-274 An Overview of the Operational Characteristics of Selected Irrigation Districts in the Texas Lower Rio Grande Valley: Brownsville Irrigation District. Megan J. Stubbs, M. Edward Rister, Allen W. Sturdivant, Ronald D. Lacewell.
- TR-275 Estimated Benefits of IBWC Rio Grande Flood-Control Projects in the United States. Allen W. Sturdivant, Ronald D. Lacewell, Ari M. Michelsen, M. Edward Rister, Naomi Assadian, Marian

Eriksson, Roger Freeman, Jennifer H. Jacobs, W. Tom Madison, James T. McGuckin, Wendy Morrison, John R. C. Robinson, Chris Staats, Zhuping Sheng, R. Srinivasan and Joshua I. Villalobos.

- 12. TR-277 Exploring Hydrodynamic Modeling of Texas Bays with focus on Corpus Christi Bay & Lavaca Bay. Jordan Furnans.
- 13. TR-278 Resources for Stormwater Managers throughout the Texas Gulf Coast: An Annotated Bibliography. John Jacob, Ric Jensen.
- TR-279 An Overview of Operational Characteristics of Selected Irrigation Districts in the Texas Lower Rio Grande Valley: Hidalgo County Irrigation District No. 2 (San Juan). Megan J. Stubbs, M. Edward Rister, Allen W. Sturdivant, Ronald D. Lacewell.
- TR-280 Estimating the Required Investment to Attain Region M Water Savings Through Rehabilitation of Water-Delivery Infrastructure - 2005 Perspectives. Ronald D. Lacewell, M. Edward Rister and Allen W. Sturdivant.
- 16. TR-282 Comparative Evaluation of Generalized Reservoir/River System Models. Ralph A. Wurbs.
- 17. TR-283 Fundamentals of Water Availability Modeling with WRAP. Ralph A. Wurbs.
- 18. SR 2004-001 The Pecos River Ecosystem Project Progress Report. Charles R. Hart.
- 19. SR 2004-002 Using Renewable Energy to Pump Water. Juan Enciso and Michael Mecke.
- 20. Newsletters: (1) New Waves, Volume 19, number 1. April 2004, (2) New Waves, Volume 16, number 2. July 2004, (3) New Waves, Volume 16, number 3. October 2004.
- 21. Newsletters: (1) Texas Water Resources, Volume 28, number 1. May 2004, (2) Texas Water Resources, Volume 28, number 2. September 2004.
- 22. Newsletters: (1) Rio Grande Basin Initiative Outcomes, Volume 3, number 1. March 2004, (2) Rio Grande Basin Initiative Outcomes, Volume 3, number 2. May 2004, (3) Rio Grande Basin Initiative Outcomes, Volume 3, number 3. August 2004.
- 23. Web sites: (1) Texas Water Resources Institute http://twri.tamu.edu (2) Dairy Compost Utilization http://compost.tamu.edu (3) Fort Hood Range Revegetation http://forthoodreveg.tamu.edu (4) North Central Texas Water Quality http://nctx-water.tamu.edu, (5) Pecos River Basin Assessment Program http://pecosbasin.tamu.edu, (6) Rio Grande Basin Initiative http://riogrande.tamu.edu, (7) Texas Congressional District GIS http://congdistdata.tamu.edu, (8) Texas Spatial Information System http://tsis.tamu.edu, (9) Texas Water Centers http://txwatercenters.tamu.edu, (10) SETAC Water Workshop http://water-workshop.tamu.edu, (11) Buck Creek Water Quality Project http://twri.tamu.edu/buckcreek, (12) Save Texas Water http://savetexaswater.tamu.edu.

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Student Support

Student Support						
Category	Section 104 Base Grant	Section 104 RCGP Award	NIWR-USGS Internship	Supplemental Awards	Total	
Undergraduate	2	0	0	0	2	
Masters	10	0	0	0	10	
Ph.D.	0	0	0	0	0	
Post-Doc.	0	0	0	0	0	
Total	12	0	0	0	12	

Notable Awards and Achievements

Publications from Prior Projects

None