Water Resources Research Center
Annual Technical Report
FY 2007

Introduction

The University of Arizona's Water Resources Research Center (WRRC) promotes understanding of critical state and regional water management and policy issues through research, community outreach and public education. A research and extension unit of the College of Agriculture and Life Sciences, the UA's WRRC is the designated state water resources research institute established under the 1964 Federal Water Resources Research Act. It is also one of five UA centers responsible for implementing the Water Sustainability Program, which receives funding from the UA's Technology and Research Initiative Fund. In addition to conducting water management and policy research and analysis, the WRRC has a strong information transfer program that includes community outreach, publications, conferences, seminars and workshops.

Research Program Introduction

The University of Arizona's Water Resources Research Center operates a research grant and information transfer program under the Water Resources Research Act, Section 104(b). The WRRC typically funds three to five small projects each year. Researchers in the social, biological, physical and engineering sciences, as well as such fields as water management, water law, economics and public health, from the three Arizona universities are invited to apply for grants. A wide range of projects have been funded over the past 40 years. In recent years, projects have emphasized improvements in water supply quality and reliability, and explored new ideas to address water problems in Arizona or expand understanding of water and water−related phenomena. A primary goal of the program is to foster the entry of new research scientists, engineers, and technicians in the water resources field. The program also promotes dissemination of research results to water managers and the public.

The WRRC also and administers competitive grants funded by the U.S. Geological Survey under Section 104(g).

Forward and Inverse Transient Analytic Element Models of Groundwater Flow

Basic Information

Title:	Forward and Inverse Transient Analytic Element Models of Groundwater Flow
Project Number:	2004AZ68G
Start Date:	9/1/2004
End Date:	8/31/2008
Funding Source:	104G
Congressional District:	7th
Research Category:	Ground−water Flow and Transport
Focus Category:	Groundwater, Hydrology, Models
Descriptors:	Ground−water, Hydrology, Models
Principal Investigators:	Shlomo P. Neuman

Publication

1. Kuhlman, Kristopher L. and Shlomo P. Neuman. “Recent advances in Laplace transform analytic element method (LT−AEM) theory and application to transient groundwater flow”, In Computation Methods in Water Resources, Volume XVI, 2006.
2. Kuhlman, K.L. and S.P. Neuman, Recent advances in Laplace−transform analytic element method (LT−AEM) theory and application to transient groundwater flow, Proc. XVIth Intern. Conf. Computational Methods in Water Resources XVI (CMWR XV), June 2005, Copenhagen, Denemark, 2006.
3. Kuhlman, Kristopher L., 2008, Laplace Transform Analytic Element Method for Transient Groundwater Flow Simulation, Ph.D. Dissertation," Department of Hydrology and Water Resources, Graduate College, The University of Arizona, Tucson, Arizona, 239 pp.

USGS-National Institutes for Water Resources Grant Program
Award 200AZ68G
Forward and Inverse Transient Analytic Element Models of Groundwater Flow
Shlomo P. Neuman PI
Brief Progress Report May 23, 2008

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

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

Dr. Kuhlman defended his dissertation successfully on April 24, 2008. His dissertation has been approved by the university and he now holds a doctoral degree. Dr. Kuhlman's dissertation will constitute our final report for this project.

Dr. Kuhlman presented his work at three conferences, including two American Geophysical Union fall meetings (2006 and 2007) and the Computational Methods in Water Resources conference in 2006, which included a publication in the conference proceedings. A paper has been accepted for publication in the Journal of Engineering Mathematics on the topic of his dissertation material, and another paper on a related non-linear application was submitted for publication to the journal Advances in Water Resources.

At least two more publications should come directly out of the work supported by this grant, as well as more applications and extensions to additional topics. These publications will be prepared in the near future.

The LT-AEM has been shown to be useful in application to aquifer test analysis and situations where a simplified, but quick, elegant and accurate solution is adequate. The programs Dr. Kuhlman has written will be available and documented as part of his dissertation and the related publications, as public domain software.

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

Basic Information

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

Publication

1. Conroy, O., A.E. Saez, D. Quanrud, W.P. Ela and R.G. Arnold. 2007. Changes in estrogen/anti−estrogen activities in ponded secondary effluent. Sci. Total Environ. 382: 311−323.
2. Zhang, J., Tomanek, M., Dong, H., Arnold, R., Ela, W., Quanrud, D., Sáez, E. 2007. Fate of Polybrominated Diphenyl Ethers, Nonylphenol and Estrogenic Activity during the Managed Infiltration of Wastewater Effluent. In Press, Journal of Environmental Engineering.
3. Conroy, Otakuye, 2007, Estrogenic and Anti−estrogenic Activity Present in Wastewater Effluent and Reclaimed Water, Ph.D. Dissertation, Chemical and Environmental Engineering, The University of Arizona, Tucson, Arizona, 327p.
4. Engstrom, Jason, 2006, The Fate of Nonylphenol and Polybrominated Diphenyl Ethers in Land – Applied Biosolids, MS Thesis, Chemical and Environmental Engineering, The University of Arizona, Tucson, Arizona, 152p.
5. Leung, Cary, 2008, Fates of Polybrominated Diphenyl Ethers and Nonylphenol in Biosolids Disposed of as Soil Amendments at the University of Arizona Marana Agricultural Center, MS Thesis, Chemical and Environmental Engineering, The University of Arizona, Tucson, Arizona, 110p.
6. Tomanek, Matthew, 2007, Fate of Polybrominated Diphenyl Ethers in Wastewater Treatment, Effluent Application to Recharge Basins, Land Application of Biosolids, and Concentrations in Dust and Air, MS Thesis, Chemical and Environmental Engineering, The University of Arizona, Tucson, Arizona, 84p.
7. Zhang, Jianmin, 2007, Fate of Estrogenic Activity and Specific Endocrine Disrupting Contaminants (4−Nonylphenol and Polybrominated Diphenyl Ethers) during Wastewater Treatment and Effluent Polishing Operations, Ph.D. Dissertation, Chemical and Environmental Engineering, The University of Arizona, Tucson, Arizona, 174p.
8. Engstrom, J., Quanrud, D., and Arnold, R. 2006. Nonylphenol and polybrominated diphenyl ethers: groundwater effects from land−applied biosolids. In: Proceedings, 5th International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water. National Ground Water Association. Costa Mesa, CA March 13−15, 2006.

9. Leung, C., Arnold, R., Ela, W., Saez, E., Quanrud, D. 2007. The fate of polybrominated diphenyl ethers in land−applied biosolids. In: Proceedings, 6th International Conference on Pharmaceuticals and EDCs in Water. National Ground Water Association. Costa Mesa, CA. October 22−23, 2007.
10. Orosz−Coghlan,P., Quanrud, D., Cleveland, C., Stinson, B., Esposito, K., Arnold, R. 2006. Reduction of estrogenic activity during advanced wastewater treatment: application of the U.S. EPA−developed luciferase reporter gene assay In: Proceedings, 5th International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water. National Ground Water Association. Costa Mesa, CA March 13−15, 2006.
11. Quanrud, D., J. Zhang, S. Teske, H. Dong, P. Orosz−Coghlan, P. Littlehat, O. Conroy, R. Arnold, W. Ela, and K. Lansey . 2004. The fate of nonylphenol and total estrogenic activity during wastewater treatment and sludge digestion: a mass balance analysis. In: Proceedings, 4th International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water. Minneapolis, MN. October 13−15, 2004.
12. Teske, S., Arnold, R., Propper, C., Buschmann, S., Quanrud, D., and Ela, W. 2007. Fate of 17b estradiol and total estrogenic activity at six municipal wastewater treatment facilities in Arizona. In: Proceedings, 6th International Conference on Pharmaceuticals and EDCs in Water. National Ground Water Association. Costa Mesa, CA. October 22−23, 2007.
13. Teske, S., Zhang, J., Ela, W., Arnold, R., and Quanrud, D. 2006. Fate of PBDEs during wastewater treatment. In: Proceedings, 5th International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water. National Ground Water Association. Costa Mesa, CA March 13−15, 2006.
14. Tomanek, M., Engstrom, J., Arnold, R., and Quanrud, D. 2007. Fate of polybrominated diphenyl ethers in conventional wastewater treatment and effluent application to recharge basins. In: Proceedings, 2007 California Section Annual Conference. WateReuse Association. Palm Springs, CA. March 4−6, 2007.
15. Zhang, J., Conroy, O., Quanrud, D., Arnold, R., and Ela, W. 2006. Understanding sample preparation for the measurement of estrogenic activity in the solids. In: Proceedings, 5th International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water. National Ground Water Association. Costa Mesa, CA March 13−15, 2006.

4. Description Information:

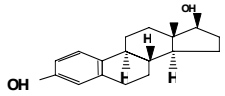
4A. Problem and Research Objectives:

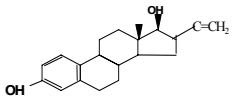
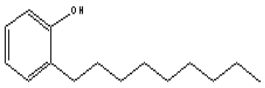
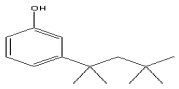
Federal and state regulatory agencies have generally encouraged the practice of biosolids disposal via addition to soil. Nationwide trends in sludge/biosolids disposal reflect increased reliance on the use of biosolids as soil amendments. In year 2001, 68 percent of the 8,650 publicly owned treatment works that generated sewage sludge in the United States disposed of biosolids via land application or distribution to the public for use as a soil amendment (National Research Council, 2002). This amounts to 3.4×10^6 dry tons of biosolids each year, or 61 percent of the sewage sludge now produced (USEPA, 1993; USEPA, 2000). This percentage is potentially much higher in semiarid portions of the southwestern United States, where perennially dry conditions typically yield organic-poor soils that benefit significantly from biosolids addition. In Arizona, 95 percent of the biosolids developed as a by-product of wastewater treatment are applied to agricultural land as soil amendments. Some 150,000 dry tons of class B biosolids are applied annually to more than 50,000 acres of Arizona agricultural land. In many parts of the western states, including Arizona, there are no viable disposal options other than land application.

The hydrophobic character of known estrogenic compounds in wastewater (Table 1) suggests that they will be strongly associated with sludges derived from wastewater treatment. There is increasing concern regarding the presence in treated biosolids of organic wastewater contaminants (OWCs), including a wide variety of pharmaceutically active compounds (PhACs), personal care products (PCPs), endocrine disrupting compounds (EDCs) and flame retardants. EDCs, especially those that act as estrogen mimics (agonists) or as antagonists, have been identified as sources of potential environmental and human health problems. Workers at the USGS have reported that treated biosolids contain a wide variety of OWCs. Fifty-five contaminants were detected in at least one biosolid product and summed OWC content ranged from 64 to 1,811 mg/kg dry weight (Kinney et al., 2006). If these results are typical of biosolids produced in Arizona and the Southwest, then land application constitutes a ubiquitous, diffuse source of organic contaminants to soil. It is possible, for example, that rainfall or irrigation of biosolids/soil mixtures can leach such compounds following land application or that they escape via overland flow during extreme wet weather events. Such outcomes could have detrimental effects on potable groundwater and surface water quality, affecting the ecological health of waters receiving these nonpoint-source pollutants.

Polybrominated diphenyl ethers (PBDEs) are a widely used type of flame retardant that have been detected in wastewater and sludge (Hale et al., 2001). PBDEs are known to interfere with thyroid hormone and have been shown to impair memory and motor skill development in animals. Because PBDEs are very hydrophobic (log K_{ow} values ranging from 4 to 9) they are expected to partition to sludge. Their fate during wastewater treatment and land application of biosolids is of significant environmental interest.

Table 1. Structures and properties of organic wastewater contaminants with estrogenic activity.

Chemical	Structure	Molecular Weight	Log K_{ow}	Relative Estrogenic Activity (YES bioassay)
17β-estradiol (E_2)		272	3.94	1.0

17α-ethinyl estradiol (EE_2)		296	4.15	1.4
4-Nonylphenol		220	4.48	$10^{-4} - 2\times10^{-4}$
Octylphenol		206	4.12	5×10^{-4}

Until recently, meaningful investigation of mechanisms for OWC removal during wastewater treatment was impeded by a lack of reliable methods for extracting hydrophobic organics from sludges and biosolids. That is, it was not possible to extract estrogens from biosolids with confidence, making it difficult to assign mechanisms (biodegradation versus phase transfer, etc.) for treatment-related improvements in water quality.

The goals of this project were to 1) develop and compare advance methods to extract OWCs from sewage sludges/biosolids/soils; 2) establish the fate of estrogenic activity, nonylphenol, polybrominated diphenyl ethers (PBDEs), and a suite of OWCs during wastewater treatment and sludge digestion processes at full-scale wastewater treatment plants; and 3) assess fate of nonylphenol, PBDEs, and OWCs after application of biosolids onto land. Nonylphenol and PBDEs were chosen for detailed analysis because they are an important estrogen mimic and thyroid mimic, respectively, that are always present in municipal wastewater.

The fate of OWCs that separate with sludge during municipal wastewater treatment was determined by extracting and measuring a suite of compounds before and after sludge digestion, dewatering and composting. Sludges and biosolids were obtained from full-scale wastewater treatment plants in Arizona and southern California.

To determine the fate of OWCs after land application of biosolids, a combination of field and laboratory studies were conducted. A series of sampling events were performed at a field site receiving biosolids to establish contaminant loss rates over time. Bench-scale laboratory columns containing soil/biosolid mixtures were used to test whether OWCs could be leached from agricultural soils receiving biosolids. This work was designed to establish the importance of mixing ratios and weathering time as determinants of compound survival and availability.

4B. Methodology

Sampling sites

Wastewater Treatment Plants. Four wastewater treatment facilities were investigated during this project. Each plant provides preliminary treatment (screening and grit removal), primary treatment (primary sedimentation and primary sludge collection), secondary treatment (bioreactors and secondary clarifiers), and chlorination/dechlorination prior to effluent discharges. Sludge from primary sedimentation is combined with secondary (waste activated) sludge for digestion. Digested sludge is dewatered via centrifugation.

Roger Road Wastewater Treatment Plant. The RRWWTP is a 40 million gallon per day (MGD) conventional treatment facility utilizing trickling filters and operated by Pima County Department of Wastewater Management. Secondary effluent is chlorinated/dechlorinated prior

to discharge to the Santa Cruz River, an effluent-dependent stream in Tucson, Arizona. The RRWWTP was utilized for study of PBDE fate during wastewater treatment.

Ina Road Water Pollution Control Facility. The 27.5 MGD pure oxygen activated sludge plant is operated by Pima County Department of Wastewater Management. The facility provides central dewatering for sludges digested both on site and at the RRWWTP. All biosolids so produced are used for land application.

Joint Water Pollution Control Plant. The 350 MGD plant is operated by the City of Los Angeles. The plant utilizes activated sludge with mesophilic anaerobic digestion and composting. At the JWPCP, a portion of the dewatered cake is stabilized by composting and sold as a soil amendment.

Hyperion Wastewater Treatment Plant. The 360 MGD plant is operated by the City of Los Angeles and utilizes activated sludge with thermophilic anaerobic digestion.

An idealized WWTP flow schematic (Figure 1) shows typical sampling points used in this project for collection of wastewater and sludge samples. The intent was to obtain sufficient samples to support a mass balance on estrogenic activity, nonylphenol, and in some cases, for a series of other trace organic wastewater contaminants. At the IRWPCF, samples were collected at ten different points along liquid and solid flowpaths. Liquid samples were 24-hour composites from automated samplers; sludge streams were hand-composited over the same 24-hour periods. Samples with appreciable solids contents were centrifuged to obtain liquid-phase and dewatered solids fractions. Composite samples were collected at IRWPCF at different points along liquid and solid flowpaths on November 17, 2005. Liquid samples were 24-hour composites from automated samplers; sludge streams were hand-composited over the same 24-hour periods. Grab samples were collected at HTP from primary sludge, wasted activated sludge, digested sludge, dewatered cake, and composted sludge.

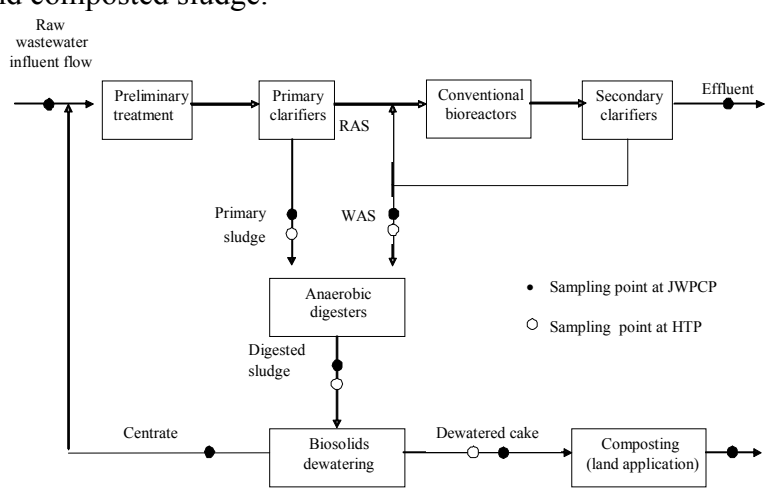


Figure 1. Idealized schematic of treatment processes and sampling locations at WWTPs included in this study. Specific sampling points for JWPCP and HTP are shown.

At the Roger Road plant, samples for measurement of PBDEs consisted of primary effluent, unchlorinated secondary effluent and combined (thickened, undigested) sludge. All samples were grab samples. Primary influent samples (2) and effluent samples (4) were collected in winter 2006-2007. Contemporary sludge samples (2) were taken before digestion. Sampling points were selected to support balances for individual PBDE congeners through the primary and secondary treatment processes.

Land Application Site. The University of Arizona Marana Agricultural Center (UAMAC) in Marana, Arizona, served as the field site for application of biosolids to agricultural soil. A portion of the facility contained plots that differed based on long-term biosolids application rates. These were designated 0X (control—no biosolids application), 1X and 3X. The 1X plots received biosolids at an annual rate that translated to 50 additional lbs of available nitrogen per acre each year. The rate of biosolids addition to 3X plots was three times as high (150 lbs of nitrogen per year per year). Biosolids were injected in March of each year as a slurry into soil about 8 in below the surface using an injection shank. Short staple cotton was grown on site.

Because soils were generally mixed to a depth of one foot via disking after biosolids addition, it was assumed that biosolids constituents, including OWCs, were well mixed through approximately the top foot of soils. The Marana facility test plots were first sampled in July 2005, four months after biosolids application. Samples were collected from the vertical walls of pits excavated at the time of sampling. Samples were collected in 1-inch increments down to a depth of one foot in each excavated pit. Four replicate pits were sampled within each test plot and corresponding samples from each depth were pooled for analysis. A second sampling event was conducted in November 2005, eight months after the annual biosolids application in March 2005. Identical collection methods were used during both sampling events. A portion of soil from each plot was air dried and packed into 4-in diameter columns designed to simulate field conditions of water addition/infiltration to test hypotheses regarding contaminant mobility in soil leachates.

Processing and analysis of liquid and solid samples

General. Liquid samples were passed through a 0.80 µm membrane filter, and filtrate was stored for subsequent analyses. Moisture in sludge and biosolid samples was partially removed by drying at 40° - 60°C for 48 hours. Water content was then determined by drying for 12 hours at 103°C. The organic separation process for samples that were predominantly liquid (raw wastewater, secondary effluent, centrate from sludge dewatering, etc.) was different. At times, the entire sample in its original form was dried in the microwave vessels and 20 mL of methanol was added for MAE. Occasionally, samples were filtered, and then applied directly to the C-18 disks and corresponding cleanup step followed.

Chemicals. All organic solvents were HPLC grade (VWR Scientific) and used as obtained. Ultrapure water was obtained via Nanopure (Barnstead, Dubuque, IA, USA) treatment. C-18 SPE cartridges were purchased from Empore, 3M. Nonylphenol, tech. 29,085 [84852-15-3] was obtained from Aldrich Chemical Company, Inc. The nonylphenol stock consisted of a mixture of isomers in unknown proportion. 17α-ethinylestradiol (EE2) [57-63-6] was obtained from Aldrich Chemical Company, Inc. Millipore 0.45 and 0.8 µm membrane filters were purchased through VWR Scientific.

Sample extraction. Organic extracts from sludges/biosolids were obtained using a microwave assisted extraction (MAE) procedure in a CEM MDS-2100 Microwave Digestion System. In general, 0.1 -0.5 g of the granular solid (dry weight) was extracted in 20 mL of reagent grade methanol using the following program: pressure was ramped from 0 to 20 psig over five minutes by heating the closed extraction vessel and held constant for 30 minutes. Reactor contents were then allowed to cool down before the liquid phase containing extracted organics was decanted off for further processing. For NP extraction, 4 grams of sample were dried and ground to a fine powder, then suspended in 23 mLs of methanol. For extraction of PBDEs, 5g of dry sample was suspended in 40 mLs of 1:1 (v/v) hexane/acetone, then

microwaved at 25 psig for 120 minutes. To lower the detection limit, PBDEs were extracted in triplicate and combined prior to additional processing steps.

Cleanup of Extracts. Post-extraction sample clean-up steps were designed to separate estrogenic compounds from other organic material that might compromise measurements of estrogenic activity and nonylphenol. Methanol-based extracts were evaporated to < 1 mL and extract residuals were diluted to ~1% methanol in Nanopure water. Hydrophobic organics in the dilute mixture were then adsorbed on C-18 SPE cartridges. The C-18 cartridges were first washed with 5 mL of 0.2 v/v methanol/water which was discarded. Estrogenic compounds were then eluted in 10 mL of 0.8 v/v methanol and saved. The extracts so obtained were directly analyzed for nonylphenol via HPLC with a fluorescence detector. The procedure blank was obtained using a blank microwave extraction step (methanol only), dilution of the methanol "extract" in Nanopure water, adsorption on a C-18 cartridge and elution, per above.

Samples extracted for NP analyses were dried, redissolved in water, and then concentrated on C-18 (reverse-phase) disks. Sorbed organics were eluted in a mixture of 0.80 v/v methanol and water. Eluate was dried and reconstituted in toluene prior to derivitization with pentafluorobenzyl bromide. The sample was then ready for NP analysis via GC/ECD.

Estrogenicity Testing: YES bioassay. The reporter gene bioassay employed was the yeast estrogen screen (YES) (DeBoever *et al*., 2001). Estrogenic activity was measured using a recombinant strain of *Saccharomyces cerevisiae.* Estrogens and estrogen mimics that pass through the cell envelope bind first to a human estrogen receptor protein and then to an estrogen response element fused to the *lacZ* gene leading to production of β-galactosidase. β-galactosidase activity is measured colorimetrically, based on cleavage of the yellow dye CPRG (chlorophenol red β-D-galactopyranoside) to yield chlorophenol red (Routledge and Sumpter, 1996). CPRG was purchased from Calbiochem.

To run the assay, yeast were grown in batch culture (32°C) to an optical density of 1.0 cm^{-1} (λ=630 nm). The growth medium was prepared by adding Aspartic acid and Threonine into minimal media. Minimal media was made by mixing the following components into 1 L of ultrapure water: KH_2PO_4 (13.61 g), $(NH_4)_2SO_4$ (1.98 g), KOH (4.2 g), $MgSO_4$ (0.2g), L-leucine (50 mg), L-histidine (50 mg), adenine (50 mg), L-arginine (20 mg), L-methionine (20 mg), L-tyrosine (20 mg), L-isoleucine (30 mg), L-lysine (30mg), L-phenylalanine (25 mg), L-glutamic acid (100 mg), Lvaline (150 mg), L-serine (375 mg), $Fe_2(SO_4)_3$ (0.8 mg). 1 L of growth medium was made with 1 L of minimal medium by adding L-Asp (109.6 mg), L-Thr (208.8 mg), glucose (0.5 g), 0.25 mL of vitamin solution and 63 µL $CuSO_4$ (20mM). Vitamin solution was made by adding thiamine (8 mg), pyridoxine (8 mg), pantothenic acid (8 mg), inositol (40 mg) and biotin (0.4 mg) into 180 mL of autoclaved water.

Samples were serially diluted across each of eight parallel rows of a 96-well plate (Costar). The procedure involved 8-10 (two-fold) dilution steps using Nanopure water as diluent, after which the liquid volume in each well was 50 µL. The yeast culture was diluted in growth media to A_{630} = 0.133, from which 150 µL was added to each well. Following a 24-hour incubation period (32°C) for cell growth and estrogen-dependent gene expression, 50 µL of cycloheximide/CPRG solution was added to each well. The solution was prepared by adding 20 mg of cycloheximide (Sigma) and 0.2 mL of a 10 mg/L CPRG solution to 5 mLs of the growth medium. Addition of cycloheximide, an inhibitor of new protein production in eukaryotes, prevented interference from CPRG, which is weakly estrogenic. The plates were then incubated for an additional 24 hours at 32°C for color development. Absorbance and light scattering were

measured at λ=570 nm and 630 nm using a plate reader (Bio-Tek Instruments, Inc., E1 x 800). Estrogen-dependent color development in each well was normalized for culture density using:

$$A_n = \frac{A_{570} - bA_{630}}{A_{630}}$$

where A_{570}, A_{630} are measured optical densities at respective wavelengths; b is the ratio of optical densities due to light scattering at 570 nm and 630 nm in the negative control series; and A_n is the normalized, estrogen-dependent β-galactosidase activity in the well.

A negative control, in which the sample-free growth medium (50 µL) was substituted for the diluted sample, was run in the last two columns of every 96-well plate. Process (negative) controls were also run. A liter of Nanopure water was passed through a C-18 disk followed by elution in 0.2 v/v (5 mL) and 0.8 v/v (10 mL) methanol/water. The latter was evaporated to dryness, and residual organics were re-suspended in water for measurement of estrogenic activity using the YES procedure. A series dilution containing concentrations of EE_2 from 5.0×10^{-12} to 1.0×10^{-7} M served as positive control for each experiment. Results from the positive control series were used to convert measured estrogenic activities in environmental samples to equivalent concentrations of EE_2 using:

$$EE_2eq = \frac{EC_{50,EE2}}{D_{50} \times C_f}$$

where $EC_{50,EE2}$ is the concentration of EE_2 that provided a half-maximal response (β-galactosidase activity) in the positive control, D_{50} is the dilution value at which the processed environmental sample provided a similar response in the YES bioassay, and C_f is the concentration factor achieved during sample processing (sample volume/final volume after separation, differential elution, drying and resuspension).

Nonylphenol. Nonylphenol was determined via HPLC-FLD. The Hewlett-Packard HPLC-FLD system (Hewlett Packard Series II, Model 1090) used for nonylphenol measurement consisted of an autosampler, solvent delivery system, reverse-phase C18 column (86-200-E3) and a fluorescence detector (1046A). The mobile phase was an acetonitrile (ACN) gradient in ultrapure water and a flow rate of 1 mL/min. The ACN gradient program was 0.30 ACN/0.70 water from 0 - 5 min; 0.40 ACN/0.60 water from 5 - 10 min; 0.60 ACN/0.40 water from 10 – 20 min; 0.80 ACN/0.20 water from 20 -25 min; and an isocratic purge from 25 - 30 min after which the eluent composition was returned to 0.30 ACN/0.7 water. The injection volume was 25 µL, and the excitation and emission wavelengths were 230 nm and 305 nm. The method detection limit was estimated as 5 µg/L. The measured recovery of NP quantification procedure including extraction, cleanup and concentration steps was 78%.

Polybrominated Diphenyl Ethers. PBDEs were prepared for analysis using EPA Draft Method 1614. After consulting EPA Methods 3620b, 3660b and 3665a (USEPA, 2003) for detailed guidance, a three-part procedure consisting of (i) sulfur elimination using TBA sulfite, (ii) treatment with sulfuric acid and (iii) passage through a mini column containing Florisil was adopted. .

Resultant extracts underwent cleanup steps to remove chemical interferences as described in the EPA's draft record 1614: *Brominated diphenyl ethers in water, soil, sediment and tissue by HRGC/HRMS* using EPA steps detailed in 3620b, 3660b, and 3665a. The modified extracts were then analyzed for PBDE congeners 28, 47, 99, 100, 153, 154, 183, and 209 via GC/ ECD. Flow data, total suspended solids (TSS), and all lab results other than PBDE content were

supplied by Pima County and confirmed in this lab. Standard calibration procedures were used in all quantitative analyses. An internal standard was generally included.

USGS Analytical Methods. UofA graduate students working with USGS staff conducted analyses for a suite of organic wastewater contaminants at Dr. Edward Furlong's laboratory at the USGS National Water Quality Laboratory in Colorado. The analytical method used is fully described in Burkhardt et al. (2006). A summary of the method is as follows:

- Extract the sediment samples using water/isopropyl alcohol on a pressurized solvent extraction system.
- Isolate the selected compounds from these extracts using a disposable, polypropylene SPE cartridge, which contains a PSDVB phase. Dry the SPE cartridges for 5 minutes. The SPE cartridges are not dried exhaustively.
- Elute the compounds of interest with a mixture of dichloromethane (DCM) and diethyl ether (DEE) at an 80:20 ratio, respectively.
- Also use the DCM–DEE to elute sorbed compounds from a Florisil/sodium sulfate SPE cartridge.
- Evaporate the extract in a hood by using a gentle stream of nitrogen to a final volume of 1 mL.
- Determine the compounds of interest in the concentrated extracts by capillary-column gas chromatography/mass spectrometry (GC/MS).

Comparison of MAE and ASE Extraction Methods. As a part of this project, the USGS (Dr. Furlong's laboratory) and the UofA performed a detailed comparison and analysis of two advanced methods for extraction of trace organics from solid samples. Microwave Assisted Extraction (MAE) and Accelerated Solvent Extraction (ASE) were evaluated using two identical sets of wastewater sludges. These were extracted at the UofA using MAE and, concurrently, at the USGS using ASE for the purpose of comparing extraction recovery efficiencies for target analytes. The purpose of this experiment was to compare the recovery efficiencies of MAE and ASE extraction methods for different types of sludge/wastewater samples and to determine whether the two extraction methods provide similar recovery efficiencies for analytes of interest.

A series of extracts were produced using MAE (UofA extraction method) and ASE (USGS extraction method). Three different sludge/biosolid samples were included in the cross comparison: centrifuged/dewatered sludge, lime stabilized sludge, and a spiked lime stabilized sludge. A duplicate lime stabilized sludge sample was included, resulting in a total of four environmental samples. A fifth test case, muffled sand, provided by USGS, was included as a blank. Each of the five sample types was prepared by USGS. The composite samples were prepared and aliquoted at the USGS. Spiking solutions and a spiking kit were shipped to UofA along with instructions to minimize variations. The timing of all sample extractions was coordinated to ensure that the time between sample aliquoting and the initiation of extraction for all methods corresponded. Replicates and a matrix spike of the limestabilized sludge for each analysis were included for QC. After extractions were performed, both labs shipped (on ice, overnight) aliquots of the resulting extracts to the other laboratory, resulting in a total of 5 MAE extracts and 5 ASE extracts for analysis in each laboratory. At UofA each extract was loaded onto a C18 disk and eluted using 20%, 50%, and 80% MeOH, resulting in three discrete sample fractions that were individually evaporated to near dryness and re-suspended in ultrapure water for estrogenic activity measurement using the yeast estrogen screen. Estrogenic responses (EE_2 equivalents) from the three fractions were summed to provide a total estrogenic activity

measurement for each sample and from each assay. The USGS did a solvent exchange step on the MAE extracts as appropriate prior to analysis for the hormones, pharmaceuticals and wastewater compounds included in the WERF project.

Hormone data were analyzed with a smaller set of isotopically labeled surrogates in this substudy because certain surrogates decayed during MAE due to deuterium exchange reactions in the heated methanol solvent system. This did not affect the ASE samples, however, data from the ASE samples were treated in the same way for the sake of comparability of the two data sets. Furthermore, since deuterium exchange is a phenomenon that exclusively affects the surrogates, it does not detract from the applicability of MAE to bioassay samples that do not contain surrogates. The only estrogenic steroid affected by this issue was estrone, although a number of the androgens and progestins were treated separately.

Recoveries of estrogenic steroids compared well between the two extraction techniques. EE2, E3, equilin, equilenin, and mestranol were not observed in unspiked sludges by either method. Low levels of diethylstilbestrol and 17α-estradiol were observed in MAE samples but not ASE samples, however they were below nominal detection limits so this does not create any inconsistency. E1 and E2 both were observed in all three unspiked samples. Within methods, variability for these compounds was 12.2% or less in replicate samples, and variability between ASE and MAE techniques was somewhat higher (2-49.6%), but at levels within a factor of five of detection limits this represents good reproducibility. Recoveries of estrogens in the spiked ASE samples were acceptable with estriol (200%) being somewhat elevated. The MAE spiked sample appeared to have been contaminated with high levels of E1 and E2; equilin and equilenin had low recovery, but the other estrogens performed well. It is likely that equilin, equilenin, and some of the androgens were not extracted well by MAE because the protocol was not initially intended or optimized for such a broad suite of analytes.

In general, the non-steroidal estrogens were present in the biosolids samples at high enough levels that concentrations spiked in were overwhelmed by ambient levels, so recovery data are not reported. Nevertheless, agreement of replicates within extraction methods was very good (4.9-28%). ASE and MAE provided comparable results for nonylphenol (NP), octylphenol (OP), and their monoethoxylates (NP1EO, OP1EO). However, ASE extracts contained significantly more nonylphenol diethoxylate (NP2EO) and beta-sitosterol. These two compounds are slightly more abundant than the lower ethoxomers. Since NP2EO (Routledge and Sumpter, 1996) and beta-sitosterol are significantly less estrogenic than NP and present at similar levels, the total estrogenicity of ASE and MAE extracts was comparable. On the other hand, bisphenol A was observed in MAE extracts, but is known to be a poor performing analyte in the USGS 5433 method and was not observed in the ASE extracts; levels were low enough that presence or absence in an extract is not likely to significantly affect the total estrogenic activity. Furthermore, although chemical analysis methods are fairly extensive, there are certainly compounds with estrogenic activity that are not targeted but could be present in samples (e.g., phthalates, phytoestrogens, certain pesticides). Therefore, the predicted estrogenic potency predicted from chemical data should be looked at as a lower bound to what may be present in a complex sample. From the chemical data generated in this cross-comparison experiment we conclude that although the MAE technique is less effective than ASE at recovering certain analytes, it is effective at extraction of the most potent estrogens, and for the compounds of most interest the extracts have similar enough chemical composition to justify direct comparison of data between the two techniques.

4C. Principal Findings and Significance

Fate of Estrogenic Activity and Nonylphenol during Wastewater Treatment. A detailed mass balance analysis was performed at the JWPCP and Hyperion WWTPs. Measurements of estrogenic activity and nonylphenol were combined with mass (solids) or volume (liquids) fluxes corresponding to various points at JWPCP and HTP to yield daily mass fluxes of estrogenic activity (as EE_2) and nonylphenol at those positions (Figure 2). From the results of the analysis, it is evident that 93 percent of the estrogenic activity in the plant influent was missing from JWPCP effluent. The EE_2 equivalent concentration of estrogenic activity in JWPCP effluent was 0.089 nM (26.4 ng/L), which is still much higher than the minimum levels known to disrupt estrogen physiology in exposed animals.

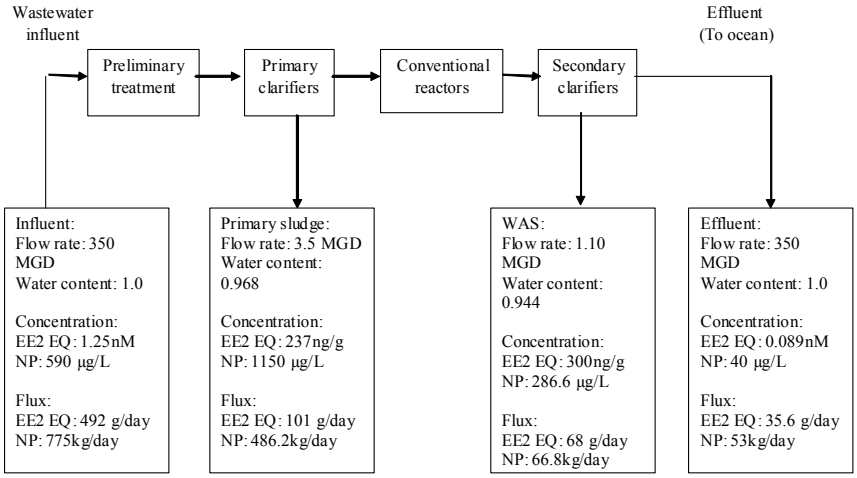


Figure 2. Mass balance of estrogenic activity and nonylphenol during primary and secondary treatment at JWPCP.

From a comparison of estrogenic activities in filtered versus unfiltered influent samples, it was apparent that more than 90 percent of the influent estrogenic activity was associated with particles removed on a 0.8 µm filter. Greater than 50 percent of the estrogenic activity lost (based on comparison of JWPCP influent and effluent concentrations) was accounted for in an extract derived from the dewatered sludge**.** There is some evidence of experimental error in estrogenic activity measurement involving sludges. Estrogenic activity in the dewatered cake was low compared to that of digested sludge before centrifugation. The mass balances on estrogenic activity around anaerobic digestion, dewatering and composting were suspect, probably because the samples were grab samples or due to the experimental errors. The flux of estrogenic activity out of the digester seems particularly high. As a consequence, it was not possible to estimate the efficiencies of individual unit operations (anaerobic digestion, dewatered and composting) for removal of estrogenic activity.

A similar overall picture emerges from nonylphenol data at JWPCP. That is, secondary treatment is capable of lowering the flux of nonylphenol from influent to effluent by more than 90 percent (here, 93%). Of the 93 percent through-plant loss, however, more than two-thirds (72%) was accounted for as extractable nonylphenol in the dewatered sludge. Considering both the dewatered cake and effluent as sinks for nonylphenol at JWPCP, all but a fourth of the influent nonylphenol was accounted for. There were more circumscribed balances around the anaerobic digester and JWPCP sludge dewatering operations. These show that mesophilic digestion and physical dewatering have a very limited effect on nonylphenol mass. That is,

extractable nonylphenol was essentially unchanged by digestion and centrifugation. A comparison of nonylphenol in primary and waste activated sludges shows that primary sludge accounts for almost 90 percent of the nonylphenol that enters the anaerobic digester. There was little or no loss of extractable nonylphenol during mesophilic anaerobic digestion. As expected, dewatering had little effect on nonylphenol levels or fluxes (Figures 3).

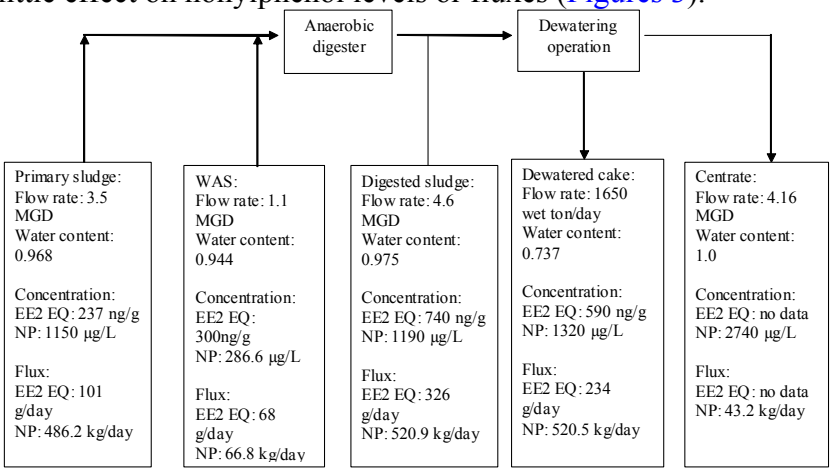


Figure 3. Mass balance of estrogenic activity and nonylphenol during the sludge handling processes at JWPCP.

A balance around the composting operation, which precedes sale of composted sludge and fertilizer/soil conditioner, suggests that 75% of the nonylphenol that enters the composting process in dewatered cake is lost, perhaps due to aerobic biochemical activity. This encouraging result should be further examined and verified in future research studies to establish the efficacy of using aerobic decomposition processes, such as composting, for nonylphenol destruction (Figure 4).

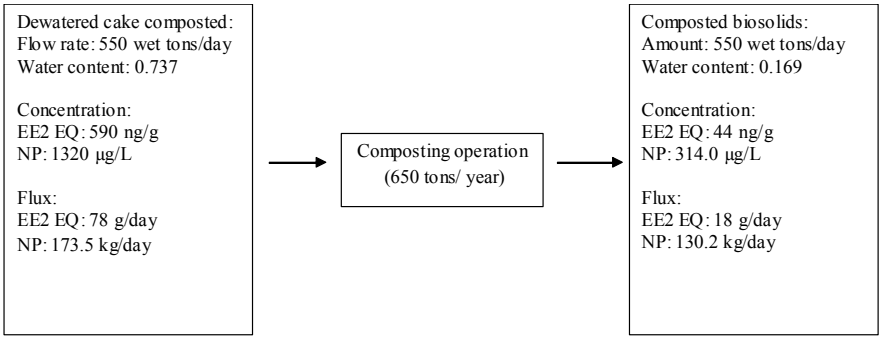


Figure 4. Mass balance of estrogenic activity and nonylphenol during the composting process at JWPCP.

Overall, the balance on nonylphenol fluxes at the JWPCP indicated that two-thirds of the nonylphenol that enters the treatment plant leaves with the dewatered cake. Aerobic biodegradation during secondary treatment may remove as much as 25 percent of the influent nonylphenol. Again, about 80 percent of nonylphenol in the JWPCP influent was associated with the particles larger than 0.8 µm. Thus, relatively low nonylphenol levels in the plant effluent (40µg/L) are more a product of suspended solids removal than of biochemical treatment of nonylphenol. It is also possible that aerobic biodegradation is effectively matched by in-plant production of nonylphenol from NPnEO.

The contribution of nonylphenol to estrogenic activity is also of some interest. YES bioassays with pure 17α-ethinyl estradiol and a mixture of nonylphenol isomers indicated that EE_2 is 5000 – 10,000 times more estrogenic than nonylphenol (data not shown). The difference in potency is balanced, at least in part, by the relatively large expected concentration of nonylphenol in wastewater and wastewater effluent. Thus, by expressing estrogenic activity in terms of an equivalent EE_2 concentration, it is possible to speculate on the contribution of nonylphenol to the YES bioassay response. Here, a factor of 1/7500 was applied to convert nonylphenol measurements to EE_2-equivalent concentrations. In the JWPCP influent, for example, the nonylphenol concentration was 5.90×10^5 ng/L, for an EE_2-equivalent concentration of 79 ng/L. Estrogenic activity in the same sample, expressed as an EE_2-equivalent concentration, was 370 ng/L, so that the measured nonylphenol concentration accounted for just over 20 percent of the estrogenic activity. In the plant effluent, nonylphenol accounted for just 2 percent of the estrogenic activity. Results suggest that nonylphenol is removed with greater efficiency than other components of estrogenic activity during conventional wastewater treatment, perhaps because the affinity of nonylphenol for organic-rich solids is greater than those of most other estrogens and estrogen mimics. In this analysis, possible matrix effects during YES measurement and possibility of synergy or antagonism among compounds contributing to estrogen activity were ignored.

The nonylphenol concentration was estimated at 1300 µg/g in the dried dewatered cake at JWPCP, and the estrogenic activity was 600 ng EE_2/g in the same sample (Figures 3 and 4). Consequently, nonylphenol accounted for perhaps 30 percent of the extractable estrogenic activity in the dewatered cake. Evidently, nonylphenol is an important component of estrogenic activity in the JWPCP wastewater and solids.

At HTP, there was little loss of estrogenic activity during thermophilic sludge digestion and subsequent dewatering operations (Figure 5). The daily mass flux values obtained for nonylphenol and estrogenic activity suggest that thermophilic sludge digestion probably offers little advantage in terms of estrogen and particularly nonylphenol destruction. The through-digestion increase in nonylphenol could have arisen from the nature of the experimental design (one-time grab samples), or from conversion of ethoxylated nonylphenol forms to nonylphenol during digestion (Ahel *et al.,* 1994). A modest reduction in estrogenic activity is apparent in the data.

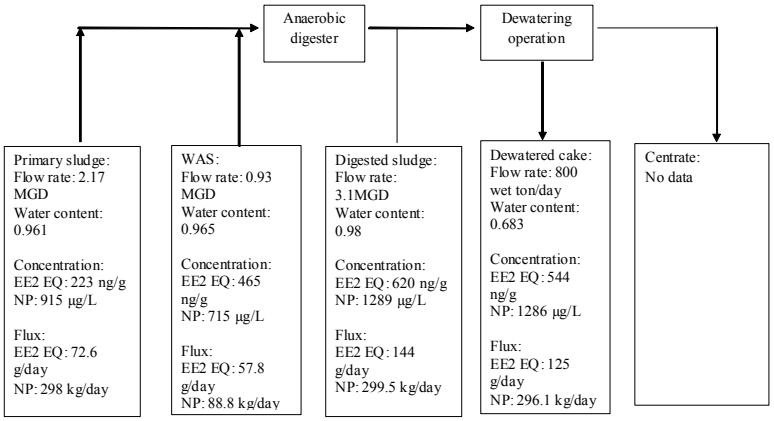


Figure 5. Mass balance of estrogenic activity and nonylphenol during the sludge handling processes at HTP

Fate of PBDEs during Wastewater Treatment. The mean concentrations of major PBDE congeners in RRWWTP influent and effluent (Figure 6) indicate that heavily brominated congeners are more successfully removed from the aqueous stream during secondary treatment. By far, the greatest removal efficiency was for BDE-209. However, when PBDEs in undigested solids (Figure 6) were included, mass balances (not shown) indicated that all congeners except BDE-209 experienced a net increase in mass during treatment. It is likely that the liquid-liquid extraction method used to initiate measurement of influent PBDEs was inadequate for extraction of influent field samples that contained high levels of suspended solids. There was also significant day-to-day variation in both influent and effluent samples, although, when extractions were performed in duplicate, results were consistent (data not shown). The extraction method was replaced with a more aggressive series of extraction steps in later experiments.

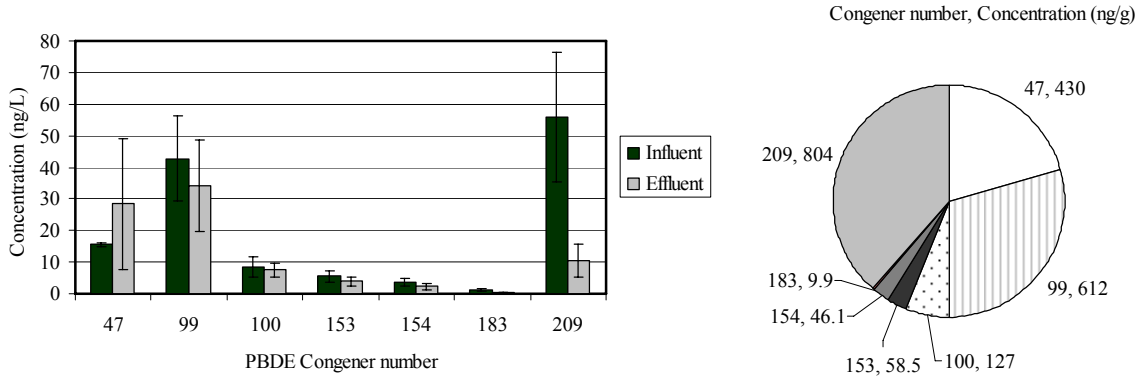


Figure 6. Average concentrations of influent and effluent (a) and thickened sludge (b) of major PBDE congeners at RRWWTP. Based on four effluent samples, two influent samples and three sludge samples.

The congener BDE-209 had the highest average concentration in RRWWTP influent and thickened sludge. Since five of the other six congeners measured presumably originated in Penta-BDE, concentration ratios among individual congeners in plant influent, effluent and sludge were compared to congener ratios in the Penta-BDE product to test hypotheses related to differential (congener-specific) sorting or transformation during wastewater treatment. Because BDE-99 was present at a suitably high concentration in all samples, comparisons were based on the concentrations of individual congeners that were normalized to that of BDE-99. Congener mass ratios were similar in plant influent, effluent, undigested sludge and the commercial Penta product (data not shown), suggesting that processes governing the physical-chemical breakdown of Penta-containing products and PBDE collection, transport and separation or transformation during wastewater treatment do not strongly differentiate among BDE-47, -99, -100, -153 and -154. Sludges accounted for 84% of the total PBDE efflux after secondary treatment processes at RRWWTP. However, the potential for biochemical transformation of PBDEs during anaerobic sludge digestion must be considered (see below) in order to compare PBDE masses entering the environment with effluent and biosolids.

Fate of Trace Organic Wastewater Contaminants during Wastewater Treatment. The fate of a suite of OWCs during wastewater treatment at the JWPCP and Ina Road facilities was evaluated. Analyses were performed at the USGS National Water Quality Laboratory under the

guidance of Dr. Edward Furlong. Three University of Arizona graduate students visited Dr. Furlong's laboratory to participate in these analyses, supporting knowledge transfer objectives of the project. Concentrations of OWCs from the JWPCP and IRWPCF plants for samples obtained through unit treatment processes are summarized in Tables 2 and 3, respectively. At the Ina road facility, hydraulic loading data was used to calculate mass fluxes for selected OWCs, permitting determination of percentage reductions through unit processes (Table 4). For those OWCs in which sufficient data was available, most were efficiently removed (>80% reduction) during wastewater treatment at the IRWPCF.

Table 2. Concentrations of trace organic wastewater contaminants through unit treatment processes at JWPCP.

Compound	Concentration (µg/kg)						
	Influent	Primary Sludge	Waste Activated Sludge	Digested Sludge	Effluent	Centrate	Dewatered Cake
phenol	ND	854	166.9	ND	ND	ND	ND
1,4-dichlorobenzene	ND	5.8	1.5	0.7	ND	ND	590
d-limonene	8.1	131.0	0.0	ND	ND	ND	ND
acetophenone	ND	25.4	9.4	ND	ND	ND	5,000
para-cresol	9.5	1,332	1,225	38.6	ND	ND	21,000
isophorone	ND	4.2	ND	ND	ND	ND	ND
camphor	ND	4.9	ND	24.8	ND	8.9	ND
naphthalene	0.2	5.8	ND	7.2	ND	3.1	1,100
isoquinoline	ND	1.4	ND	ND	ND	ND	ND
indole	4.4	52.3	164.0	1.4	ND	8.7	3,200
2-methylnapthalene	0.3	18.0	ND	5.3	ND	2.0	1,600
1-methylnapthalene	0.2	12.9	ND	4.0	ND	2.1	1,200
skatol	4.9	22.4	4.9	ND	ND	1.2	2,400
2,6-dimethylnapthalene	0.5	17.2	ND	4.5	ND	1.4	ND
BHA	ND	0.3	ND	ND	ND	ND	ND
N,N-diethyltoluamide(DEET)	2.2	2.6	1.2	1.6	1.4	1.7	ND
diethylphthalate	12.0	23.7	ND	ND	ND	ND	ND
4-tert-octylphenol	10.2	19.7	ND	63.7	ND	12.9	22,000
tributylphosphate	1.7	1.6	ND	0.6	ND	0.5	ND
benzophenone	8.0	27.5	ND	4.1	ND	2.5	ND
para-nonylphenol-total	292.0	1,587	144.8	2,080	7.5	617.9	530,000
tri(2-chloroethyl)phosph	0.7	ND	ND	ND	ND	ND	ND
4-n-octylphenol	1.3	0.6	ND	ND	ND	4.5	ND
phenanthrene	1.8	7.5	0.5	2. 3	ND	0.8	740
Anthracene	2.0	4.6	ND	1.1	ND	0.7	ND
tonalide(AHTN)	20.6	162.3	97.5	54.7	4.9	18.1	28,000
galaxolide(HHCB)	2.6	78.2	10.8	7.2	0.8	2.2	18,000
carbazole	0.3	2.2	ND	ND	ND	0.3	ND
4-cumylphenol	0.5	0.8	ND	ND	ND	0.5	ND
OPEO1	893.2	3,225	131.9	ND	ND	ND	ND
bromacil	ND	3.9	ND	ND	ND	ND	ND
metolachlor	ND	0.7	ND	ND	ND	ND	ND
NPEO1-total	172.9	16,224	17.7	14.9	6.0	16.9	11,000
anthraquinone	ND	1.7	ND	ND	0.6	ND	ND
fluoranthene	ND	0.6	0.4	0.2	ND	0.1	ND
triclosan	29.2	56.6	13.6	28.4	ND	13.6	6,300
pyrene	ND	0.5	1.6	0.5	ND	0.2	310
bisphenolA	2.7	90.2	3.4	8.3	ND	2.9	ND
OPEO2	4.1	ND	ND	ND	ND	ND	ND
NPEO2-total	145.1	1,842	27.1	ND	ND	12.7	3,400
ethanol,2-butoxy-,phosph	13.0	44.4	ND	1.7	ND	2.5	ND

triphenylphosphate	0.3	1.7	ND	ND	ND	ND	ND
diethylhexylphthalate	27.2	203.5	36.1	31.8	ND	12.7	30,000
benzo(a)pyrene	ND	ND	ND	ND	ND	0.1	220
3-beta-coprostanol	0.006	901.5	122.9	269.9	ND	0.014	140,000
cholesterol	0.012	1,549	101.2	144.6	ND	0.025	43,000
beta-sitosterol	0.001	352.1	52.4	96.4	ND	0.002	130,000
stigmastanol	ND	366.2	ND	ND	ND	ND	18,000

Table 3. Concentrations of trace organic wastewater contaminants through unit treatment processes at the Ina Road WPCF.

Compound	Concentration (µg/kg)								
	Influent	Primary Effluent	Primary Sludge	Waste Activated Sludge	DAFT Sludge	Digested Sludge	Effluent	Centrate	Gravity Thicken Sludge
phenol	36.23	2.27	1,384	ND	490.0	ND	ND	12.92	1,800
1,4-dichlorobenzene	0.63	0.23	4.34	0.64	ND	ND	ND	0.29	ND
d-limonene	7.52	1.03	37.67	0.73	ND	ND	0.18	ND	500. 0
acetophenone	17.15	ND	ND	ND	ND	ND	ND	ND	2,600
para-cresol	421.1	1.90	15,537	5,767	17,000	ND	ND	0.46	150,000
isophorone	ND	ND	ND	0.12	ND	ND	ND	ND	ND
camphor	1.79	1.00	5.63	ND	ND	5.93	ND	1.99	ND
naphthalene	ND	0.11	ND	ND	ND	ND	ND	3.82	ND
isoquinoline	ND	ND	ND	ND	ND	ND	ND	ND	ND
indole	76.21	4.75	1,053	364.2	2,900	103.4	0.06	38.77	4,700
2-methylnapthalene	ND	ND	0.33	ND	ND	0.39	ND	0.13	ND
1-methylnapthalene	ND	ND	ND	0.11	ND	0.44	ND	0.07	ND
skatol	4.16	ND	107.6	333.9	520.0	ND	0.20	ND	30,000
2,6-dimethylnapthalene	ND	ND	ND	ND	ND	0.52	ND	ND	ND
BHA	ND	ND	ND	ND	ND	ND	ND	ND	ND
N,N-diethyltoluamide(DEET)	2.58	1.40	12.00	0.51	ND	1.45	2.50	0.91	ND
diethylphthalate	0.23	19.94	ND	ND	ND	ND	ND	ND	ND
4-tert-octylphenol	18.7	4.34	72.89	3.74	ND	25.50	ND	2.19	230.0
tributylphosphate	ND	ND	0.71	0.57	ND	ND	1.60	0.15	ND
benzophenone	3.60	2.90	26.48	12.14	76.0	8.27	1.70	1.19	430.0
para-nonylphenol-total	2264	486.0	4,982	474.7	8,800	2,687	3.30	228.6	23,000
prometon	ND	ND	ND	ND	ND	ND	ND	ND	ND
atrazine	0.21	ND	ND	ND	ND	ND	ND	ND	ND
tri(2-chloroethyl)phosph	0.72	ND	ND	0.96	ND	ND	1.50	0.16	ND
pentachlorophenol	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-n-octylphenol	2.46	ND	4.06	0.14	ND	ND	ND	ND	ND
diazinon	ND	ND	ND	ND	ND	ND	ND	ND	ND
phenanthrene	0.07	0.05	ND	0.14	ND	1.03	0.00	0.11	ND
Anthracene	0.07	0.05	ND	ND	ND	0.14	0.01	ND	ND
tonalide(AHTN)	52.96	14.33	400.4	235.2	960.0	103.4	8.90	7.36	5,200
galaxolide(HHCB)	7.04	2.05	76.88	39.34	150.0	17.92	2.18	0.95	960.0
carbazole	ND	ND	ND	ND	ND	ND	ND	ND	ND
4-cumylphenol	ND	ND	ND	ND	ND	ND	ND	ND	ND
OPEO1	318.8	ND	2,998	1366	ND	ND	4.00	ND	66,000
metalaxyl	ND	ND	ND	ND	ND	ND	ND	ND	ND
bromacil	0.17	ND	ND	ND	ND	ND	ND	ND	ND
metolachlor	ND	ND	ND	ND	ND	ND	ND	0.99	ND
chlorpyrifos	ND	ND	ND	ND	ND	ND	ND	ND	ND
NPEO1-total	317.5	73.59	2,109	832.2	13,000	47.55	27.10	4.97	25,000
anthraquinone	0.19	ND	ND	ND	ND	ND	ND	ND	ND
fluoranthene	ND	ND	3.38	1.97	ND	5.66	0.01	0.07	ND
triclosan	41.45	16.73	317.7	86.49	1,500	46.17	1.50	6.86	3,000
pyrene	ND	ND	ND	2.40	ND	4.80	ND	ND	ND
bisphenolA	ND	ND	ND	ND	ND	ND	ND	0.82	ND
OPEO2	ND	ND	ND	ND	ND	ND	ND	ND	ND
NPEO2-total	236.7	ND	1153	637.4	4,400	ND	56.00	ND	20,000
tri(dichlorisopropyl)pho	ND	ND	ND	ND	ND	ND	1.60	0.29	ND
ethanol,2-butoxy-,phosph	13.28	3.99	75.70	12.61	ND	15.16	30.00	9.24	ND
triphenylphosphate	0.47	0.10	5.60	0.43	ND	0.29	1.00	ND	ND
diethylhexylphthalate	60.61	19.24	520.3	467.9	2,000	17.23	4.80	20.88	7,900
tetrabromodiphenylether	0.99	ND	123.0	ND	ND	ND	ND	ND	ND

benzo(a)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-beta-coprostanol	1.11	0.05	0.41	0.10	ND	ND	8.00	ND	1.40
cholesterol	2.19	0.06	0.92	0.27	ND	ND	12.00	0.04	4.60
beta-sitosterol	0.014	0.002	0.066	0.006	ND	ND	ND	ND	0.29
stigmastanol	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 4. Percent reductions of selected organic wastewater contaminants through unit treatment processes at the Ina Road WPCF.

Organic Wastewater Contaminant	Log K_{ow}	Influent to Effluent	Across Primary Clarifier	Across Activated Sludge	Across Anaerobic Digester	Across Entire plant
indole	1.14	99.9	34.1	-	94.6	99.1
tri(2-chloroethyl)phosphate	1.78	-	-	-	-	-
N,N-diethyltoluamide(DEET)	2.02	6.8	3.7	-5.3	-	9.9
benzophenone	3.18	54.5	-12.8	28.5	95.3	54.9
OPEO1	4.12	98.8	-	55.7	-	-
NPEO1-total	4.17	91.8	34.8	43.3	99.5	91.7
NPEO2-total	4.21	77.2	-	-	-	-
2,6-dimethylnapthalene	4.45	89.8	-	-	-	91.2
Anthracene	4.46	96.4	-	88.1	-	89.8
para-nonylphenol-total	4.48	99.9	61.1	96.4	81.5	99.1
camphor	4.5	-	36.5	-	-	-
d-limonene	4.57	-	-	-	-	-
triphenylphosphate	4.59	-	-	-	-	-
Triclosan	4.76	96.5	17.3	75.1	96.2	95.9
ethanol,2-butoxy-,phosphate	4.78	-	11.3	-	-	-
skatol	4.88	95.4	-	-	-	-
tonalide(AHTN)	5.70	83.8	27.5	9.3	100.0	84.3
galaxolide(HHCB)	5.90	70.2	0.90	-6.7	95.4	69.7
cholesterol	7.00	-	70.9	-	-	-
diethylhexylphthalate	7.50	92.4	21.4	-10.9	99.5	92.2
3-beta-coprostanol	8.82	-	-	-	-	-

Fate of Nonylphenol after Land Application of Biosolids. In the bench-scale laboratory column study, soil concentrations of nonylphenol decreased during a four-month period of monitoring (Figure 7). Columns containing the 1X and 3X field soils were sampled at approximately 6-week intervals. At each point shown, soils were withdrawn from the top four inches of the respective columns. Initial NP concentrations were 4.6 $mg \cdot kg^{-1}$ (dry weight) and 1.7 $mg \cdot kg^{-1}$ for the 3X and 1X columns. After four months, NP concentrations had decreased to 1.5 and 1.2 $mg \cdot kg^{-1}$, respectively.

Column leachates were continuously collected and analyzed for NP in order to determine a mass balance. Leachate NP concentrations were never higher than about 7.5 µg/L and decreased to 1.5 µg/L after four months. Leachate concentrations derived from the 1X and 3X columns were similar (Figure 8). The mass balances on the columns indicated 0.1-0.4% of the NP lost was due to leaching. Thus, almost all of the NP mass lost from the columns was biodegraded.

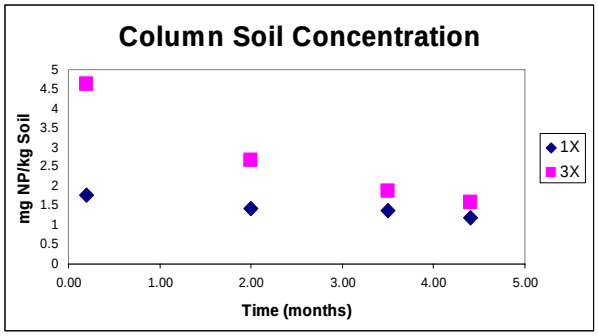


Figure 7. Time dependent levels of 4 nonylphenol in laboratory simulations of field soils amended with biosolids. The 1X and 3X labels refer to biosolids addition levels (see text).

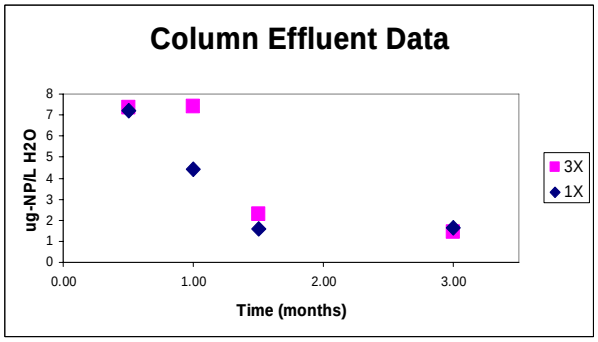


Figure 8. 4-Nonylphenol concentrations in leachates derived from columns containing agricultural soils amended with biosolids. The 1X and 3X designations refer to biosolids loading rates.

Profiles of NP concentration in soils collected from the Marana Agriculture Center field site (Figures 9) also indicate that NP concentrations decreased with time. The concentration at the four-inch depth decreased from 1.6 mg·kg^{-1} in July (3X soil sample) to 0.6 mg·kg^{-1} in November. NP loss from other samples was less dramatic, and concentrations at the 12-inch depth may have been stable, perhaps due to lack of an aerobic microflora at that depth. The July and November concentrations in the 4-inch depth samples were similar to values obtained in the column samples, suggesting that the time-dependent decreases in 4-nonylphenol were similar in the field and column simulations. Overall, results from the laboratory and field experiments indicated that NP is effectively biodegraded after land application of biosolids, with half lives on the order of a few months.

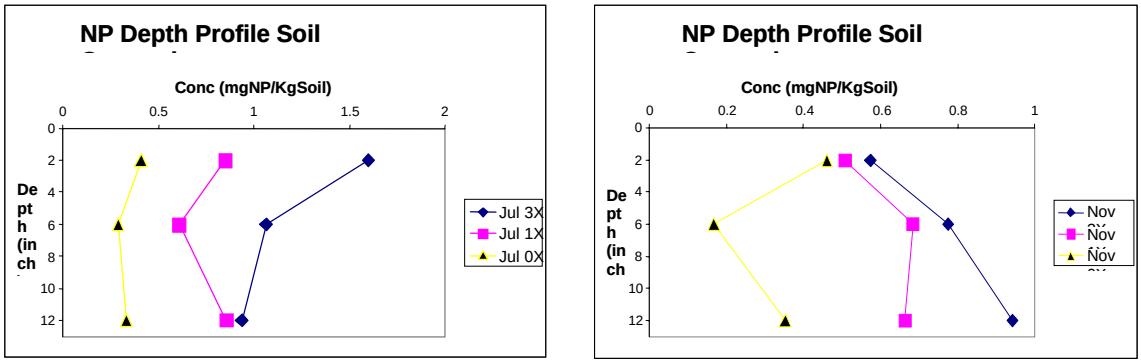


Figure 9. NP concentration versus depth in Marana agricultural soils for the July 2005 (a) and November 2005 (b) sampling periods. Designations in the legend refer to biosolids load in the plots sampled.

It is noteworthy that levels of NP in the unamended control soil samples were all non-zero. Results suggest that all plots at the Marana agricultural site may have occasionally received biosolids amendments, or that there are mechanisms (airborne transport or runoff) for transport of NP from biosolids-amended to unamended plots. Alternatively, NP could be a residual from pesticide applications.

PBDEs in biosolids and soils amended with biosolids. Profiles of the primary Penta-BDE congeners in the top foot of UAMAC agricultural soils (Figure 10) indicate that BDE-47 and -99 were the dominant congeners present and that, although PBDEs were present throughout the depth interval, the highest concentrations were at 2-8 inches depth. The position of maximum

concentration corresponded to the depth of biosolids injection, unaffected by PBDE transport or attenuation mechanisms. Depth-dependent data for the 0X, 1X and 3X plots indicate that nominal biosolids application rates were relatively poor indicators of PBDE concentrations in soils. That is, the control plot contained surprisingly high concentrations of major Penta-BDE congeners, and concentrations in the 1X and 3X plots were similar. There is no ready explanation for this. Contaminant transport could have occurred during infrequent, strong rainfall events, and, in fact, soil transport with runoff during periods of heavy rain was observed (data not shown). Other transport mechanisms are more difficult to envision. It is possible; however, that operator error or indifference over the 20-year period of sludge application at UAMAC was responsible.

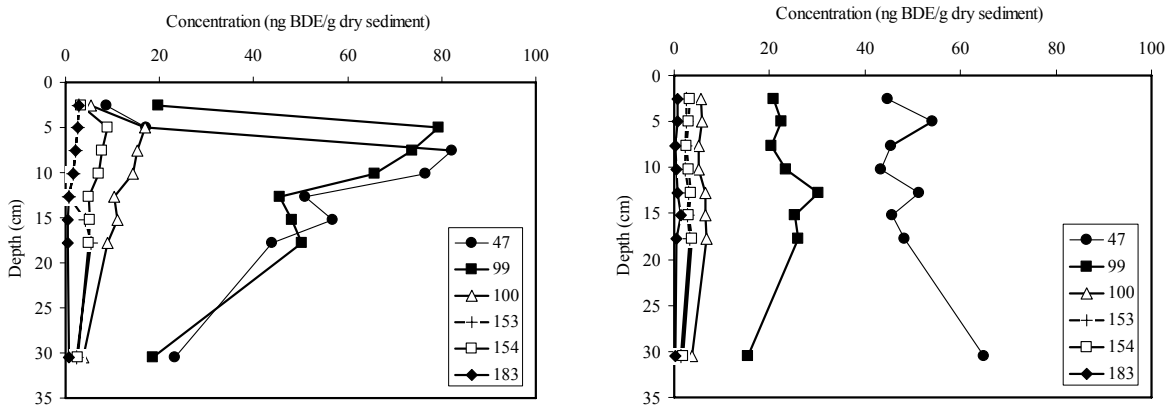


Figure 10. Profiles of major PBDE congeners in the top foot of UAMAC soils in July 2005. Biosolids application rates in the soils sampled provided (a) 150 lb nitrogen/acre year (3X), (b) 50 lb nitrogen/acre year (1X).

The highest concentrations of individual congeners were on the order of 100 ng/g dry soil (BDE-47 and -99 in the 3X profile from July 2005). These concentrations are similar to the highest sediment levels at the SRF. Not surprisingly, PBDE concentrations in digested, dewatered sludge at IRWQCF were frequently more than an order of magnitude higher. Comparison of the nominal rates of biosolids addition to the 1X and 3X plots with the measured PBDE profiles provides a crude balance on PBDEs at the field site and insight relative to the long-term fate of PBDEs in land-applied biosolids. Balances were undertaken for BDE-47 and -99 only since the relatively high concentrations of these congeners in the UAMAC soils were comfortably within the range of the analytical methods employed. The 1X plot nominally received 0.366 kg of dry sludge per square meter per year. If all the PBDEs were retained in the top foot of soil, the consequent increment to BDE-47 concentration throughout that depth interval would average 0.70 ng/g per year (based on a BDE-concentration of 0.806 mg/kg in digested sludge and a dry bulk soil density of 1.38 g/cm^3). At an average concentration of 1.95 mg/kg in digested sludge, the annual increment to the average BDE-99 concentration at the 1X application rate would be 1.7 ng/g (5.1 ng/g for the 3X plot). By averaging the concentrations of BDE-47 and BDE-99 over the soil profiles at UAMAC it was possible to calculate periods of application necessary to accumulate the PBDE masses present in the 1X and 3X plots. The exercise was based on an assumption that BDE-47 and -99 are conserved. Results indicate that from 5-80 years of sludge application would be necessary to accumulate congeners to the concentrations measured in UAMAC soils. The highest values are a consequence of the high

levels of BDE-47 measured in the 1X plot in both the July and November sampling periods. Other calculated periods were from 5-22 years. Results suggest that both BDE-47 and -99 are persistent in agricultural soils despite the level of microbial activity that is expected following the addition of biosolids. Minimum half times for congener disappearance are on the order of decades or longer.

Since 85-95% of the PBDEs in wastewater are transferred to biosolids produced during wastewater treatment, their fate in agricultural soils amended with biosolids is of particular environmental interest. In the United States, about 60% of the biosolids produced in publicly owned treatment works is disposed of via land application, and in agricultural states like Arizona, the percentage is much higher. The mass balance on PBDEs in UAMAC soils is tentative at best since there is no long-term record of organic contaminant concentrations in IRWQCF biosolids. Nevertheless, PBDEs extracted from the top foot of UAMAC soils probably account for the entire mass of PBDEs applied during the last 5-20 years. Periodic mixing has complicated efforts to investigate PBDE transport in agricultural soils, and there may be significant contributions to total PBDEs in soil strata deeper than one foot. Neither limitation alters the principal result of the study, i.e. that all congeners accumulate in soils for decades. Opportunities for human exposure may arise (i) when soil particles become airborne, as is frequently observed in semi-arid agricultural areas; (ii) during infrequent periods of heavy rainfall and overland soil transport; and (iii) via the food chain when biosolids are used to fertilize the growth of animal fodder. The very long periods over which PBDEs and perhaps other trace organic contaminants in wastewater accumulate in the environment suggest that caution is warranted in the assessment of related impacts on human and environmental health.

Thus, comparison of sludge and soil concentrations of PBDE congeners strongly suggests that PBDEs are stable in agricultural soils amended with biosolids and accumulate over periods on the order of decades. Conversely, comparison of the July and November analytical results suggests that PBDEs disappear in these soils with half times on the order of months. Additional field monitoring is necessary to develop a single model for PBDE behavior in soils amended with biosolids.

Soil samples obtained from the Marana field site were analyzed for a suite of 56 OWCs at the USGS Water Quality Laboratory. A total of 11, 14, and 30 compounds were detected in the 0X, 1X, and 3X soils, respectively. Compound concentrations as function of depth detected in the 1X and 3X soils are listed in Tables 5 and 6, respectively. Compound concentrations did not show trends with depth, likely due to the mechanical disking performed following each annual biosolid application.

Table 5. Concentrations (ug/kg) of organic wastewater contaminants detected as function of soil depth (inches) in 1X biosolid land application plots at the UA Marana Agricultural Center.

Compound	1.5	2.5	3.5	4.5	5.5	6.5	12
acetophenone	ND	ND	ND	ND	ND	40	ND
para-cresol	100	ND	ND	ND	ND	ND	ND
Indole	570	200	230	460	740	270	210
Skatol	130	ND	92	ND	ND	ND	26
BHA	ND	ND	250	ND	ND	ND	ND
diethylphthalate	ND	ND	ND	ND	270	ND	ND
phenanthrene	ND	9.6	ND	ND	ND	ND	15
Anthracene	ND	ND	ND	ND	ND	ND	11
OPEO1	ND	ND	ND	ND	24000	42000	ND
fluoranthene	ND	ND	ND	ND	ND	ND	13

Pyrene	ND	ND	ND	ND	ND	ND	9.3
diethylhexylphthalate	ND	ND	ND	ND	ND	72	ND
cholesterol	ND	ND	ND	ND	0.068	ND	ND
beta-sitosterol	5400	ND	ND	ND	ND	ND	ND

Table 6. Concentrations (ug/kg) of organic wastewater contaminants detected as function of soil depth (inches) in 3X biosolid land application plots at the UA Marana Agricultural Center.

Compound	0.5	1.5	2.5	3.5
phenol	ND	ND	ND	66
1,4-dichlorobenzene	ND	ND	96	8
d-limonene	ND	ND	620	83
acetophenone	ND	290	ND	100
para-cresol	59	ND	490	110
naphthalene	ND	ND	45	5
indole	570	2500	6500	760
1-methylnapthalene	ND	ND	39	ND
skatol	110	250	1200	220
4-tert-octylphenol	ND	ND	ND	15
para-nonylphenol-total	1200	ND	10000	1800
phenanthrene	ND	ND	23	ND
Anthracene	ND	ND	24	ND
tonalide(AHTN)	170	520	1100	300
galaxolide(HHCB)	84	320	660	150
carbazole	ND	ND	130	18
NPEO1-total	ND	ND	670	ND
anthraquinone	ND	ND	ND	67
fluoranthene	7.1	ND	130	12
triclosan	90	ND	ND	200
pyrene	7.8	ND	130	10
bisphenolA	120	1300	2600	920
OPEO2	ND	ND	330	ND
diethylhexylphthalate	420	1200	1500	280
tetrabromodiphenylether	ND	ND	1500	56
benzo(a)pyrene	ND	ND	190	13
3-beta-coprostanol	1800	4600	0.96	0.18
cholesterol	1900	6600	1.9	0.33
beta-sitosterol	2400	8900	ND	ND
stigmastanol	ND	4000	ND	ND

Summary

WWT and sludge digestion. Estrogens and other OWCs were detected in biosolids from municipal treatment plants. Activated sludge wastewater treatment was able to remove 25% of influent nonylphenol by biodegradation. However, the majority of nonylphenol is transferred to sludge during wastewater treatment; two-thirds of the influent nonylphenol was found in biosolids after mesophilic anaerobic digestion. Thermophilic (high temperature) anaerobic sludge digestion provided little additional benefit for removal of estrogenic activity and nonylphenol. Ten out of 14 monitored OWCs were removed by >80% during activated sludge wastewater treatment. However, brominated flame retardants are not significantly degraded during wastewater treatment, rather, they are incorporated into sludge and then largely survive anaerobic digestion.

Land application. Field and laboratory studies of land application showed that nonylphenol biodegrades in soil with a half-life of a few months. In contrast, brominated flame-retardants are recalcitrant and largely accumulate in soil over time with half-lives of decades or longer.

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

Basic Information

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

Publication

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

Progress Report: USGS-NIWR 104G Project # 2005AZ114G

April 29th, 2008

Chemolithotrophic Denitrification: The Missing Link in the Biogeochemical Arsenic Cycle?

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Ron Oremland, USGS, Menlo Park, CA

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

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

Work during the last year of the project tested the impact of nitrate in reducing the mobility of arsenic in a sand sediment column (SF1) fed with a mixture of Fe(II) and As(III), which represent the species of iron and arsenic in anoxic groundwater. A control column (SF2) fed with only nitrate and As(III) was run in parallel. The results of this continuous flow experiment confirmed that the oxidation of iron by chemolithotrophic denitrifiers leads to the formation of iron oxides that serve as sorbents of both As(III) and As(V) (Figures 1A and 1B).

The graph demonstrates that the iron in the effluent of SF2 was predominately composed of Fe(II); whereas the effluent of SF1 contained only small amount of Fe(III). The total iron concentration in the SF1 effluent was considerably lower than in the corresponding influent due to its continued adsorption/precipitation on the surface of sand. These findings indicate that in nature nitrate should be expected to decrease the mobility of arsenic by two mechanisms: *1)* microbially catalyzed oxidation of arsenite to arsenate, 2) microbial oxidation of ferrous iron to ferric iron oxides which are effective arsenic sorbents. Furthermore, our results suggest that nitrate supplementation to groundwater could be used as an effective approach for the bioremediation of arsenic. Considering the levels of arsenic found in contaminated groundwater, the concentrations of nitrate are well below the federal drinking water standards for this nitrogen compound.

Significant effort was also dedicated to identify the microorganisms responsible for the anoxic oxidation linked to denitrification in four enrichment cultures developed in our research using inocula from different sources (anaerobic pond sediments, anaerobic reactor sludge; sludge from a continuous As-oxidizing denitrifying bioreactor). The different cultures were maintained in a mineral medium supplemented with As(III) and nitrate under a CO_2/N_2 atmosphere. No yeast or other organic amendments were added to the medium. Microbial cultures were characterized utilizing different microbial molecular ecology techniques, including denaturing gradient gel electrophoresis (DGGE), fluorescence in situ hybridization (FISH), sequencing of 16S DNA clone libraries. DGGE fingerprints revealed that in spite of the fact that the medium only contained nitrate and arsenite, the enrichments cultures consisted of various microorganisms. Sequencing of the 16S DNA clone libraries constructed for the different enrichment cultures revealed that sequences closely related to those of bacteria in two different bacterial genera were dominant in the cultures. The relative abundance of microorganisms in those two groups in the various cultures was determined by FISH utilizing specific probes designed in our study.

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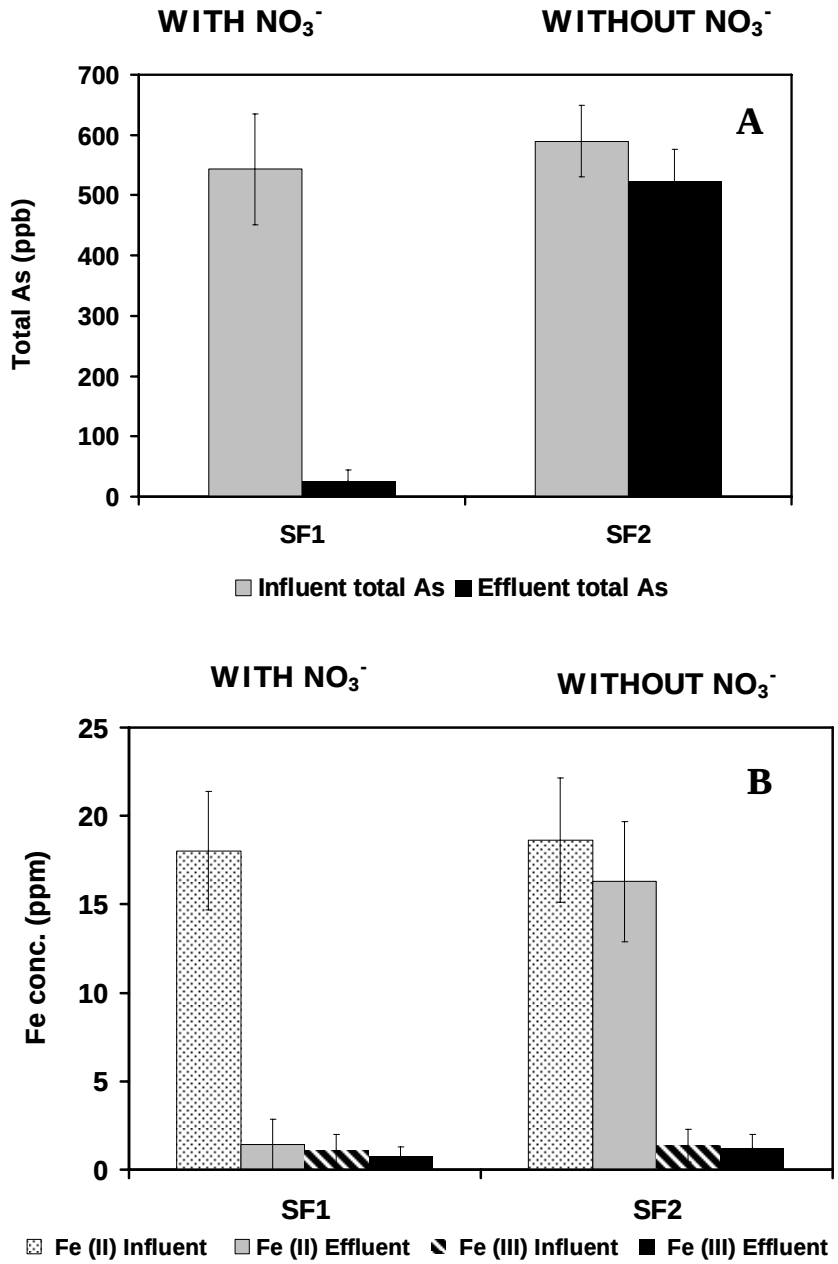

Figures 1A and 1B. Average concentration of arsenic in the influent (grey block) and effluent (solid block) of reactors SF1 and SF2 (**Panel A**). Average concentration of ferrous iron (dotted block) and ferric iron (stripped block) in the influent, and average concentration of ferrous iron (grey block) and ferric iron (solid block) in the effluent of continuous bioreactors SF1 and SF2 (**Panel B**). SF1 and the control bioreactor SF2 were fed with As(III) (6.7 μM) and Fe(360 μM), in addition the feed of reactor SF2 was supplemented with nitrate (2.0 mM). Both reactors were packed with sand as 95% of the empty bed volume and inoculated with 2.94 g VSS/l anaerobic sludge obtained from a As(III)-oxidizing chemolithoautotrophic denitrifying reactor.

Riparian Vegetation Response to Cessation of Groundwater Pumping, Lower San Pedro River, Arizona

Basic Information

Title:	Riparian Vegetation Response to Cessation of Groundwater Pumping, Lower San Pedro River, Arizona
Project Number:	2007AZ190B
Start Date:	3/1/2007
End Date:	2/28/2008
Funding Source:	104B
Congressional District:	5
Research Category:	Not Applicable
Focus Category:	Ecology, Hydrology, Conservation
Descriptors:	None
Principal Investigators:	Julie Stromberg

Publication

1. Katz, G.L., J. Haney, C. Paradzick, D. B. Harris. In press (2009). Mitigation, restoration, and endangered species: restoring river flows to the Lower Basin. In J.C Stromberg and B. Tellman (editors) Ecology and Conservation of the San Pedro River. University of Arizona Press.

4. DESCRIPTION INFORMATION

A. Problem and Research Objectives:

Restoration of physical conditions and processes has been increasingly emphasized in ecosystem restoration. This approach assumes that once the physical environmental conditions thought to underpin ecosystem characteristics are restored, the biotic ecosystem components will recover spontaneously without human intervention (i.e., "the myth of the field of dreams", Hildebrand et al. 2005). This assumption, in turn, relies upon speculation that physical and biological ecosystem changes are reversible and will follow predictable trajectories, and that we understand the time scales of such change. This strategy has yielded positive results in many settings but for a variety of reasons the expected results may not always be achieved.

Because riparian communities persist in dynamic environments typified by fluvial disturbance, they can be characterized as resilient ecological systems. Such resilience implies that riparian systems have the capacity to recover and reassemble quickly following disturbance. For example, riverine marshes developed rapidly on moist alluvial surfaces following a large winter flood on the Hassayampa River, Arizona (Stromberg et al. 1997). If mechanisms conferring resilience also apply in the context of restoration, hydrologic improvement should lead to ecosystem recovery on relatively short time scales. On the other hand, if riparian degradation is sufficient to cross thresholds in ecosystem characteristics and functions, recovery to the original resilient state may be difficult or may not follow predicted trajectories (Suding et al. 2004).

Riparian vegetation is strongly influenced by both the surface and sub-surface water flow regime. Tree recruitment, growth, and mortality are dependent on hydrologic conditions in the riparian zone. Herbaceous riparian plants are also influenced by hydrology, including flood patterns, surface flow permanence, and groundwater depth. Access to shallow groundwater or to groundwater discharge is associated with increased species richness or the presence of specific plant assemblages in a variety of settings, including boreal rivers and montane riparian meadows. Shallow groundwater levels are associated with perennial streamflow on rivers in the Sonoran and Chihuahuan deserts, and with high cover and richness and abundance of herbaceous wetland species.

Alterations of water regimes, including changes to surface flood patterns and subsurface hydrology (e.g. lowered water table elevations), have resulted in decline of various types of riparian plant communities on desert rivers. A number of authors have suggested that riparian vegetation should recover spontaneously following hydrologic restoration at degraded sites, and this has occurred where flood flows have been designed to achieve specific goals such as regeneration of pioneer trees (Hughes and Rood 2006). Most tests of this idea, however, have focused on restoration of flood flows, or minimum instream surface flows. In contrast, the strategy of restoring groundwater levels to achieve riparian restoration objectives has received less attention.

Groundwater levels are acknowledged to influence riparian restoration outcomes, but few published examples of restoration projects focus on groundwater level recovery. On incised mountain streams in the Great Basin, Nevada, USA, water table depth influenced the effects of restoration burn treatments on *Artemisia*-invaded riparian meadows; sites with low water tables (due to draining by stream incision) appeared to have crossed an abiotic threshold and were no longer capable of supporting meadow vegetation (Wright and Chambers 2007). In similarly impacted meadow systems in the northern Sierra Nevada, California, USA, restoration projects on incised streams have manipulated fluvial geomorphology (i.e., filled incised channels, constructed new un-incised channels) as a means to raising riparian water tables (Loheide and Gorelick 2007).

Our research project focused on restoration efforts implemented by The Arizona Nature Conservancy on the lower San Pedro River (LSPR), an important conservation corridor in southeastern Arizona, USA. The restoration efforts were based on the assumption that riparian degradation on an un-dammed desert river could be reversed by a management strategy focused on restoration of groundwater levels and base flows via cessation of alluvial groundwater pumping (Katz et al. in press). Many reaches of the LSPR sustain perennial streamflow and shallow alluvial water tables, conditions that maintain cottonwood-willow (*Populus fremontii-Salix gooddingii*) forests (Lite and Stromberg 2005) and riverine marshlands (Stromberg et al. 2005). Riparian forest patches support breeding populations of the endangered southwestern willow flycatcher and provide habitat for many other wildlife species. However, many reaches of the LSPR have been degraded historically by groundwater pumping for irrigation and mining activities (Haney 2005). In some areas, groundwater

and surface water levels in the riparian zone have declined below threshold levels needed to sustain cottonwood-willow forests and emergent wetlands. In such areas, *Tamarix ramosissima* and *Hymenoclea monogyra* shrublands dominate the floodplain, and the stream channels are wide and dry, supporting little herbaceous vegetation or aquatic life (Figure 1). While the riparian zone has been impacted by a variety of human activities (e.g., livestock grazing, ATV use), hydrologic alterations from groundwater pumping are thought to have had an over-riding influence on ecosystem characteristics.

The primary goal of the restoration projects were to improve site hydrologic conditions (i.e., increase water table elevations, baseflow volume, and extent of perennial flow) as a means to improving aquatic and riparian habitat conditions (Haney 2005). The primary goals of our study were twofold: First, to more comprehensively describe reference (target restoration) conditions, by contrasting streamside plant communities between perennial-flow and nonperennial-flow sites. The second goal was to assess vegetative response to restoration on the LSPR during the first five years of reduced alluvial groundwater pumping, by comparing streamside herbaceous vegetation between restoration and reference sites. We asked: (1) What are the characteristics of streamside herbaceous structure and composition at perennial reference sites ? (2) How have site hydrology and vegetation responded to the cessation of groundwater pumping at LSPR restoration sites?

B. Methodology:

Study river. This study was conducted on the San Pedro River, an un-dammed river that flows northward from its headwaters in Sonora, Mexico, to its confluence with the Gila River near Winkelman, Arizona. The San Pedro River is spatially intermittent; perennial reaches with year-round surface flow are interspersed with intermittent reaches characterized by dry channels for part of the year.

Study sites. Data were collected data at six restoration sites and six reference sites on the LSPR for five years (2003-2007) following the initiation of the hydrologic restoration project. Restoration study sites were located at two farms purchased by The Nature Conservancy of Arizona (TNC), where historic alluvial groundwater pumping was curtailed to meet restoration objectives. Three sites were located at the 870 hectare Three Links Farm purchased in 2003, formerly containing 425 hectares under irrigated agriculture with groundwater pumping rates of approximately 3,950,000 cubic m per year (Katz et al. in review). Three restoration sites were

located at the 214 hectare H&E Farm, where groundwater pumping rates were approximately 2,710,000 cubic m per year prior to farm purchase in 2001 (Haney 2005, Katz et al. in press). At both farms, floodplain terraces formerly supporting mesquite (*Prosopis velutina*) bosques were cleared and used for crop agriculture. Direct impacts of agriculture did not occur on the active floodplain, inset below the level of the terraces, where our research was conducted. The reference sites were located upstream and downstream of the restoration sites, in areas that spanned a range of hydrologic conditions.

Vegetation sampling. Streamside herbaceous vegetation was sampled annually during the pre-monsoon summer dry-season (late May – early June). In the dry season, herbaceous riparian vegetation patterns most strongly reflect base flow and groundwater hydrology, as opposed to being influenced by precipitation or flood pulses. The streamside zone was defined as the zone of direct influence of the low-flow stream channel, including channel bars, benches and streambanks, and inclusive of areas with shallow water (up to 10cm) and emergent aquatic vegetation. At each site data were collected at three stream locations, separated by a stream distance of 100m. Percent cover of each herbaceous species was estimated within 1-m2 plots (5 per stream location, 15 total per site) using modified Domin-Krajina cover classes.

Plants were identified to species using Kearney and Peebles (1960), and recent taxonomic treatments published as part of the Vascular Plants of Arizona project. Species were classified according to water availability needs using wetland indicator scores for the Southwest (Region 7). Wetland indicator scores signify the probability that a species will occur in a wetland environment. For our study, obligate and facultative wetland species were grouped as hydric, facultative and facultative upland as mesic, and non-wetland as xeric. Plants also were categorized plants into six functional groups based on combinations of life span (annual vs. perennial) and water needs categories (Bagstad et. al. 2005).

Hydrologic monitoring. Groundwater depth at the restoration sites was measured quarterly in monitoring wells. Surface flow presence was assessed once per year, during the summer pre-monsoon dry season. These data were used to categorize sites as perennial or nonperennial.

Analysis. Several vegetation metrics (total herbaceous cover, species richness, weighted wetland indicator score, relative cover of non-native species, and relative cover of species within the six functional groups) were compared (1) between

perennial and non-perennial sites and (2) between perennial reference sites and each of the groups of restoration sites (i.e. Three Links Farm restoration sites and H&E Farm restoration sites). Differences were analyzed with pairwise t tests, using a Bonferroni adjustment, after log-transforming data (where necessary) to better approximate a normal distribution. For data that could not be normalized, non-parametric pair-wise comparisons were conducted using Wilcox Rank Sum tests with a Bonferroni adjustment. These statistical analyses were conducted using either SAS v. 9.1 or R. We also compared the restoration sites individually to the perennial reference sites (which represent the target conditions for restoration) by expressing restoration site metrics as a proportion of the mean perennial reference site value, by year.

Plant community composition was analyzed with non-metric multidimensional scaling (NMDS) based on Bray-Curtis distance and using plant frequency data (i.e. percentage of plots occupied by a species during each year) for the 170 species encountered along the active channel during the study period. Pearson correlation coefficients were used to assess species correlations with axes produced by the NMDS ordination. Using this same dataset, cluster analysis was used to identify site groups. Significance of species indicator values was assessed with Monte Carlo tests, using 1000 iterations. Multivariate analyses were conducted with PC-ORD v. 5.

C. Principal Findings and Significance:

<u>Characteristics of reference sites (i.e., restoration target conditions).</u> Compared to the non-perennial sites, perennial-flow sites had higher herbaceous cover, higher species richness, lower weighted-average wetland indicator scores (indicating greater relative abundance of wetland plants), and higher relative cover of two of the six functional types (hydric perennials and hydric annuals). In contrast, non-perennial sites had higher relative cover of mesic perennials and xeric annuals. These finding are consistent with those of Stromberg et al (2005).

An additional plant community trait that emerged as a useful metric for assessing restoration success was the degree of year to year variability in plant community composition. The perennial-flow sites belonged to a distinct group in the cluster analysis, and were characterized by high constancy of plant species across time and space. In contrast, the non-perennial sites were much more dispersed within the ordination space, and individual sites showed considerably more year-to-year variability in species composition.

Dominance by native species is often stated as a measure of restoration success (e.g., Long et al. 2004) but in this study relative cover of non-native species was high(on the order of 70%) and did not differ between perennial and non-perennial sites. In some hydrologically altered riparian systems, increased native dominance might indicate the return of physical conditions to which the species are adapted, a phenomenon that has been observed for some woody riparian species (Sher et al. 2002). On the other hand, non-native species are abundant in the herbaceous riparian flora of Arizona, and are especially plentiful within the hydric functional group (Stromberg et al. in press). Therefore, streamside dominance by native herbaceous species is not necessarily equated with increased moisture availability on the LSPR.

Plant community changes at restoration sites. According to most vegetation metrics, Three Links Farm currently supports vegetation similar in structure and composition to that of the perennial reference sites. Mean streamside herbaceous plant cover, species richness, wetland indicator score, and relative cover of all plant functional groups at the Three Links Farm restoration sites are similar to target conditions. Further, the Three Links Farm restoration sites tend to group with the perennial reference sites compositionally, as indicated by ordination results and cluster analysis.

In sharp contrast, the H&E Farm restoration sites show little evidence of shifting towards conditions similar to those of the perennial reference sites. The H&E Farm restoration sites have lower streamside plant cover and species richness, and higher (i.e., drier) wetland indicator score, than target conditions. Relative cover of hydric perennials and hydric annuals is lower that target conditions, while relative cover of xeric annuals is higher. Temporal trajectories do not indicate convergence towards the species composition of reference sites. In the cluster analysis, the H&E Farm sites group separately from the perennial reference sites.

Barriers to restoration success. The lack of detectable recovery at H&E Farm could be due to several factors. It could be caused by an incorrect understanding of historic site conditions (e.g., if the reach was always ephemeral due to geologic factors) or by the presence of unidentified restoration barriers or thresholds (Hobbs 2007). Alternatively, the hydrologic and biotic systems at H&E Farm may be characterized by slow rates of change, but not true stability. It is possible that the time required for hydrologic recovery in this system is simply longer than our five-year study period. Groundwater pumping for irrigation occurred over many decades, and it

may be unreasonable to expect aquifers to recover within years (Filippone and Leake 2005). This intrinsically slow rate of hydrologic recovery may have been exacerbated by recent drought, further delaying the return of hydrologic conditions that will eventually drive vegetative shifts. If this is the case, then once drought conditions diminish, ecosystem recovery will likely proceed, albeit in a slow and perhaps episodic manner.

Because ephemeral channel recharge is episodic, recharge by this mechanism occurs in a pulsed fashion (Pool 2005), and groundwater recovery dependent on this process is likely to occur in a stair-step pattern. H&E Farm may typify such conditions, where depleted alluvial groundwater on a losing reach is being slowing and episodically recharged by floodwaters. Indeed, the increased water table elevations observed after monsoon flooding in 2006 suggest that, should such events continue to occur in the future, repeated delivery of seasonal moisture might incrementally replenish alluvial groundwater in this reach. Such a response could ultimately result in ecosystem recovery, if thresholds necessary to support vegetation typical of perennial reference sites are crossed. In this system, different hydrologic thresholds may be relevant for different riparian ecosystem components, and the same thresholds may not apply to both degradation and restoration.

In addition to slow hydrologic recovery, slow biotic response to changed physical conditions could contribute to the lack of a positive restoration outcome at H&E Farm. For example, seed availability might limit the rate of biotic change, since reproductive material of extant plants will be readily available at a site, while that of off-site species may not be. Dispersal limitation was thought to play an important role in producing contrasting patterns of riparian response to flow restoration on two floodplains in California, USA (Trowbridge 2007), and in constraining alluvial grassland restoration in Germany (Bissels et al. 2004). For desert rivers in Arizona, perennial reaches do have diverse soil seed banks that could provide propagules for restoration via hydrochory (Stromberg et al. 2008); viable seeds of wetland plant species also have been found in ephemeral reaches of spatially intermittent rivers, although the abundance of these propagules decreased with distance downstream of a perennial reach in one survey (Stromberg, unpub. data). Restoration sites at H&E Farm are several kilometers from the nearest upstream perennial reach. However, because the LSPR is undammed and characterized by a dynamic flood regime, longitudinal

connectivity is fairly high in this system and dispersal limitation is unlikely to be the primary cause of the lack of vegetation change at H&E Farm.

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Compound Specific Isotope Analysis of Natural Attenuation Activity in Chlorinated−Solvent Contaminated Aquifers

Basic Information

Title:	Compound Specific Isotope Analysis of Natural Attenuation Activity in Chlorinated−Solvent Contaminated Aquifers
Project Number:	2007AZ198B
Start Date:	3/1/2007
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	Arizona District 7
Research Category:	Ground−water Flow and Transport
Focus Category:	Groundwater, Water Quality, Toxic Substances
Descriptors:	None
Principal Investigators:	Mark Brusseau

Publication

4. Description Information

A. Problem and Research Objectives

The sustainability of potable water supplies is a critical issue in Arizona, given the recent and ongoing population increase, economic expansion, and arid climate. A major issue influencing water-resources sustainability is the contamination of vital groundwater supplies by hazardous chemicals. Such contamination reduces the quantity of groundwater available for use as potable water, and also poses a risk to human health and the environment. In Arizona, chlorinated solvents, including tetrachloroethene (PCE), trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC), are the primary contaminant at 43 of 48 State and Federal Superfund sites. In aggregate, these sites comprise billions of liters of contaminated groundwater. Accordingly, these chlorinated-solvent contaminated sites pose a significant and long-term risk to the sustainability of potable groundwater in Arizona. Remediation of polluted soil and groundwater at chlorinated-solvent contaminated sites is therefore of immediate importance in protecting groundwater resources in the state of Arizona. Of particular interest is the development of simple, low cost, easily applicable remediation strategies that will achieve cleanup goals for these sites.

Remediation of polluted soil and groundwater at chlorinated-solvent contaminated sites in Arizona is of prime importance for ensuring safe and clean potable water resources. Unfortunately, remediation of chlorinated-solvent contamination has proven to be a costly, complex, and challenging task. Chlorinated solvents occur naturally as immiscible liquids that are denser than water, and once they enter the subsurface, they become trapped in soil pores and are difficult to locate and remove. As a result, they serve as a long-term source of contamination in the subsurface. Several studies commissioned by the National Research Council (NRC) conclude that the presence of immiscible liquid is generally the single most critical factor constraining remediation of sites contaminated by organic compounds (NRC, 1994, 1997, 1999, 2000, 2004). The National Research Council recently re-analyzed the human toxicity of trichloroethene. Based on their analysis, they have recommended that the legally enforceable maximum contaminant level (MCL) of TCE be reduced from 5 μg/L (parts per billion) to 1 μg/L (NRC, 2006). Clearly, this reduction in

the MCL would have a significant impact on all sites contaminated with TCE.

Recently, monitored natural attenuation (MNA), a process that uses intrinsic transformation and retention processes while carefully monitoring contaminant conditions to control and shrink groundwater plumes has come into favor as a low-cost approach for site remediation. Over the past decade, MNA has been successfully used at many sites contaminated with petroleum hydrocarbons. Due to the unique complexities presented by chlorinated solvents, MNA has been more difficult to implement for chlorinated-solvent contaminated sites. However, field studies have shown that MNA can be successfully used for such sites if the appropriate transport and transformation regimes exist (Buscheck et al. 1997; Parsons, 1999; Kampbell et al, 2001).

Because MNA relies on intrinsic processes, accurate site characterization is critical for its successful implementation. Accordingly, formal protocols addressing the implementation of MNA place high importance on site characterization (e.g. Wiedemeier et al., 1998). There are three major questions to address regarding the feasibility and viability of MNA for a given site. These are 1) Are natural attenuation processes occurring at the site? 2) Is the rate and magnitude of natural attenuation sufficient to accomplish the cleanup objectives and be protective of human health and the environment? 3) Will natural attenuation be sustainable over the long time frames typically required for successful application of MNA? Developing accurate methods to assess these three questions is of fundamental importance to the success of MNA. The particular complexities and challenges of chlorinated-solvent contamination necessitate a greater amount of information to accurately characterize the site (NRC, 2000). Additionally, the USEPA has now recognized that the protocols for chlorinated-solvent contaminated sites need to be much more region and site specific (USEPA, 1999).

Typically, the dominant attenuation process for most sites is microbial transformation of the contaminant. Therefore, characterizing the occurrence, rate, and magnitude of microbial transformation processes is a critical element in evaluating MNA feasibility. Currently, such characterizations are based on evaluating the spatial and temporal distribution of contaminant concentrations, electron acceptors and donors, and degradation products in site groundwater, which is typically referred to as a geochemical “fingerprint” of

microbial activity. This approach involves a high degree of uncertainty because it is difficult to assess the potential impact of abiotic transformation processes, sorption, dilution, and mass transfer processes upon the observed geochemical measurements. More direct determination of microbial transformation processes can be accomplished by using site groundwater or sediment samples in laboratory microcosm studies. This method has the advantage of more directly evaluating the contribution of microbial processes to attenuation, but proves difficult and time consuming in practice, with specific challenges in relating laboratory results to the field. The development of low-cost methods that could be rapidly applied to the field to accurately assess microbial transformation would greatly enhance the ability to determine MNA feasibility for specific sites.

A potential low-cost, rapid method for directly identifying the presence of biological transformation processes is Compound Specific Isotope (CSI) analysis. This method takes advantage of the natural fractionation of carbon isotopes during biological transformation. All carbon-containing compounds contain a mixture of ^{12}C and ^{13}C. The initial naturally occurring ratios of ^{12}C and ^{13}C are altered as the contaminant is biodegraded because microbial metabolism kinetically prefers the lighter ^{12}C. This fractionation results in an enrichment in the heavier ^{13}C for the original contaminant. Furthermore, the degradation product (such as TCE produced from biodegradation of PCE) is initially enriched in ^{12}C. Abiotic transformation processes do not exhibit significant isotopic fractionation, and thus, changes in $^{13}C/^{12}C$ ratios are a reliable indicator of biological transformation of the target contaminant. In recent years, several laboratory studies have successfully demonstrated the reliability of this method (Slater et al., 1998, 2000; Dayan et al., 1999; Hunkeler et al., 1999, 2002; Sherwood-Lollar et al., 1999; Bloom et al., 2000; Barth et al., 2002; Chu et al., 2004). Additionally, pilot-scale field studies have also been conducted, including demonstrations of CSI at chlorinated-solvent contaminated sites (Sherwood-Lollar et al., 2001; Vieth et al., 2002; Kirtland et al., 2003). However more research is necessary to further characterize the applicability of this promising technology to chlorinated-solvent contaminated sites in Arizona.

The goal of this project is to evaluate a simple and broadly applicable method to assess the feasibility of using MNA at chlorinated-solvent contaminated sites in Arizona.

The availability of such a method would greatly enhance the ability to quickly and effectively evaluate sites, thereby providing valuable information for site owners and regulators.

B. Methodology

The Park/Euclid WQARF site in Tucson was used as a model Arizona chlorinated-solvent contaminated site for this study. The Park-Euclid site is located approximately 1 km S-SW from the University of Arizona (UA) and has both perched and regional aquifers. Prior operation of a commercial dry cleaning facility resulted in the contamination of the perched aquifer with PCE. This aquifer is not used for potable-water supply. Contamination of the regional aquifer occurred through a pair of former water-supply wells. The regional aquifer is the main source of potable water supply for the Tucson Basin. The nearest water-supply wells are located 0.7 km north (downgradient) of the inferred plume edge and are used by the UA. Analysis of the Arizona Department of Environmental Quality (ADEQ) database shows that the original PCE contamination in subsurface has evolved into a mixture containing PCE and several compounds typically associated with PCE biotransformation (TCE, DCE, and VC). Generally, PCE concentrations have decreased over the last ten years, while TCE concentrations have remained constant. Accumulation of DCE isomers (mainly *cis*-1,2-DCE) is observed in most of the wells. Conversely, VC has been observed in only three wells and only since 2001. This suggests that PCE is undergoing biotransformation and that DCE transformation is the limiting step. The Park-Euclid site has been the focus of prior chlorinated-solvent remediation studies conducted by the PI's research group. Our prior research has included microcosm studies to demonstrate reductive dechlorination activity in groundwater samples obtained from the site. In addition, polymerase chain reaction analysis of samples collected from the site has demonstrated the presence of bacteria from the genus *Dehalococcoides. Dehaloccoccoides* sp., which are the only known genus capable of converting PCE or TCE to ethane. A good correspondence has been observed at the site between the presence of *Dehalococoides* and the occurrence of ethene, which is the final degradation product for reductive dechlorination of chlorinated-solvent contaminants (Hendrickson et al. 2002).

Compound specific isotope analysis is done by isolating a compound of interest via

gas chromatography (GC), oxidizing it to CO_2 via combustion, and determining the relative ratios of naturally occurring isotopes in an Isotope-Ratio Monitoring Mass Spectrometer (IRMS). The aggregate process is commonly referred to as GC/C/IRMS. This allows determination of a $^{13}C/^{12}C$ ratio, which can then be used to assess the presence or absence, and rate and magnitude, of biological activity. The results of the CSI analysis were compared to the data we have gathered from our prior studies using other characterization methods.

Both ^{13}C and ^{12}C exist naturally in the environment, with ^{12}C representing approximately 98.89% of the earth's carbon, and ^{13}C representing approximately 1.11% (Meckenstock et al., 2004). Because of kinetic isotope effects, biologically transformed chemical species demonstrate a deviation from this ratio. For ^{13}C, this deviation is defined as:

$$\delta^{13}C = (R_s/R_{std}-1) \times 1000$$

where R_s is the $^{13}C/^{12}C$ ratio of the sample and R_{std} represents the $^{13}C/^{12}C$ ratio of the standard. Biological transformation processes show a siginificant kinetic isotope effect, or the increase of the $^{13}C/^{12}C$ ratio. These effects depend on the preferential use of lighter isotopomers in enzymatically catalyzed reactions, which leads to unequal distribution of isotopomers in substrates and reaction products.

Groundwater samples were collected in triplicate from the Park-Euclid site in December of 2007. All sampling adhered to EPA methods. These samples were shipped on ice to the Colorado Plateau Stable Isotope Lab (CPSIL) in Flagstaff, AZ, where they were analyzed for both $\delta^{13}C$ and aqueous concentration of PCE, TCE and cis-1,2-DCE. GeoTrans, Inc., the ADEQ consultant for the Park-Euclid site, collected concurrent groundwater samples using EPA Method 8260B as part of their semi-annual monitoring program.

C. Principal Findings and Significance

Aqueous concentration data collected for the Park-Euclid site shows a shift in the chlorinated ethene composition over time (Fig 1). Higher chlorinated ethenes such as PCE and TCE have decreased over the last 7 years, while the daughter product of TCE

biotransformation, cis-1,2-DCE has increased, then decreased. The daughter product of cis-1,2-DCE biotranformation, VC, has increased recently. Additionally, the final product of complete reductive dechlorination, ethane, has been observed at the site, and in increasing levels since 2005. These data illustrate the geochemical fingerprint of reductive dechlorination, and suggest that biotransformation is active at the Park-Euclid site. Additionally, the increasing concentrations of VC and ethene suggest that the previously limiting step, biotransformation of cis-1,2-DCE to VC, is now occurring.

The $\delta^{13}C$ data collected for the Park-Euclid site further corroborate that biodegradation is occurring at the site (Fig 2). A relationship has been established between cis-1,2-DCE concentration and cis-1,2-DCE $\delta^{13}C$, which suggests that cis-1,2-DCE is being actively reduced to VC. Previous data from 2005 shows that as cis-1,2-DCE decreases in concentration, the relative enrichment of ^{13}C increases. The increase in normalized $\delta^{13}C$ is a product of the reductive chlorination, and shows that the observed overall concentration decrease is the result of biotransformation as opposed to other dilution and dispersion mechanisms. Data from the same wells collected in 2007 shows a shift along the same trend established by the 2005 data, and demonstrates continual reductive dechlorination.

These results are significant in that they show a previously unobserved temporal trend at the field scale. Prior studies on reductive dechlorination have established single time point relationships between decreasing concentration and isotope fractionation. The results of the current study establish a temporal trend in reductive dechlorination, and serve as evidence of reductive dechlorination in the Park-Euclid perched aquifer. Taken in concert with the established shift in chlorinated ethene composition in the perched aquifer, these data strongly suggest that natural attenuation is occurring at the site. Additionally, the results indicate that CSIA is an effective and easily implementable site characterization tool that can provide data useful for assessing MNA feasibility under site conditions that are common to Arizona.

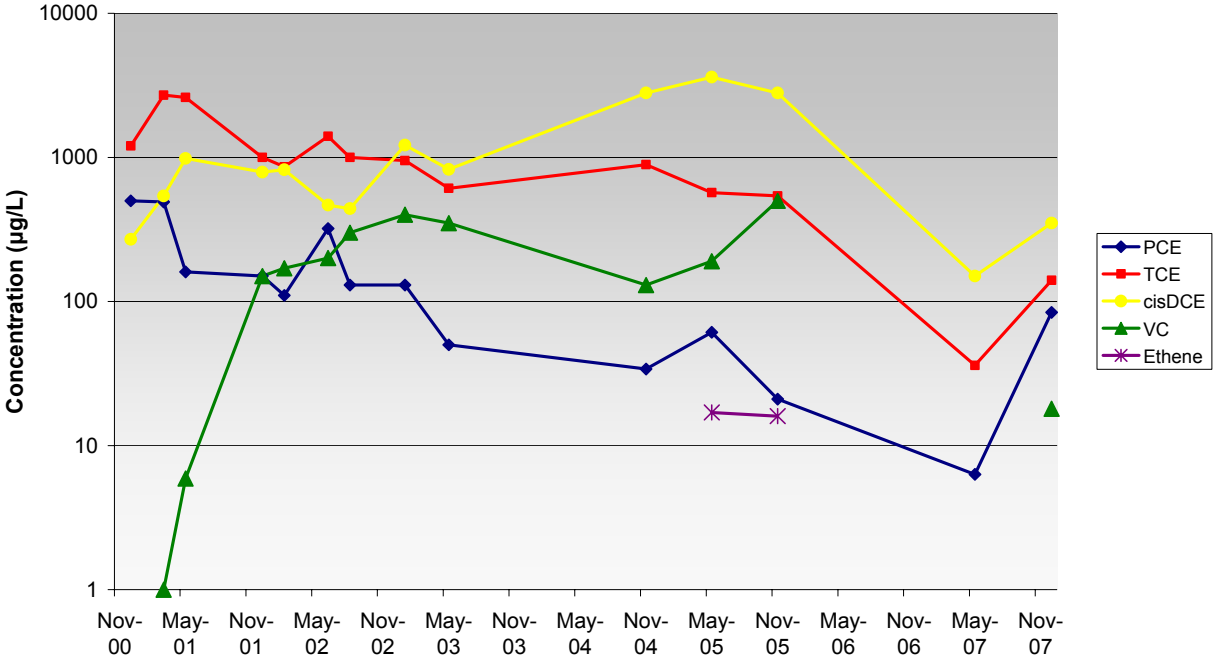

Figure 1: Aqueous concentrations of chlorinated solvents at well PEP-9.

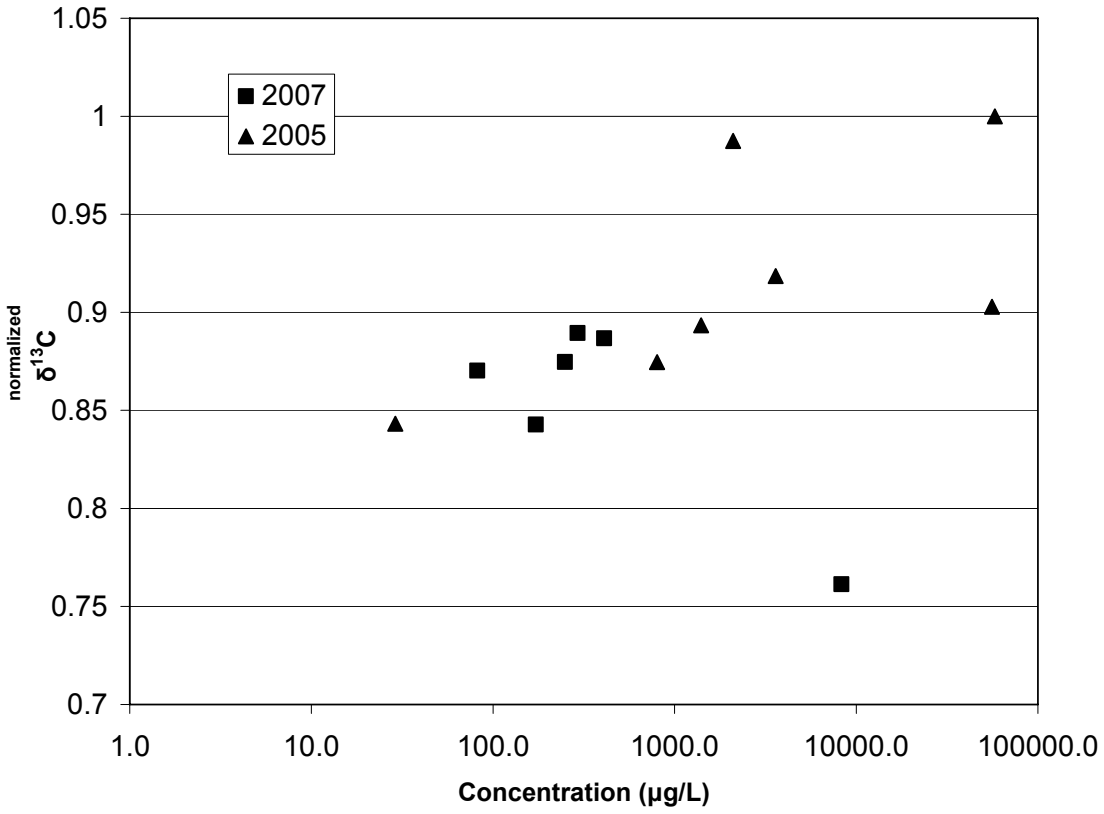

Figure 2: Normalized $\delta^{13}C$ as a function of aqueous concentration for cis-1,2-DCE. $\delta^{13}C$ values are normalized by the least enriched value observed at the Park-Euclid site.

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Sources of Nitrate in Groundwaters of the Tucson Basin

Basic Information

Title:	Sources of Nitrate in Groundwaters of the Tucson Basin
Project Number:	2007AZ213B
Start Date:	3/1/2007
End Date:	2/29/2008
Funding Source:	104B
Congressional District:	7
Research Category:	Water Quality
Focus Category:	Geochemical Processes, Nitrate Contamination, Hydrogeochemistry
Descriptors:	
Principal Investigators:	Thomas Meixner

Publication

1. Dejwakh, N. 2008. Sources of Nitrate to Tucson Groundwaters, MS Thesis. Department of Hydrology and Water Resources University of Arizona, Tucson, Arizona 45pp.

4. Descriptive Information

4. A. Problem and Research Objectives

Due to the dependence on groundwater for domestic, industrial and commercial use, the quality of groundwaters is of critical importance in the arid regions of the world including the Southwest United States. Nitrate is a common contaminant to groundwaters around the world. In Arizona, nitrate contamination is the leading cause of the removal of wells for domestic use from production. Waters with excess nitrate are not only associated with the destruction of wildlife by causing eutrophication of aquatic ecosystems, they have also been known to cause mothers to give birth to babies with blue-baby syndrome. The Environmental Protection Agency (EPA) has set the maximum contaminant level (MCL) for nitrate in drinking water to 0.71 mmols/L or 10mg of NO_3-N/L. In light of these health concerns, the sources, sinks and processes affecting nitrate concentrations in Tucson's groundwater were investigated.

The literature accounts for four major sources of nitrate to groundwaters and streams. A typical source of nitrate includes fertilizers, mainly from the addition of nitrogen as a nutrient to agricultural fields and lawns, and flushed through irrigation losses. Another major source is manure/septic wastes composed of organic nitrogen that oxidizes and mixes with runoff. In addition, a great deal of N cycling occurs in the soil level where organic matter originating from vegetal sources are decomposed (mineralization) and nitrified by organisms. Finally, recent studies conducted in urban settings (Southern California) and areas of limited hydrological activity (Atacama Desert) have shown significant atmospheric deposition of nitrate from marine origins, photochemical reactions and the combustion of fossil fuel.

Nitrates are lost from soil and groundwater systems through different processes. One nitrate consumption process is denitrification where organisms break down nitrate into dinitrogen gas. Studies have shown denitrification to occur in both surface water and groundwater with anoxic conditions and organic matter present. Immobilization is another known pathway of N loss in which organisms in the soil take up nitrate and ammonium and convert it to organic N (opposite of mineralization). Like organisms, plants (including crops) also take up nitrate as a nutrient to generate biomass. Finally, leaching, the pathway by which nitrate is transported by recharge waters, represents not only a loss of nitrate to the soil but also a source to groundwaters. Leaching can be significant due to nitrate's high mobility.

Traditionally, two isotopes of nitrate ($\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$) are used to differentiate between different sources and to determine processes affecting nitrate (Kendall). Studies have measured enriched $\delta^{18}O$ in atmospheric nitrate, generally enriched $\delta^{15}N$ in manure/septic nitrate, low $\delta^{15}N$ and $\delta^{18}O$ in soil nitrate and isotopic mass ratios for fertilizers overlapping with the atmospheric isotopic ratios. In addition, denitrification can be estimated with $\delta^{18}O$ and $\delta^{15}N$ increasing on a 1:2 ratio. The recent development of a technique involving the $\delta^{17}O_{NO3}$ signature allows better constraint on the proportion of atmospheric derived nitrate. Although most processes fractionate the O molecules in NO_3 with mass-dependence, giving $\delta^{17}O$ a direct relation to $\delta^{18}O$, atmospheric photochemical reactions fractionate oxygen molecules mass-independently resulting in a more enriched $\delta^{17}O_{NO3}$ due to their ozone origin.

In the Tucson basin, there are no perennial streams other than effluent dominated Santa Cruz River. Groundwater is disconnected from surface waters with depths to water table between 38-52 m along the Rillito River and 42-47 m near the Santa Cruz River. Studies have shown that significant groundwater recharge occurs along the Rillito River flood plain where runoff from both undeveloped (mountain front) and developed (residential, commercial) land flows during

rain events (Eastoe et al.). Recharge also occurs from treated wastewater along the Santa Cruz River. In addition to wastewater, golf courses, agricultural activity, houses with septic tanks, landfills and atmospheric deposition (combustion of fossil fuel) are possible N sources in the basin. Based on these source waters, Rillito groundwater nitrate is expected to be derived from soil nitrification and atmospheric processes, with some minor fertilizer and human waste influence. The Santa Cruz groundwater nitrate is expected to be predominantly from human waste. We employ chemical data and the $\delta^{17}O$ enhancement to the dual isotopic system to answer a few questions: (1) How important is sewage-derived nitrate in Tucson's groundwater? (2) Is denitrification affecting groundwaters? And (3) what proportion of nitrate is atmospherically derived?

4. B. Methodology

Study Area

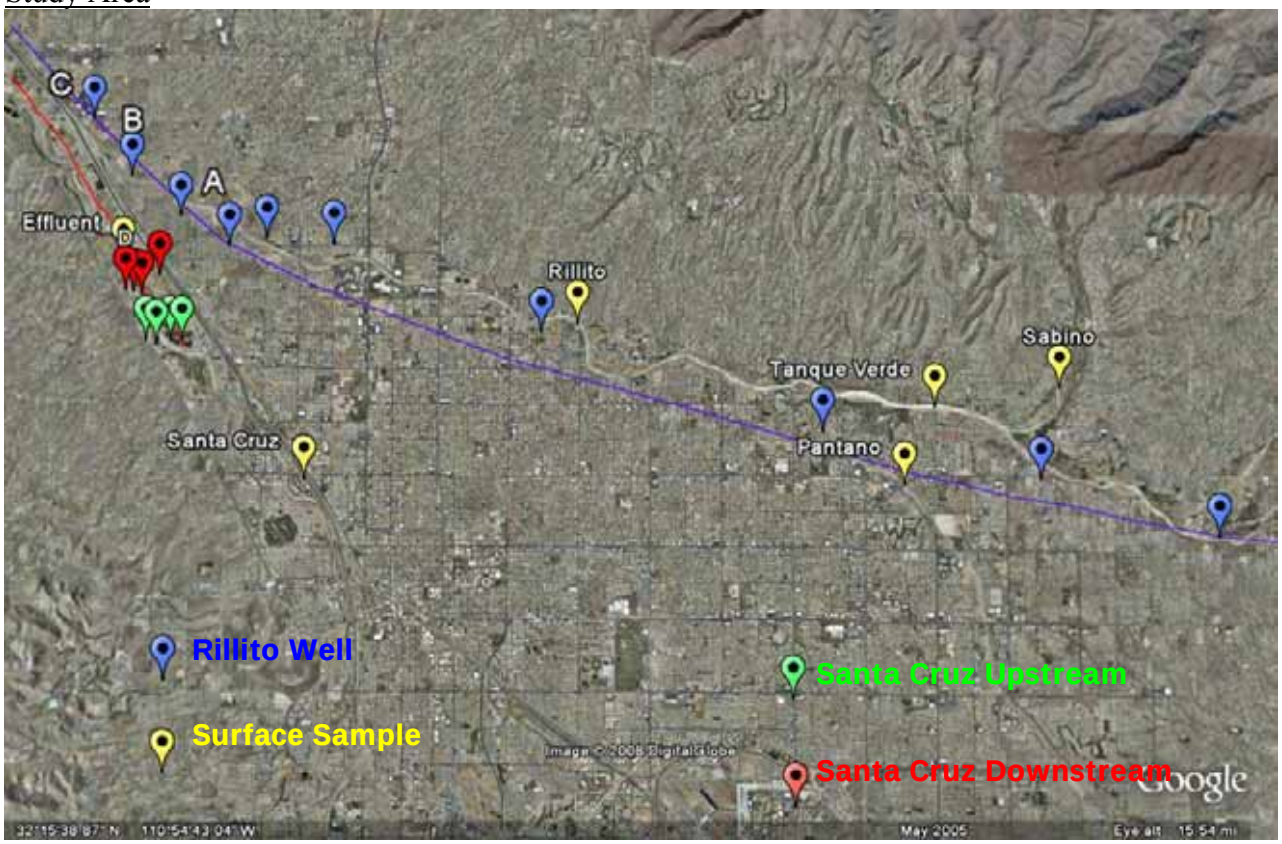

Figure 1. Wells sampled along the Rillito River (blue markers), along two Santa Cruz River cross-sections immediately downstream (green markers) and further downstream (red markers) from the wastewater treatment plant. Runoff samples collected in major washes (yellow markers) during a summer rain event.

In a study conducted in Tucson, geochemical and isotopic data were employed to distinguish groundwater regions based on their age, origin and flow paths. The general flow gradient was determined to be from east and southeast to west and northwest Tucson. Based on this study, samples were collected on a flow path along the Rillito River. This flow path

permitted the investigation of nitrate sources in waters originating from urban and mountain sources.

Since another significant source of recharge to Tucson's groundwater is treated effluent, groundwater beneath a wastewater effluent fed wash, the Santa Cruz River was investigated. To examine both lateral and longitudinal processes, two well cross-sections were selected along the Santa Cruz, one near the Roger Road Wastewater Treatment Plant and the other one 1.2 Km downstream (See Figure 1). The depths to water table increase along the Rillito River from 38 to 52m. Along the Santa Cruz, the water table varies between 42 and 47m below the land surface.

Sampling

Previous research (Kendall et al., Silva et al.) determined that 100-200 μmoles of $[NO_3]$ was needed for the analysis of nitrate isotopes $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$. Based on analysis of groundwater nitrate concentrations obtained from Tucson Water, 4 liters of water was sampled at each well (2 2-liter HDPE bottles were used) for the combined analysis of anions, nitrate isotopes, and water isotopes ($\delta^{2}H_{H2O}$ and $\delta^{18}O_{H2O}$. In addition, a 125ml amber glass bottle sample was collected for the analysis of Total Nitrogen (TN) and Dissolved Organic Carbon (DOC).

With the help of the City of Tucson, wells were selected along the Rillito River and along the two Santa Cruz River cross-sections. With the aid of an extensive well map, a list of all production and monitoring wells of interest was created and shared with Tucson Water's field specialists. Many wells were removed from the list either because they were not in operation or had technical difficulties associated with them. Nearly twenty wells were selected for sampling.

With the help of Tucson Water field technicians, a one-time sampling campaign was conducted and completed in three days. All production wells were running, and hence, the requirement of purging three well casings before sampling was already met. For the monitoring wells, a measure of the water table depth was taken, and, utilizing the well casing depth and diameter, three well casings was purged before sample collection. In addition, the pH, conductivity and dissolved oxygen were measured using handheld field meters. Although dissolved oxygen was measured immediately after pumping, the measurements were taken in open air.

In addition to groundwater samples, surface waters were sampled to obtain the pre-infiltration concentrations and isotopic signatures of possible source waters. Samples were collected from the Rillito River and other ephemeral channels during a summer rain event. The other ephemeral washes, Tanque Verde, Sabino Canyon, and Pantano Wash were sampled before their discharge into the Rillito River. In addition, samples were collected from the wastewater-fed Santa Cruz River and from the Colorado River water imported through the Central Arizona Project water, currently used to recharge Tucson's groundwater.

Sample analysis

After collection, the samples were returned to the lab, filtered and stored at 4 ºC in the dark. Within two days, the sample alkalinity was analyzed by end point titration. The samples were then analyzed for anions (fluoride, chloride, nitrite, bromide, nitrate, sulfate and phosphate) using Ion Chromatography (Dionex).

Once nitrate concentrations were determined, the volume containing 150□mols (100-200 μmols needed) of $[NO_3]$ was calculated for each sample. These sample volumes were then passed through ion-exchange columns to capture all nitrate and other anions in the sample (See Appendix A for details). The columns were then shipped to the Department of Earth and

Atmospheric Science at Purdue University for nitrate isotopic analysis. As described by Silva et al. (2000), the nitrate was eluted from the column, precipitated to $AgNO_3$ and converted to gas (N_2 and O_2). The nitrate isotopes $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ and were measured by isotope ratio mass spectrometry (IRMS). In addition, the water isotopes $\delta^{2}H_{H2O}$, and $\delta^{18}O_{H2O}$ were measured at the University of Arizona Environmental Isotope Laboratory.

Isotopic signatures

Four main sources of nitrate to aquatic systems are atmospheric N, fertilizers, soil nitrification and manure/septic. In the past, attempts were made to distinguish these sources based on their $\delta^{15}N$ isotopic signatures. Due to the overlapping $\delta^{15}N$ signatures of different sources, this approach was not successful and was greatly improved by coupling $\delta^{15}N$ with $\delta^{18}O$ of nitrate (Figure 2). Fertilizer nitrate has $\delta^{18}O$ near 22 ± 3‰. Although manure/septic and soil N have overlapping $\delta^{15}N$ and $\delta^{18}O$ ranges, studies have shown that manure/septic nitrates tend to have more enriched $\delta^{15}N$, at times exceeding 20‰. Soil nitrates have $\delta^{15}N$ values generally between 3 and 10‰ (Figure 2). Precipitation nitrate has the most enriched $\delta^{18}O$ ranging from 25‰ to 70‰. Because many processes fractionate $\delta^{18}O_{NO3}$ at the soil interface, the elevated atmospheric signature is often lost.

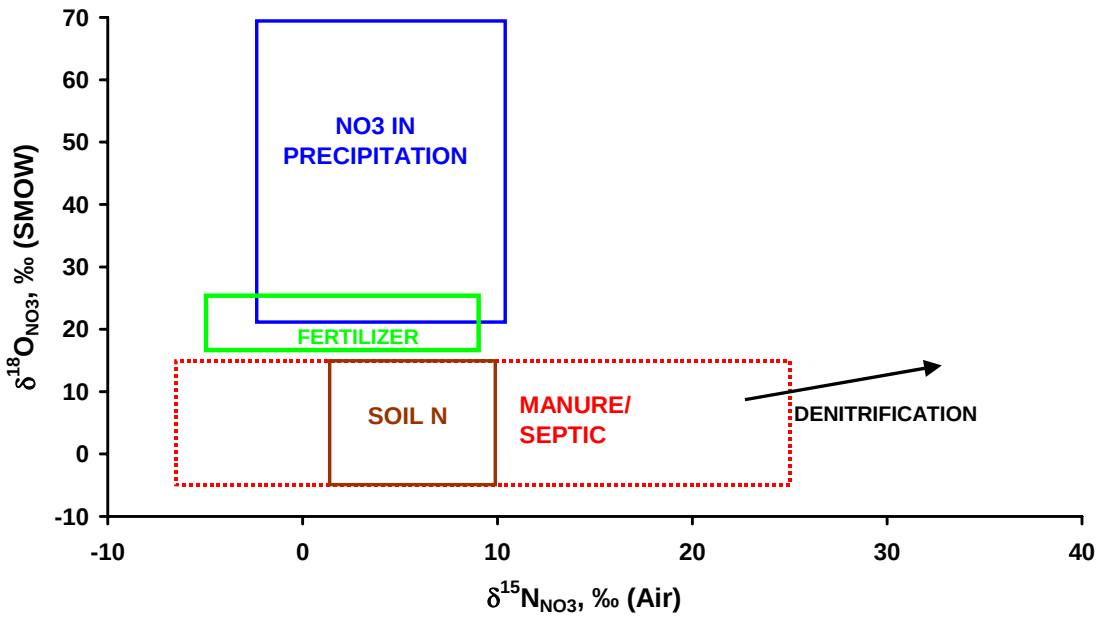

Figure 2. Dual isotopic plot $\delta^{18}O$ vs $\delta^{15}N$ showing the ranges of sources of nitrate. Precipitation nitrate has the most enriched $\delta^{18}O$. Although with similar mass ratios, manure/septic N can usually be distinguished by a more enriched $\delta^{15}N$ signature. More difficult to tease apart are nitrates from fertilizers and precipitation. Denitrification follows a 1:2 increase of $\delta^{18}O$ with respect $\delta^{15}N$.

In addition to determining sources of nitrate, isotopic data are useful for determining whether nitrates are affected by any fractionating reaction. For example, denitrification processes can be discerned with an increase of both $\delta^{18}O_{NO3}$ and $\delta^{15}N_{NO3}$ on a 1:2 slope along a flow path (Figure 2). Furthermore, in biologically mediated denitrification, organisms reduce nitrate and produce N_2 gas changing nitrogen from N^{+5} to N^{0} state. Electron donors are required to achieve this end. Typically, organic matter is the electron donor, and during the redox reaction, it is

oxidized from C^0 to C^{+4} (Equation 1). To determine the organic pool present in the groundwater, samples were analyzed for total organic carbon (TOC) and total nitrogen (TN).

Atmospheric nitrate characterization

In most reactions, fractionations are mass dependent in that they occur because of differences in isotopic mass ratios. For example, the resultant $\delta^{17}O$ in kinetic and equilibrium reactions is directly related to $\delta^{18}O$ via:

$$\delta^{17}O = 0.52 \times \delta^{18}O \quad (1)$$

However, atmospheric studies have found that in photochemical reactions occurring in the atmosphere, $\delta^{17}O$ fractionate mass independently giving it a distinctly enriched isotopic signature:

$$\delta^{17}O > 0.52 \times \delta^{18}O \quad (2)$$

This distinction in fractionation can be employed to quantify atmospheric from terrestrially (kinetic and equilibrium) derived nitrate. The difference between measured and expected $\delta^{17}O$ from kinetic and equilibrium reactions ($\delta^{17}O = 0.52 \times \delta^{18}O$) is termed $\Delta^{17}O$ (capital delta seventeen O):

$$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O \quad (3)$$

The enrichment in $\delta^{17}O$ for atmospherically derived compounds (e.g. NO_3, SO_4…) is a result of atmospheric photochemical reactions (See Appendix B). Atmospheric deposition studies conducted in southern California and Chile have measured a $\delta^{17}O$ range of 60-65‰ in atmospheric nitrate samples, whereas terrestrially derived nitrate had very small $\delta^{17}O$.

A model suggests that as atmospheric nitrate deposits and mixes with terrestrial nitrate in the soil, its $\delta^{17}O$ signature decreases. If the nitrate mixture were to undergo further fractionation by different terrestrial processes (immobilization, denitrification), its $\delta^{17}O$ will change parallel to the terrestrial fractionation line with a 0.52 slope as expressed in Equation 6, thereby preserving its original $\Delta^{17}O$ signature. Since so many processes can corrupt the $\delta^{18}O_{NO3}$ signature, the $\Delta^{17}O$ conservation is ideal to trace back the proportion of atmospheric nitrate present in a sample.

Results: Wastewater influence

Upstream Rillito River groundwater has low nitrate (~0.2 mmols/L) with concentrations increasing and reaching the EPA's MCL for nitrate (0.71 mmols/L or 10mg NO_3-N/L) near the confluence with the Santa Cruz groundwater (Sample A, Figure 3). Concentrations then decrease further downstream to pre-Santa Cruz groundwater influence concentrations (Samples B, C). The Santa Cruz samples have higher nitrate concentrations with four of the nine samples reaching or exceeding the MCL and an overall increase in nitrate from upstream to downstream, with average concentrations of 0.5 and 1.5mmols NO_3/L, respectively.

In a previous dissertation conducted on the recharge of Santa Cruz River sewage waters, chloride (and chloride/bromide ratios) was found to be a good tracer of wastewater (Esposito, 1993). Chloride data for the treated wastewater stream was obtained and its elevated range is used as an end-member for tracing wastewater. The low chloride runoff samples create a clear distinction between wastewater and runoff as source waters (Figure 3). The groundwater chloride data reveal that Santa Cruz samples and Rillito samples A and C are influenced by wastewater recharge. Peculiarly, sample B, between A and C, has very little wastewater influence.

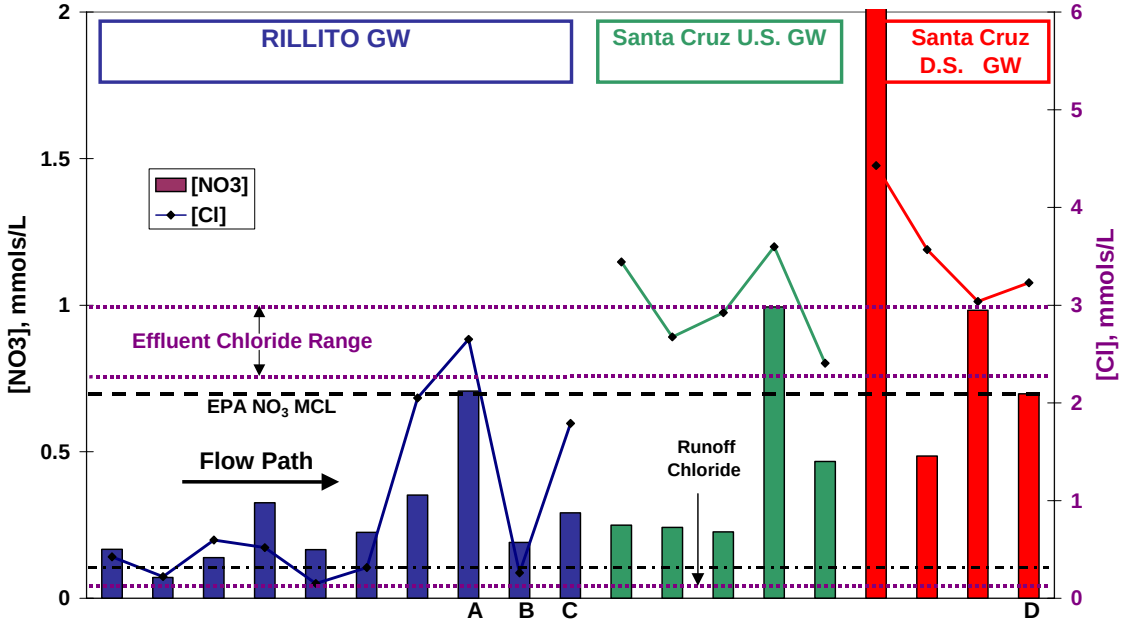

Figure 3. Nitrate (bars, left axis) and Chloride (connected dots, right axis) concentrations along Rillito groundwater flow path (blue), at the upstream (green) and downstream (red) Santa Cruz cross-sections. The lines shown are the EPA's nitrate MCL (broken line), the chloride concentration range for the wastewater effluent stream (upper dotted lines) and the runoff chloride level (lower dotted line). All Santa Cruz samples and Samples A and C are influenced by wastewater recharge due to their high level of chloride.

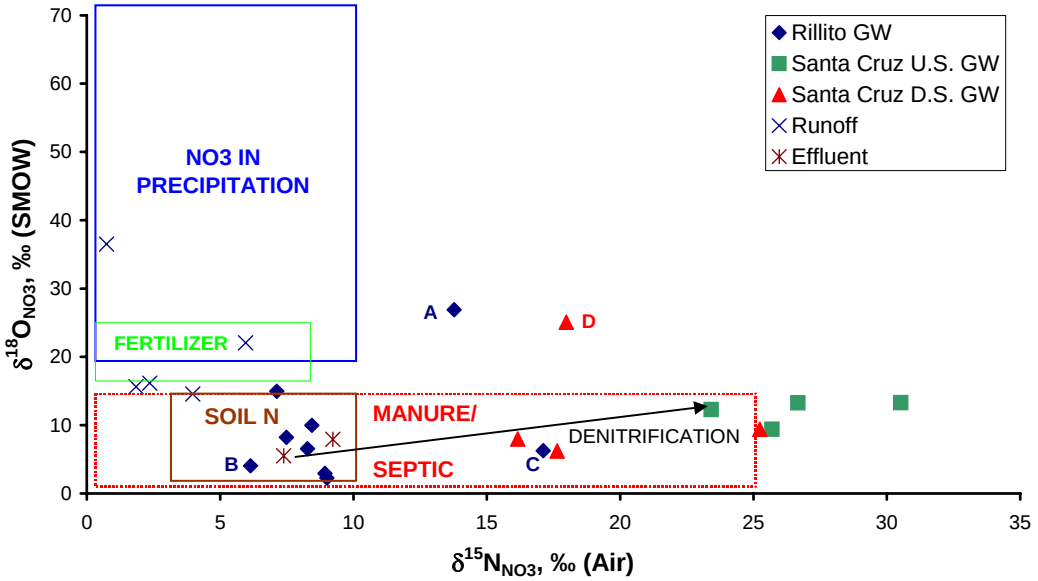

Figure 4. Dual isotope plot $\delta^{18}O$ vs. $\delta^{15}N$ of data showing the ranges of sources of nitrate. Most Rillito groundwater samples plotted with the Soil N range and the Santa Cruz samples within the manure/septic range with a denitrification trend from stream level to groundwater. The runoff data plotted near the lower values of the precipitation range.

Results: Sources of Nitrates

When determining the source of nitrate to water, the use of the dual isotopic system is essential. Although all sources have overlapping $\delta^{15}N$ ranges, precipitation nitrate can be differentiated based on its enriched $\delta^{18}O$ signature. In addition, several studies have been successful in teasing apart soil N from manure/septic nitrate based on an enriched manure/septic $\delta^{15}N$ (Kreitler). The runoff samples plot within or near the lower portion of the precipitation $\delta^{18}O$ range (17-22‰). The depleted $\delta^{18}O$ may be due to mixing with fertilizer and/or soil nitrate or by nitrate cycling at the soil level (immobilization, mineralization). The Rillito groundwater samples generally fall within the soil nitrification range ($\delta^{15}N$=6-9‰ and $\delta^{18}O$=1-10‰).
The isotopic signatures of the samples collected along Santa Cruz sewage stream fell within the lower Manure/Septic range. As expected, the Santa Cruz groundwater samples are within the range of manure/septic with elevated $\delta^{15}N$>16‰.

Sample C has an enriched $\delta^{15}N$ signature. As observed with the chloride data, this is probably due to mixing with wastewater (elevated $\delta^{15}N$). Samples A and D have peculiar isotopic signatures (Figure 4). Similar to Sample C, their $\delta^{15}N$ are within the range for Soil N and Manure/Septic mixing. However, their $\delta^{18}O$ are enriched and likely influenced by a third end-member: atmospheric nitrate. Sample B was not affected by sewage recharge (Figure 3) and had isotopic mass ratios within the soil N range.

Results: Denitrification

The Santa Cruz samples follow a denitrification trend along the recharge flow path from the treated wastewater stream level to the groundwater, as $\delta^{18}O$ increases with increasing $\delta^{15}N$ on a 1:2 slope (Figure 4). Denitrification rates were higher upstream, with $\delta^{15}N$ enrichments up to 19‰ and 54% of nitrate removal, than downstream with 11‰ enrichments and additional nitrate measured. Denitrification is very likely due to the high amount of DOC measured in the wastewater effluent and Santa Cruz groundwater.

Significant amounts of DOC have been consumed between the effluent stream level and the groundwater with 88% and 67% removal rates upstream and downstream, respectively. TN average removal rates along the Santa Cruz recharge pathway were 76% upstream and 21% downstream. Both TN and DOC followed similar trends with nitrate concentrations.

Results: Atmospheric proportions

As expected, the runoff samples have the most atmospheric nitrate proportion with up to 43% (Figure 5). Samples A and D are the groundwater samples with the greatest atmospheric input (6%) and are shown to have undergone the most terrestrial fractionation (Figure 5). Interestingly, these samples have some of the highest nitrate concentrations. The Santa Cruz upstream samples have undergone more terrestrial fractionation than the downstream samples.

The Rillito groundwater had higher atmospheric proportions than the Santa Cruz groundwater samples, up to 6%. Average atmospheric percentages for the Rillito, Santa Cruz upstream and downstream were 3.5%, 1.4%, and 2.3% respectively. Although Rillito groundwater samples had the highest atmospheric percentages, their actual atmospheric derived concentrations (0.01 mmol/L average) were within the range of the upstream (0.007 mmol/L average) and downstream (0.02 mmol/L average) Santa Cruz samples. Samples A and D had the most atmospheric nitrate.

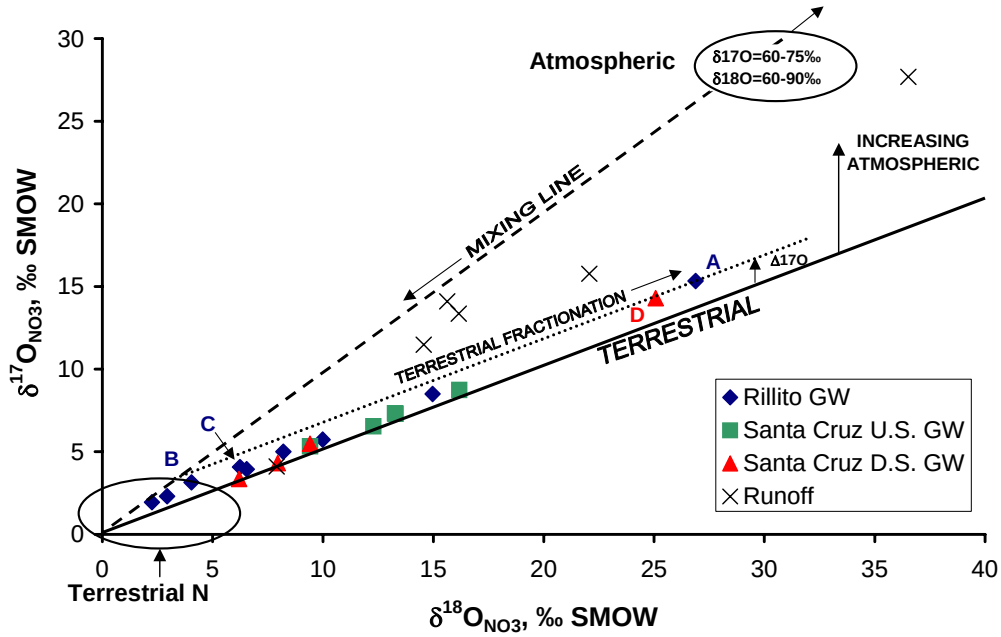

Figure 5. Plot of $\delta^{17}O$ vs $\delta^{18}O$ showing the atmospheric-terrestrial N mixing line and the terrestrial fractionation line. The greater the vertical deviation from the terrestrial fractionation line ($\Delta^{17}O$) the greater the atmospheric influence. The furthest away from the terrestrial N range, the greater is the effect of terrestrial fractionation. Runoff samples have the most atmospheric influence. Among groundwater samples, A and D had the most atmospheric input and underwent the most terrestrial fractionation.

Since both fertilizers and precipitation have elevated $\delta^{18}O_{NO3}$, the atmospheric imprints are removed from the nitrate $\delta^{18}O$ signatures to better constrict the different sources and processes affecting groundwater nitrate concentrations. Nearly all corrected $\delta^{18}O$ are within the soil N and manure/septic range. Runoff samples were the most affected by this change. The atmospheric correction of samples A and D still result in their $\delta^{18}O$ being higher than soil N and manure/septic ranges (Figure 6). Other processes may have enriched their $\delta^{18}O$.

Discussion: Sewage influence to groundwater

Rillito groundwater has low nitrate concentrations (0.2 mmols/L), increasing downstream at the proximity of the Santa Cruz. Two of the samples (A and C) have elevated isotopic signatures. This elevation is due to mixing with sewage recharge waters, as shown by their elevated chloride concentrations. Sample B is peculiar as it is between samples A and C and is not affected by sewage waters (soil N isotopic signature and low chloride). This result could be due to geologic features isolating this well from surrounding groundwater.

All Santa Cruz groundwater samples are affected by wastewater recharge waters (high chloride and $\delta^{15}N$). Whereas the main source of nitrate to the Rillito groundwater is terrestrial nitrification, Santa Cruz groundwater nitrate is predominantly from wastewater with significantly higher nitrate concentrations (1 mmols/L average) than Rillito groundwater (0.2 mmols/L average). The Rillito groundwater is contaminated with nutrient-rich recharge waters near the Santa Cruz River, with sample A from a well a mile away from the Santa Cruz River reaching the MCL of 0.71 mmols/L.

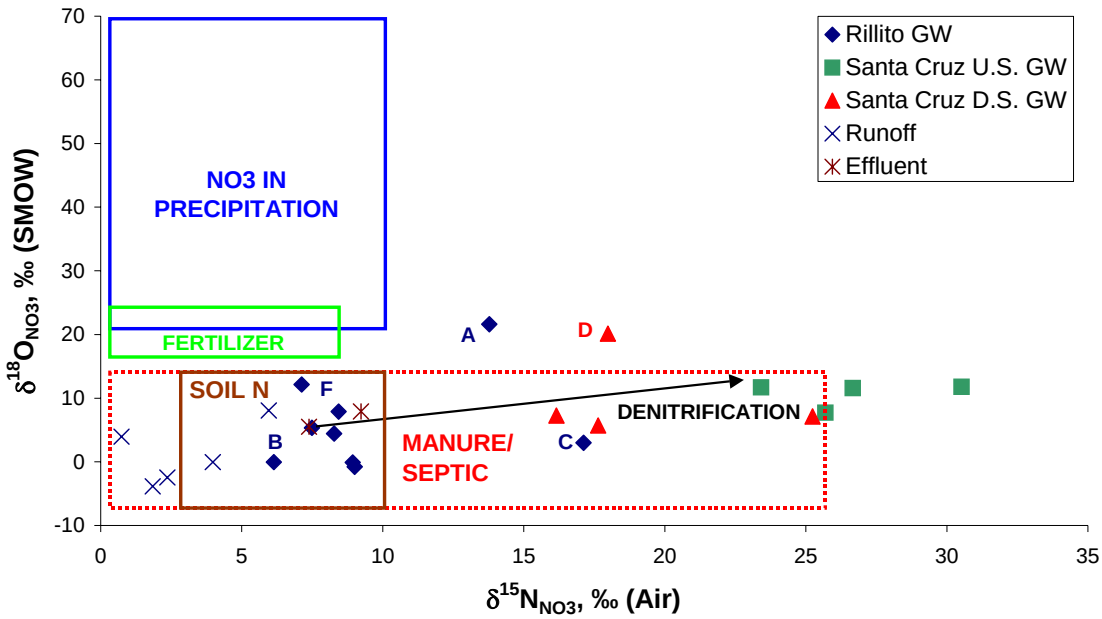

Figure 6. Dual isotope plot after removal of atmospheric imprint to the $\delta^{18}O$ signatures (Equation 12). Nearly all $\delta^{18}O$ signatures are within the soil N and manure/septic range. Other processes are affecting samples A and D.

Due to continuous stream flow, greater hydrologic connectivity between surface water and groundwater is achieved in the Santa Cruz River than in the Rillito River. This enhances the transport of nutrients from treated wastewater to the aquifer. More groundwater nitrate contamination is expected to occur with time.

Results: Denitrification

The Santa Cruz groundwater isotopic signatures show a denitrification trend along the stream to groundwater path, with upstream samples being more denitrified (ε = 19‰) than downstream samples (ε = 11‰). This result is reinforced with upstream samples having less nitrate (76% removal), and organic mater (88% removal) than the wastewater stream. A previous project showed Santa Cruz River recharge waters to undergo denitrification at the seepage level and then nitrification of ammonia in the vadose zone before recharging the aquifer (Esposito). The upstream cross-section wells are near the Sweetwater Recharge Facility where ponds are filled with treated effluent water that percolate and replenish a perched aquifer. Reclaimed water used to irrigate lawns in parks and golf courses all over Tucson is pumped from this aquifer. Ponds follow wet/dry cycles encouraging nitrification during dry periods and denitrification during wet periods (Chipello). This soil aquifer treatment (SAT) creates ideal conditions for denitrifying bacteria to thrive. Possible nitrogen removal processes explaining the low upstream groundwater concentrations are the denitrification during SAT and plant uptake.

Due to the influence of wastewater treatment plant effluent discharged on the Santa Cruz River, higher nitrate, TN, and DOC concentrations are measured in the downstream transect. Their isotopic signatures showed denitrification affecting nitrate compositions, although to a lesser extent than the upstream samples. Interestingly, this observation is reinforced by $\delta^{17}O$ data showing that these samples underwent less terrestrial fractionation then upstream samples. From stream to groundwater, lower removal rates are measured in downstream samples (21% TN and

67% DOC removal) along with an increase in nitrate (46% increase). Higher groundwater nitrate concentrations may be due to lower denitrification rates (no SAT), greater leaching, and ammonia nitrification in the vadose zone. Beside from recent sewage effluent, another possible source to these groundwaters may be from the flushing of vadose zone nitrate from mid-20th century large agricultural fields in the area that were irrigated with sewage waters. Higher moisture content, nutrient sources from wastewater and vegetation density in the Santa Cruz system makes it a biogeochemical hot spot for N cycling with denitrification in the seepage zone, nitrification in the vadose zone, plant uptake and mineralization.

Results: Atmospheric proportion

The atmospheric component of Tucson groundwater nitrates is minor. Up to 6% atmospheric nitrate was measured in samples A and D. Although Rillito samples have the highest atmospheric percentages (Rillito average 3.5% > 1.9% Santa Cruz average), their atmospheric concentrations (average 0.01mmols/L) were similar to the Santa Cruz samples (average 0.013 mmols/L). While the highest atmospheric nitrate concentrations were measured in wastewater-influenced waters (up to 0.04 mmols/L), the ones affected the most by denitrification had the least amount of $[NO_3]_{atm}$ with average of 0.004 mmols/L (Figure 7). A good example of wastewater recharge waters having more $[NO_3]_{atm}$ is samples A and B. Although both samples have some of the highest percentages of atmospheric nitrate, sample B had a much lower nitrate concentration (0.009<0.04mmols/L) due to very little wastewater influence.

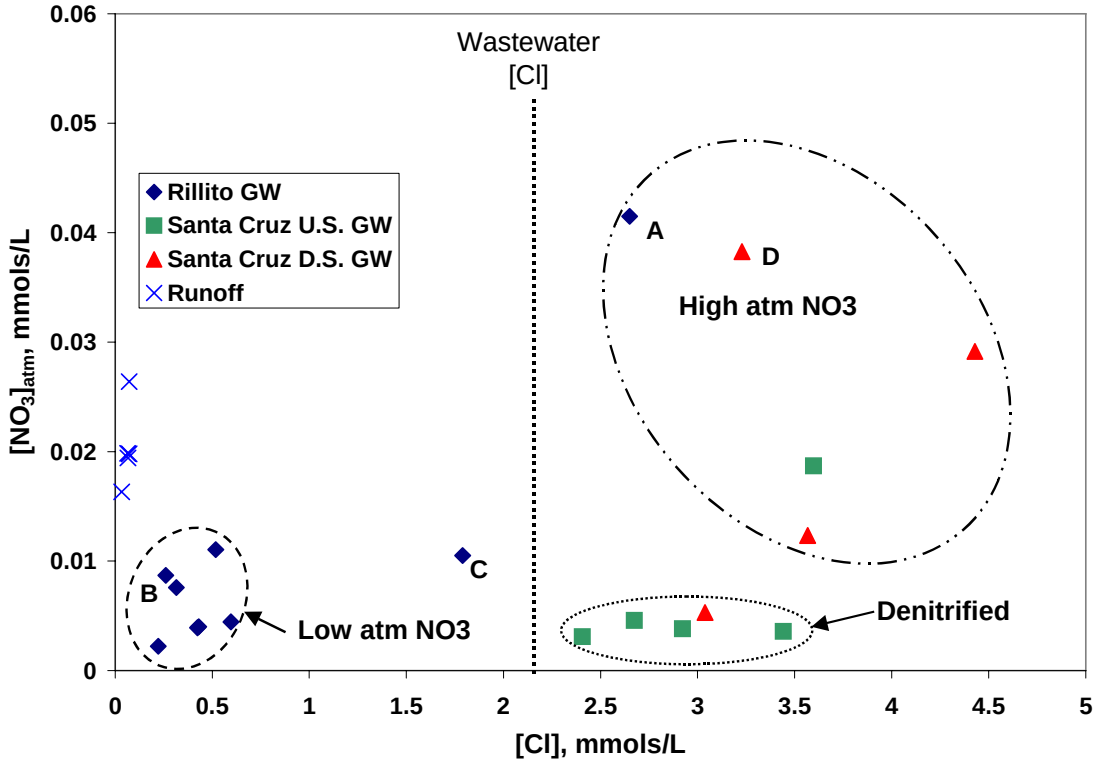

Figure7. Atmospheric nitrate vs. chloride concentrations. The wastewater chloride (dotted line) distinguishes samples with wastewater influence from those with little to no influence. Greater atmospheric nitrate is measured in wastewater recharge waters (0.03 mmols/L) than beneath the Rillito (0.007 mmols/L), except where denitrification is significant (0.004 mmols/L).

Samples A and D have the highest $\delta^{18}O$ signatures and we hypothesized that this was due to mixing with atmospheric nitrate. To check this hypothesis, we removed the atmospheric imprint but they still had relatively enriched $\delta^{18}O$. Several mechanisms can explain their signatures. First, there are likely errors in estimating their atmospheric proportion and this source may have been underestimated. Second, these samples may be influenced by both denitrification and atmospheric nitrate mixing. The pre-denitrified nitrate may have had isotopic signatures similar to wastewater effluent (sample D) and fertilizers (sample A) or a mixture of both. Third, another process that affects $\delta^{18}O_{NO3}$ is nitrification, which has been shown to occur before recharging the aquifer. Experiments have shown that, during the oxidation of nitrate, bacteria produce nitrate obtaining 2/3 of the oxygen molecules from water and 1/3 from O_2. Therefore, $\delta^{18}O_{NO3} = (2/3) \times \delta^{18}O_{H2O} + (1/3) \times \delta^{18}O_{O2}$. For example, with conditions where $\delta^{18}O_{H2O} = -5‰$ and $\delta^{18}O_{O2} = 23‰$, then $\delta^{18}O_{NO3} = 4.3‰$. On the other hand, if $\delta^{18}O_{H2O} = 0‰$ and $\delta^{18}O_{O2} = 60‰$, then $\delta^{18}O_{NO3} = 20‰$. One way to get enriched $\delta^{18}O_{H2O}$ is through evaporation, which is found to affect groundwater and may be even more significant at the soil level where nitrification and denitrification likely occur. Fourth, analytical errors may have occurred during sample processing. Fifth, their enriched $\delta^{18}O_{NO3}$ may be due to a combination of processes including mixing with atmospheric nitrate, nitrification, denitrification and analytical errors. The greater surface-groundwater connection in the Santa Cruz area may explain the larger atmospheric nitrate concentrations. More atmospheric (and wastewater) nitrate can potentially make it to the groundwater due to higher infiltration rates.

4. C. Principal Findings and Significance

To investigate sources of nitrates to Tucson groundwater, two hydrologically distinct systems were analyzed. The Rillito groundwater represents recharge of mountain precipitation waters that occurs depending on the season and the storm size. On the other hand, the Santa Cruz groundwater reflects uninterrupted recharge of wastewater effluent. Where up to 50 years old waters have been measured in the Rillito groundwater, we expect the Santa Cruz groundwater to be younger due a short residence time along the recharge path of 14 days. Several implications may be made from this study. These results are relevant for mid-size cities (1 million population) located in arid climates with little to no agricultural activity and no perennial surface water flow (no surface water-groundwater connection). Little atmospheric nitrate reaches the aquifer. Due to minimal vegetation density and soil moisture content, little nitrate concentrations are measured in the groundwater. In addition, not only do larger sources of nitrate originate from wastewater, the greater hydrologic connectivity between surface water and groundwater created by a perennial stream accelerates the transport of solutes, including nitrates, to groundwater and enhances nutrient cycling along the recharge path due to increased biological activity.

Geospatial Analysis of Urban Thermal Gradients: Application to Tucson Arizona's Projected Water Demand

Basic Information

Title:	Geospatial Analysis of Urban Thermal Gradients: Application to Tucson Arizona's Projected Water Demand
Project Number:	2007AZ219B
Start Date:	3/1/2007
End Date:	6/30/2008
Funding Source:	104B
Congressional District:	Seventh
Research Category:	Climate and Hydrologic Processes
Focus Category:	Water Use, Management and Planning, Climatological Processes
Descriptors:	
Principal Investigators:	Christopher A Scott, Andrew C. Comrie, Stephen Yool

Publication

1. Title **Geospatial Analysis of Urban Thermal Gradients: Application to Tucson Arizona's Projected Water Demand**

2. Principal Investigators

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3. Congressional District Fifth

4. Description Information

A. Problem and Research Objectives

Urban heat island and climate change-driven warming across the Southwest have implications for water use. Researchers and planners have paid inadequate attention to spatial and temporal patterns in urban warming or their implications for urban water demands, particularly for outdoor residential irrigation. This study investigated urban warming and water use in the Tucson, Arizona basin. The research objectives were:

1. Characterize spatial (x,y,z) and temporal (t) trends in Tucson's thermal profile from Landsat TM imagery over the period 1984 – 2006. Derive critical threshold temperature exceedances; and for the Spring 2005 period, identify the persistence of warming anomalies.

2. Spatially correlate temperature vs. outdoor water demand (disaggregated from total household demand) and reclaimed water for landscaping, correcting for elevation z, based on 1984 – 2006 (as the historical calibration/ validation phase) followed by future projections through 2030 (in spatially explicit form) and 2050 (in aggregate form).

3. Compile datasets of surface temperature, exceedances and persistence and make them available over the Internet for use by managers, planners, public health officials, ecologists, and researchers.

B. Methodology

Data Sources

i. Archival Landsat Thematic data – accessed from the Arizona Regional Image Archive (aria.arizona.edu). Figure 1 shows the images acquired. Only those images with antecedent precipitation less than 300 mm in the 90-day period preceding the image date as recorded at the Campbell Ave. station were used for analysis in order to minimize the effects of vegetation greening resulting from natural precipitation.

ii. Climatological data – accessed from the National Climatic Data Center (ncdc.noaa.gov) and the Arizona Meteorological Network (ag.arizona.edu/azmet). Table 1 lists the meteorological stations used for the urban warming analysis.

iii. Water use data – section water supply data for 2000-2006 made available by Tucson Water

Table 1. Meteorological Stations and Data Analyzed

Station	Urban/ Nonurban	Data Analyzed
Campbell Ave. #28796	Urban	Tmin, Tmax, Precip, ET_o
Tucson WFO #28815	Urban	Tmin, Tmax, Precip
Tucson Intl Airport #28820	Urban	Excluded (cold air drainage)
Anvil Ranch #20287	Nonurban	Tmin, Tmax, Precip
Cascabel #21330	Nonurban	Tmin, Tmax, Precip
Oracle 2SE #26119	Nonurban	Tmin, Tmax, Precip
Santa Rita Exp Range #27593	Nonurban	Tmin, Tmax, Precip
Safford	Nonurban	Tmin, Tmax, Precip, ET_o

Landsat Images were registered and rectified to an orthophoto derived street map shapefile from Pima Co. Dept. of Transportation resulting in root mean square error RMSE < 15 m (equivalent to half the minimum pixel resolution).

Vegetation Cover

Normalized difference vegetation index was calculated from TM imagery using atmospherically corrected band 3 (red) and band 4 (near infrared) radiances as follows:

$$NDVI = (B4-B3) / (B4+B3)$$

Thermal Profiles and Gradients

Surface temperatures were retrieved from TM band 6 (thermal infrared) by converting thermal brightness temperatures into thermodynamic (kinetic) temperatures. We accessed an ASTER image from 5/26/2001, with a processed emissivity layer at 90m. The Landsat NDVI for 6/18/2001 (closest date to the ASTER image) was resampled from 30 m to 90 m, and a per-pixel regression of Landsat NDVI vs. ASTER NDVI yielded $R^2 > 0.98$ indicating reliable NDVI results. Subsequently, we regressed ASTER emissivity vs. Landsat NDVI (with $R^2 > 0.36$) and selected the quadratic equation with the best fit in the NDVI range of interest. Finally, kinetic temperature maps were calculated from emissivity and radiant temperatures as:

$$T_{kinetic} = E^{0.25} * T_{radiant}$$

Urban Warming Trend Analysis

Meteorological data from stations listed in Table 1 were analyzed over the 1969-2006 period and the 1984-2005 period (the latter corresponding to the period of Landsat record). Monthly trend analysis of urban Tmin and Tmax were compared to nonurban Tmin and Tmax. The urban – nonurban difference provides the rate of warming resulting from urban heat island processes.

Water Use in Tucson

(Analysis in process)

Public Access to Data Generated by this 104B Project

A website has been developed to make metadata, data, and images available to researchers and agency staff. The website is provisionally hosted at:

http://www.stattosoftware.com/urbanheat/

This will be migrated to an arizona.edu domain before project completion.

C. Principal Findings and Significance

(in process, results to be completed June 30, 2008)

Interim results are as follows: the NDVI-emissivity relation (Figure 2) is considered robust for the NDVI range of interest (0.2 ~ 0.7). Additional work is being completed to finalize the NDVI maps that also serve as the basis for the $T_{kinetic}$ product (see Figure 3 for interim examples of early and late-TM period maps).

Quantification of the urban heat island is shown in Tables 2 and 3 (and graphically in Figures 4 and 5), for 1969-2006 and the Landsat period of record 1984-2005, respectively. The 1984-2005 urban-nonurban differences are lower than for 1969-2006 for the pre-monsoon period of interest (May and June). Further analysis of NDVI imagery and surface temperatures for established urban development areas within Tucson vs. newly developed areas will permit analysis of the degree to which outdoor irrigation depresses urban temperatures. This has significance for adaptation to warming, but also for Tucson's water budget.

Additional analyses were undertaken of reference evapotranspiration (ET_0) trends over time for one of the same urban stations (Campbell Ave. #28796) and for the closest nonurban station (Safford) for which ET_0 data were available. These results, presented in Figure 6, are significant because they indicate that the most rapid increases over the time period 1987-2002 occur during the pre-monsoon months of February – April, but with only a modest increase in May and declining trends the remainder of the year. Little difference is discernible between urban and nonurban ET_0, suggesting that minimum temperature as measured by our Landsat TM analysis is only part of the effect on evapotranspiration and thereby on outdoor residential irrigation demand.

Table 2. Annualized temperature trends (linear slope coefficients of **monthly mean minima** at urban and nonurban sites (deg C yr-1), **1969-2006,** and their differences with significance

Month	Urban	Nonurban	Difference	Significance*
Jan	0.065	0.024	0.041	c
Feb	0.065	0.004	0.061	c
Mar	0.089	0.023	0.066	c
Apr	0.099	0.034	0.066	c
May	0.109	0.054	0.055	c
Jun	0.090	0.038	0.051	c
Jul	0.045	0.016	0.029	c
Aug	0.051	0.021	0.030	c
Sep	0.061	0.021	0.040	c
Oct	0.068	0.031	0.037	c
Nov	0.059	0.024	0.035	b
Dec	0.018	-0.013	0.030	c
Annual	0.059	0.017	0.042	c

2 urban stations (Campbell Ave #28796, Tucson WFO #28815) & 4 nonurban stations (Anvil Rnch #20287, Cascabel #21330, Oracle 2SE #26119, Santa Rita Exp Rng #27593)

*Difference significant:
(a) at 0.05
(b) at 0.01
(c) at 0.001

Table 3. Annualized temperature trends (linear slope coefficients of **monthly mean minima** at urban and nonurban sites (deg C yr-1), **1984-2005,** and their differences with significance

Month	Urban	Nonurban	Difference	Significance*
Jan	0.060	0.058	0.002	
Feb	0.031	-0.003	0.034	b
Mar	0.053	0.000	0.053	c
Apr	-0.003	-0.081	0.077	c
May	0.030	0.024	0.006	
Jun	0.022	0.011	0.011	
Jul	0.074	0.038	0.036	c
Aug	0.034	0.015	0.019	b
Sep	0.097	0.071	0.026	b
Oct	0.009	-0.024	0.034	b
Nov	0.034	0.025	0.008	
Dec	-0.001	-0.010	0.009	
Annual	0.009	-0.010	0.020	b

2 urban stations (Campbell Ave #28796, Tucson WFO #28815) & 4 nonurban stations (Anvil Rnch #20287, Cascabel #21330, Oracle 2SE #26119, Santa Rita Exp Rng #27593)

*Difference significant:
(a) at 0.05
(b) at 0.01
(c) at 0.001

5. Publication Information

Articles in Refereed Scientific Journals

The following are indicative titles for manuscripts in progress:

Water demand under urban heat island and climate change in Tucson, Arizona
Christopher Scott, Eve Halper, Stephen Yool, Andrew Comrie

Correlating urban water demand, remotely sensed surface temperature and vegetation in an arid environment. Eve Halper et al.

Other Publications

Two conference presentations have been made (or are planned):

Water demand under urban heat island and climate change in Tucson, Arizona, 2000-2006. By Christopher Scott, Eve Halper, Stephen Yool, Andrew Comrie. Abstract submitted for "Changing Waterscapes and Water Ethics for the 21st Century", Arizona Hydrological Society and American Institute of Professional Geologists, 3rd International Professional Geology Conference, September 20 – 24, 2008, Flagstaff, Arizona.

Correlating urban water demand, remotely sensed surface temperature and vegetation in an arid environment. By Eve Halper. Presented at American Association of Geographers Annual Meeting, April 15-19, 2008, Boston, Massachusetts.

Other Project Outreach

Tucson urban heat island and vegetation indices. Presented to GEOG 490/590 "Remote Sensing for the Study of Planet Earth" class at Univ. Arizona, May 1, 2008.

6. Student Support

Section 104 Base Grant supported one PhD student (Eve Halper, PhD candidate, Dept. of Geography & Regional Development, University of Arizona).

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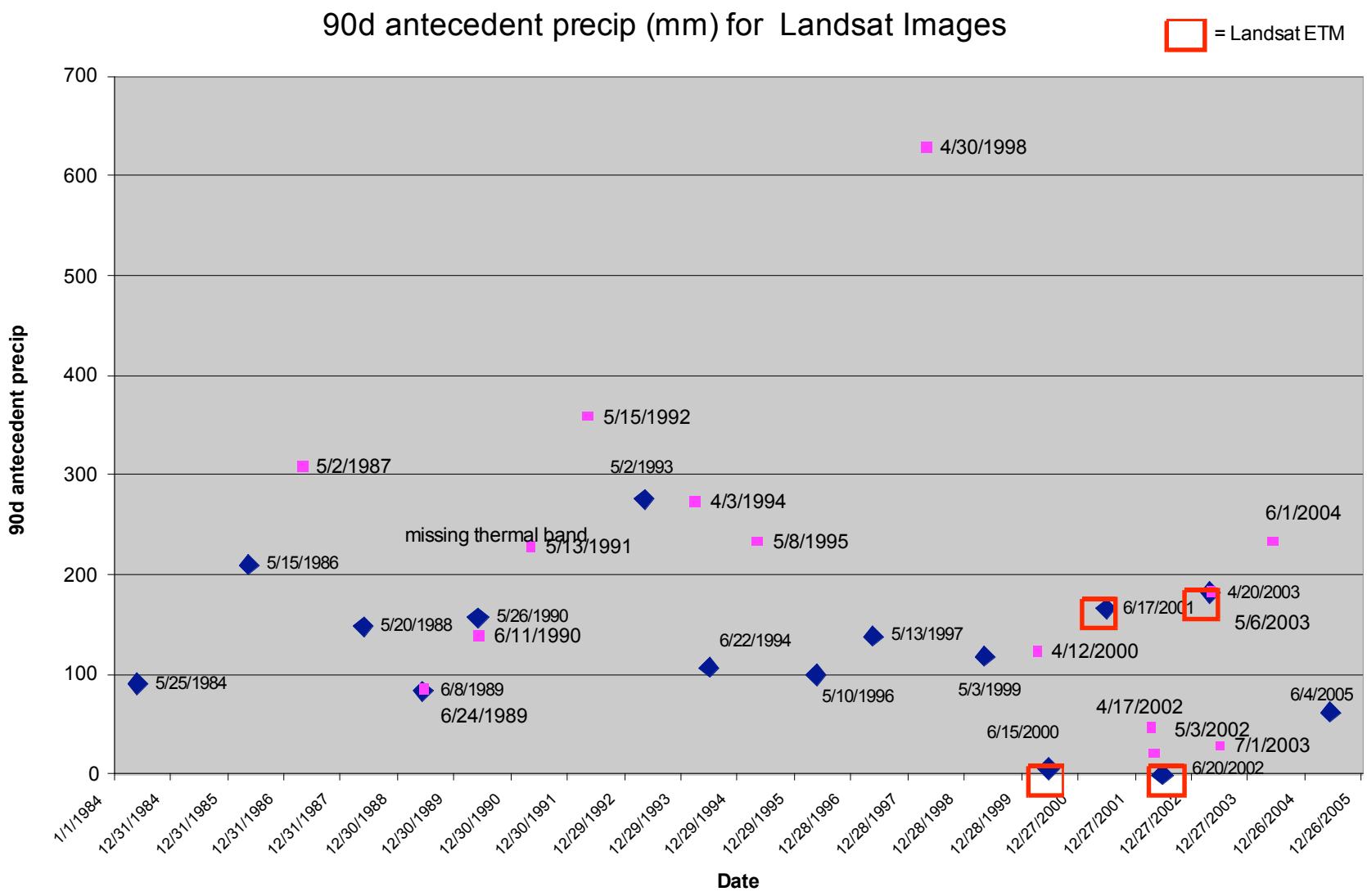


Figure 1. Landsat TM Image Acquisition Dates and 90-day Antecedent Precipitation

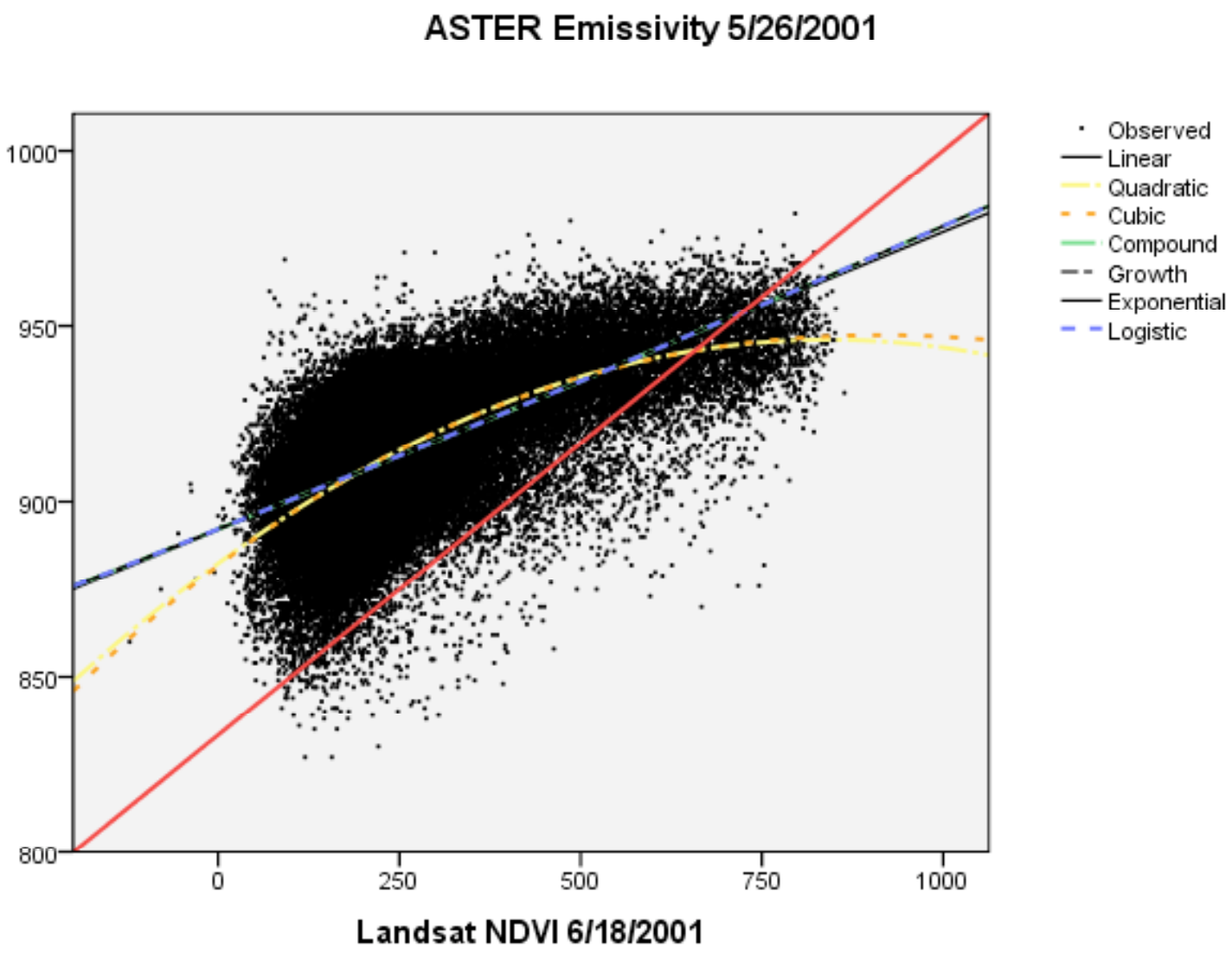


Figure 2. NDVI (Landsat) to Emissivity (ASTER) Correlation

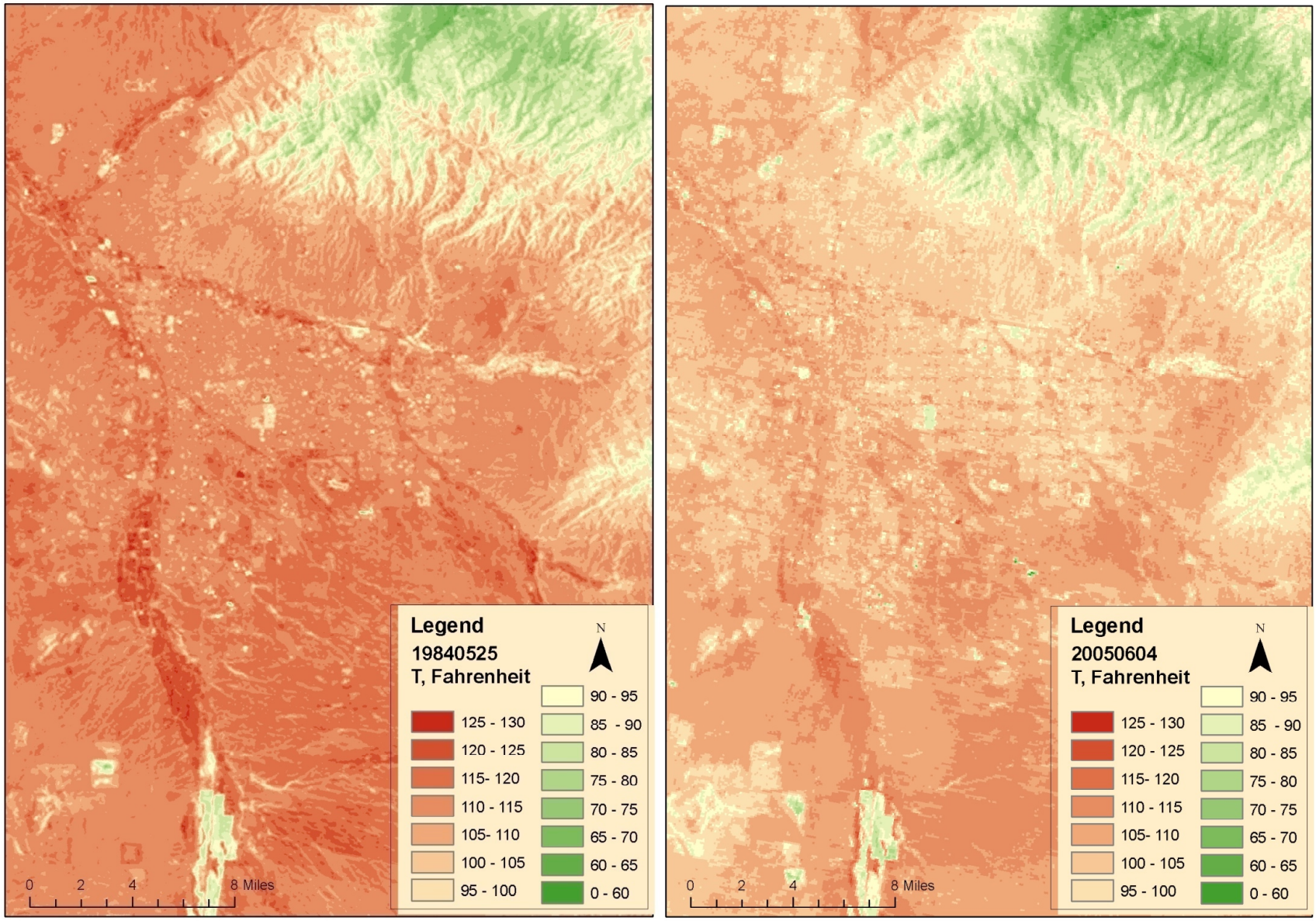


Figure 3. Kinetic Temperature (a) May 25, 1984 and (b) June 4, 2006 *(INTERIM DATA ONLY; TO BE CORRECTED)*

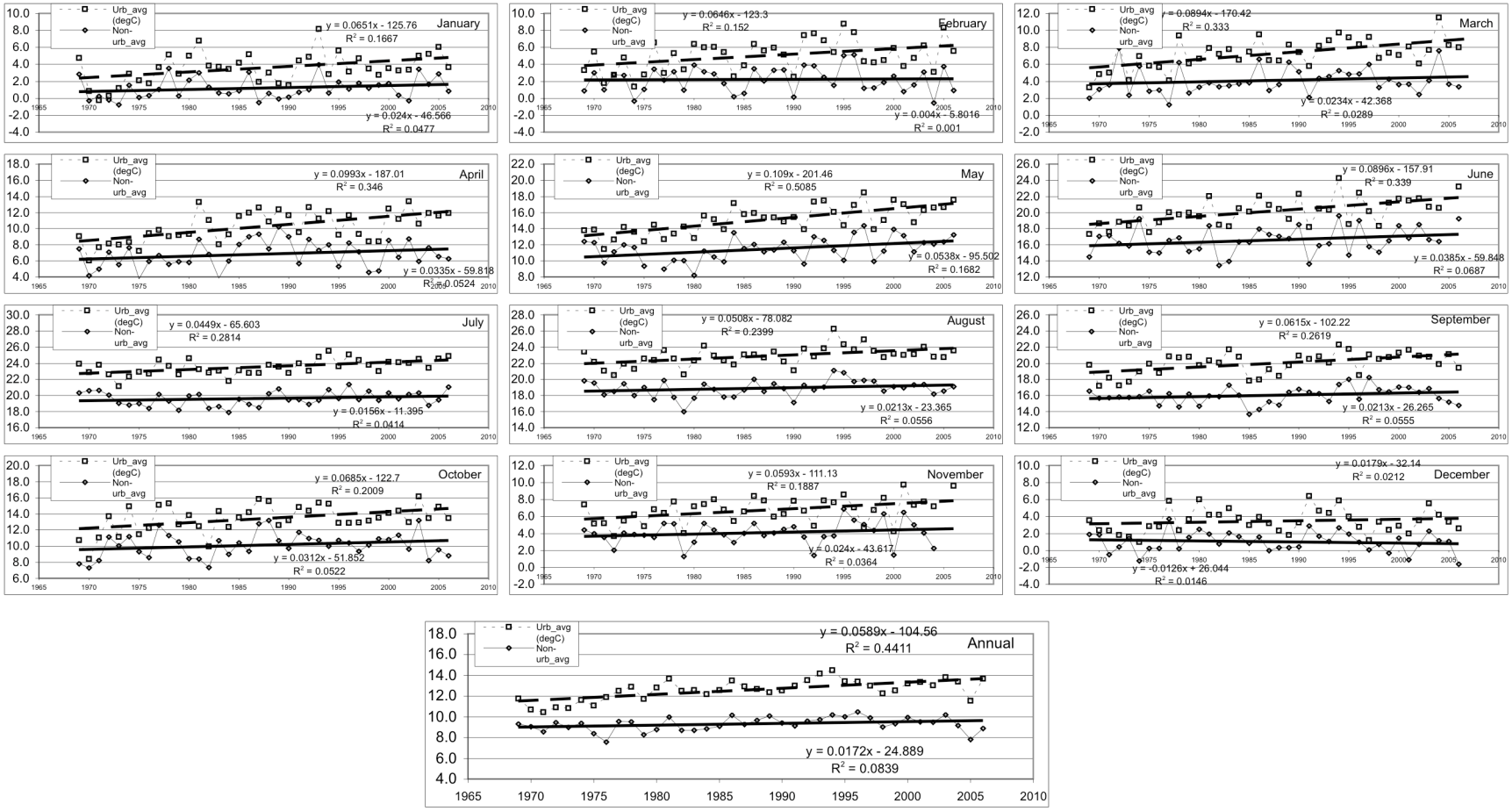


Figure 4. Urban and Nonurban Minimum Temperature (deg C), 1969-2006

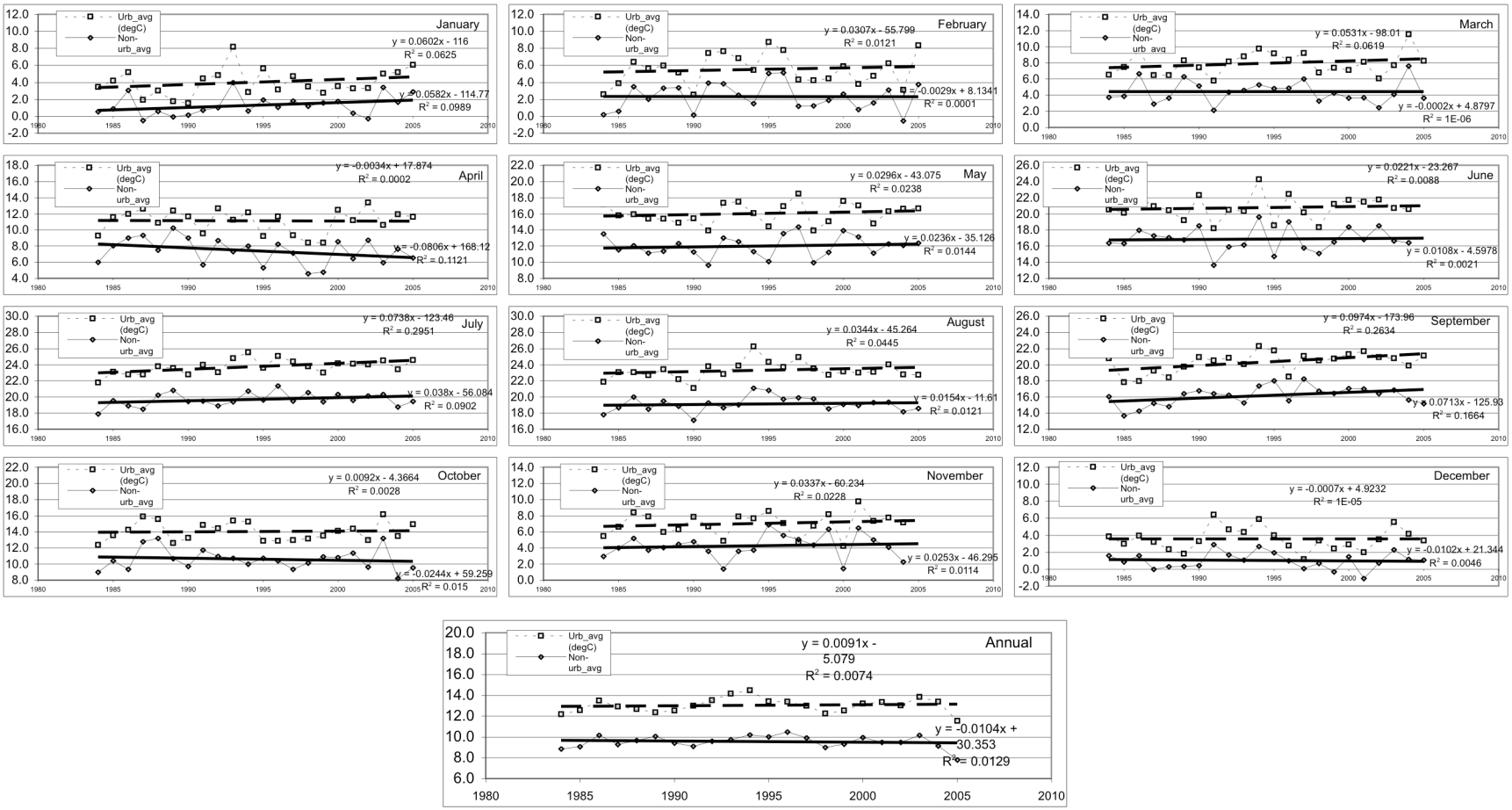


Figure 5. Urban and Nonurban Minimum Temperature (deg C), 1984-2005

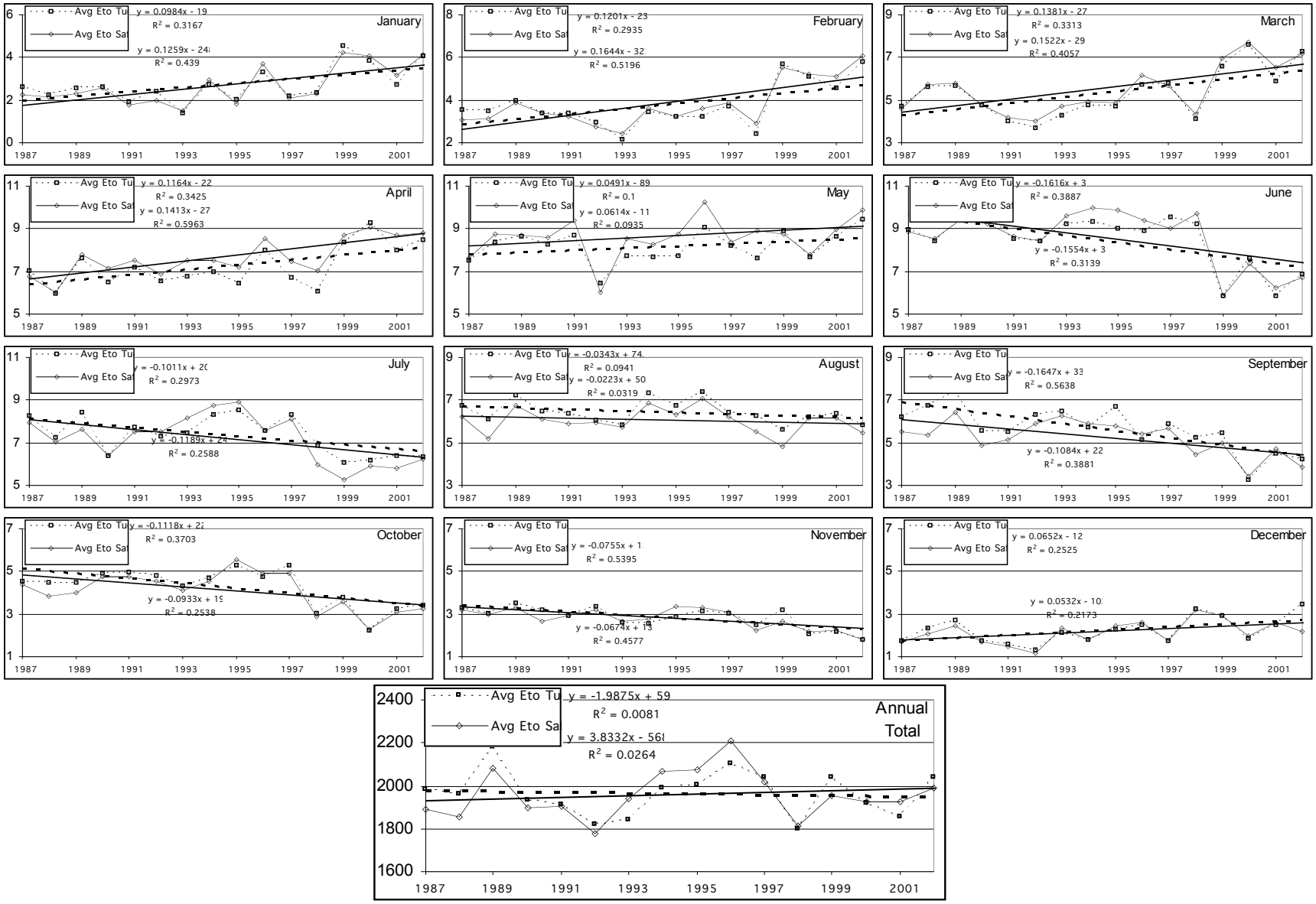


Figure 6. Urban and Nonurban Reference Evapotranspiration (mm), 1984-2005

Modification of conventional wastewater treatment processes for estrogen removal

Basic Information

Title:	Modification of conventional wastewater treatment processes for estrogen removal
Project Number:	2007AZ221B
Start Date:	3/1/2007
End Date:	2/28/2008
Funding Source:	104B
Congressional District:	Seventh
Research Category:	Water Quality
Focus Category:	Wastewater, Treatment, Water Quality
Descriptors:	None
Principal Investigators:	David Matson Quanrud, Robert Arnold, Martin Milan Karpiscak

Publication

1. Teske, S., Arnold, R., Propper, C., Buschmann, S., Quanrud, D., and Ela, W. 2007. Fate of 17b estradiol and total estrogenic activity at six municipal wastewater treatment facilities in Arizona. In: Proceedings, 6th International Conference on Pharmaceuticals and EDCs in Water. National Ground Water Association. Costa Mesa, CA. October 22−23, 2007.

4. Description Information:

4A. Problem and Research Objectives:

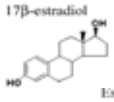
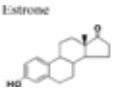
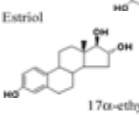
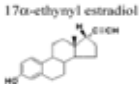
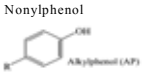
The presence of estrogens and estrogen mimics in municipal wastewater is widely acknowledged. There are several well documented cases in which continuous exposure to estrogenic compounds in surface waters impacted by treated wastewater has resulted in feminization of male fish. Impacts on human health are less certain and much debated.

A number of significant studies suggest that the primary estrogens in wastewater can be efficiently removed during wastewater treatment. Detailed relationships between effluent estrogenic activity and treatment plant design and/or operational characteristics remain to be established. Nevertheless, regulation of such compounds/activity in wastewater effluent is likely to receive attention among public agencies in the next few years.

The project conducted an in depth comparison of treatment process configuration and performance at two wastewater treatment plants in Pima County Arizona. Facilities were selected to provide contrasting biochemical processes and a range of through-plant organic removal efficiencies. Results provide guidance for selection and operation of processes for control of trace organic contaminants in wastewater.

More specifically, the project was an investigation of wastewater treatment processes that were expected to reduce the activities of estrogenic compounds in wastewater. The processes examined were (i) membrane biological treatment and (ii) activated sludge treatment. Both were studied under nitrifying conditions that were thought likely to produce biochemical transformations of aromatic trace contaminants such as those that contribute to estrogenic activity (Table 1).

Table 1. Properties of some natural estrogens and xenoestrogens found in wastewater.

	Mol. Wt (g/mol)	Water Sol. (mg/L)	Log K_{ow}	Relative estrogenic activity
17β-estradiol 	272.4	13	4.01, 3.10, 3.94	1.00
Estrone 	270.4	13	3.43, 3.13, 3.38, 2.45	0.38
Estriol 	288.4	32	2.81, 2.6, 2.55	2.4×10^{-3}
17α-ethynyl estradiol 	296.4	4.8	3.67, 4.15	1.19
Nonylphenol 	220.4	1.16	5.92	2.5×10^{-5}

This study was primarily a monitoring project. Attenuations of estrogenic activity at the Randolph Park Wastewater Treatment Plant and the Ina Road Pollution Control Facility were measured. Randolph Park is operated for biological control of effluent nitrogen levels through nitrification and partial denitrification using membrane bioreactor technology (MBR). MBR is designed to facilitate accumulation of biomass and increase solids retention times during biological treatment of wastewater. Flow schematics for the Randolph Park and Ina Road wastewater treatment facilities are provided in Figure 1a and 1b, respectively.

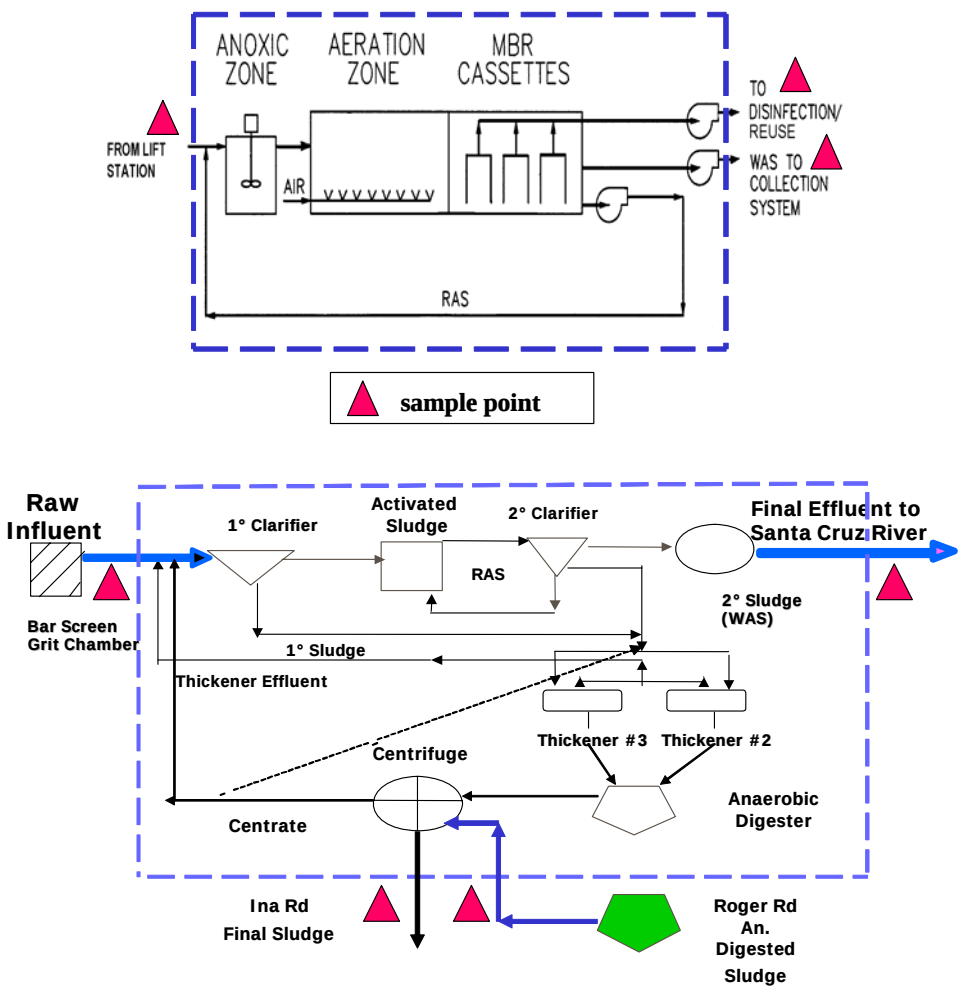


Figure 1. Participating wastewater treatment facilities: Randolph Park membrane bioreactor (a) and Ina Road activated sludgeWPCF (b). Both facilities are located in Tucson, Arizona.

Project data support selection of treatment processes and operational parameters for trace contaminant control. Results will be particularly useful for dischargers to effluent-dependent streams such as the Santa Cruz River and in situations in which potable water reuse applications are under consideration.

4B. Methodology

General: Operating parameters of the two Arizona municipal wastewater treatment plants included in the study are listed in Table 2. Plant sampling points were limited to influent, effluent and digested or undigested sludge. The data were used to produce mass balances on total estrogenic activity at each facility. Total estrogenic activity was measured using the yeast estrogen screen (YES bioassay) of Routledge and Sumpter (1996) as amended by DeBoever *et al*. (2001). This is a yeast-based *in vitro* bioassay in which total estrogenic activity is converted to an equivalent concentration of a known estrogenic compound–17α-ethinyl estradiol (EE_2), an oral contraceptive. The experimental design made it possible to measure plant performance in terms of influent-to-effluent improvements in water quality. However, because prominent

estrogenic wastewater contaminants are moderately hydrophobic (Table 1), measurement of estrogenic activity in solids derived from wastewater treatment (digested or undigested sludge) was necessary to distinguish between biochemical transformations and physical removal mechanisms.

Table 2. Wastewater Treatment Plant Operating Parameters.

	Randolph Park	**Ina Road**
Processes (Biological/Digestion)	Denitrification/Nitrification/ Membrane bioreactor and no digester.	Activated sludge with 100% oxygen and anaerobic digester.
Flow (MGD)	2.775	20.650
Solids Retention Time (days)	10	0.41
BOD Removal (%)	99.0	93.6
SS Removal (%)	98.1	93.6
Total Nitrogen Removal (%)	97.1	(1.6)

Samples were taken on two occasions at the Randolph Park facility to obtain influent, effluent and waste solids during the first four months of the study. These were analyzed for total estrogenic activity. Similar sets of measurements were made at the Ina Road Pollution Control Facility. That plant will be upgraded for nitrogen control in the near future. Consequently, this work constituted a baseline study from which comparisons can eventually be made after plant performance is upgraded. Sample timing and parameters measured were identical to those measured at Randolph Park. Sampling points were analogous to those at Randolph Park and supported through-plant balances on total estrogenic activity.

All samples were processed prior to measurement of total estrogenic activity (Figure 2). The influent solids content of raw wastewater and hydrophobic character of known estrogenic wastewater contaminants (Table 1) motivated the measurement of both dissolved (filterable) and particulate contributions to the total influent concentrations of E_2 and total estrogenic activity. Influent solids were separated via a combination of centrifugation (20 minutes, RCF = 17,000) and filtration using a 0.7 µm glass fiber filter. Both the liquid (filterable) and solid fractions were then extracted and analyzed. Previous work indicated that suspended solids in treated wastewater provide a negligible contribution to overall estrogenic activity (data not shown). Non-filterable solids from effluent samples were discarded without further processing.

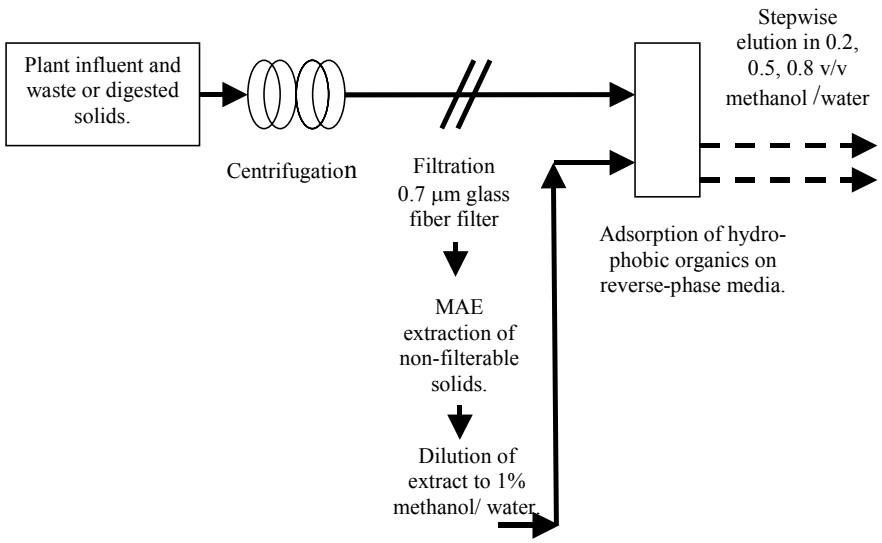


Figure 2. Sample processing schematic for measurement of total estrogenic activity in liquid and solid samples.

After centrifugation/filtration, all solid samples (sludges and non-filterable solids) were extracted in methanol using a microwave-accelerated extraction (MAE) procedure. About 1 gram (dry weight) of solid was suspended in 20 mLs of methanol and extracted at constant pressure (20 psig for 30 min.) using a CEM-MDS 2100 Microwave Digestion System. Extracts were then diluted to 1 percent methanol with pure water, and hydrophobic organics, including estrogenic contaminants, were separated using a reverse-phase (C-18 octadecyl) resin (Empore, 3M). A stepwise elution procedure was used to fractionate adsorbed organics based on relative hydrophobicity and to minimize interferences from matrix organics, including many of the toxicants that would alter estrogen-dependent response in the YES procedure. Eluate fractions consisted of 10 mLs of 0.20, 0.50 and 0.80 (volume fraction) methanol in water.

After C-18 resin adsorption/stepwise elution, the resultant 90 samples (all plants, all sampling points and sample fractions) were split between Northern Arizona University for measurement of E_2 and the University of Arizona for measurement of total estrogenic activity. By preparing samples as described, it was possible to determine the relative contributions of solid and liquid fractions to E_2 and total estrogenic activity in plant influents, compare E_2 concentrations to total estrogenic activities and so forth.

Centrifugation/filtration: Samples were separated into liquid and solid portions using a Beckman centrifuge with a JA-10 rotor (20 minutes, RCF = 17,000). The liquid portions were then decanted off and filtered with a 3.0 µm Pall glass fiber filter. The filtrate was refiltered using 0.7 µm Pall glass fiber filters.

Separation on C-18 resin: Hydrophobic organics were extracted from 0.7 µm-filtered samples using 47-mm C-18 disks (3M Empore) preconditioned with two 10-mL volumes of 100% ethyl alcohol (Aaper) and 10 mL of Nanopure (Nanopure Infinity) water. Organics adsorbed on the C-18 disks were sequentially eluted using 10 mL of 0.2 (volume fraction CH_3OH) methanol/water solution followed by 10 mL of a 0.5 methanol/water solution and then 10 mL of 0.8 methanol/water solution. Eluates were dried under nitrogen gas and redissolved in Nanopure water to yield final concentration factors of 200-500x for analysis using the YES assay. Samples to be analyzed for E_2 were redissolved in 100% methanol.

Extraction procedure (solids): A microwave-assisted extraction (MAE) procedure was utilized. Extraction vessels were charged with approximately 1 g (dry mass) of sample and 20 mLs of methanol. Extractions were performed using a CEM MDS 2100 microwave digestion system at 20 psig for 30 minutes. Reactor contents were then cooled for 45 minutes inside the microwave unit before liquids were decanted into muffled glass vials. Methanol extracts were evaporated to 1 mL under nitrogen gas. Methanol MAE extracts were diluted to ~ 1% methanol (v/v) in Nanopure water before organics were separated on C-18 octadecyl disks (Empore, 3M). Adsorbed organics were separated via differential elution in a stepwise methanol gradient, dried and resuspended in water or methanol, per above.

Yeast Estrogen Screen (YES) Bioassay: The YES bioassay of Routledge and Sumpter (1996) as modified by de Boever *et al*. (2001) was used to measure estrogenic activity. Each sample concentrate was serially diluted across 10 wells of a 96-well micro-titer plate (Costar). Each dilution series was initiated by placing 100 µL of sample concentrate in the first well of a single row. Fifty µL was transferred to the second column and mixed with 50 µL of Nanopure water (2-fold dilution per step). The process was repeated across each row to produce a maximum dilution factor of 2^9. Fifty µL of Nanopure water that was pretreated via passage through the C-18 resin was added to wells 11 and 12 of each row to serve as (negative) process controls. The 8 rows of each 96-well plate provided replicate data (n = 8) for estimation of experimental error. A standard series was developed in a similar manner with each set of measurements using concentrations of EE_2 from 1.0×10^{-7} to 5.0×10^{-12} M. The *Saccharomyces cerevisiae* strain used was provided by John Sumpter of Brunel University, Oxbridge, U.K.

Yeast cells were grown in the Routledge/Sumpter medium to (A_{630}) 1.0 cm^{-1}. The culture was then diluted in the same medium to an absorbance (A_{630}) of 0.133 cm^{-1}, and 150 µL of the diluted suspension was added to each well of the 96-well plate (total volume 200 µL). The resultant A_{630} value in each well was then about 0.10 cm^{-1}. Plates were incubated for 24 hours at 32º C for growth of *S. cerevisiae* and estrogen-dependent expression of *lacZ*. At that point, 50 µL of cycloheximide/CPRG (chlorophenol red β-D-galactopyranoside) solution consisting of 3 mL of autoclaved Nanopure water, 2 mL of 10 mg/mL cycloheximide, and 200 µL of 10 mg/mL CPRG was added to each test well. Following an additional 24-hour incubation at 32º C for β-galactosidase-dependent color development, absorbance was measured at 570 nm (β-galactosidase activity) and 630 nm (turbidity). The contribution of cell-dependent light scattering to A_{570} measurements was determined by measuring the ratio of A_{570}/A_{630} (here defined as R) in the negative control wells. β-galactosidase activity was then corrected to $A_{570} - R \times A_{630}$.

Dose-response curves were plotted for environmental samples and the positive (EE_2) control. A Student's t-test was used to identify a "first response". The first response (FR) is defined here as the highest dilution (or lowest concentration) in which a one-way Student's t-test indicates a significant difference ($t > t_{crit}$) in the means of sample replicates (or positive controls) and the negative controls. Measurements were considered different than control data (rejection of null hypothesis) at $\alpha \leq 0.005$. A similar approval was adopted to determine the onset of toxicity using light scattering (A_{630}) data. That is, A_{630} values were compared to those of the negative control series using a one-way test. The onset of toxicity was apparent when the sample dilution series produced values that were significantly lower than the negative controls ($\alpha \leq 0.005$).

The following procedure was used to convert FR data to determine EE_2 concentrations:

- Determine the highest dilution at which the mean A_{630} of the sample group was less than that of the negative control series. This dilution was the "first toxicity" dilution (FT). FT+1 is then the first dilution at which there was no distinguishable sample toxicity.
- If the FT+1 dilution was greater than the FR dilution, the sample was classified as toxic, and the estrogenic activity of the sample was not estimated. When the FT+1 dilution was less or equal to than the FR dilution, the FR dilution was accepted as a valid assay result. The sample first response (FR) was then converted to an equivalent concentration of EE_2 using:

$$\mathbf{EEQ = EC_{FR}/(FR * CF)}$$

where CF is the initial concentration factor of the sample extract, EC_{FR} is the lowest concentration of EE_2 in the standard series that produced a statistically significant response, and FR is the highest sample dilution with a statistically significant response. EEQ is the sample estrogenic activity, expressed as an equivalent concentration of EE_2.

4C. Principal Findings and Significance

Digested sludge extracts were generally more toxic than samples derived from liquids. Sample estrogenic activities (equivalent concentration of EE_2) are compiled in Table 3. A plant-by-plant description of results, including balances of total estrogenic activity, is provided below.

Table 3. Summary of total estrogenic activity measurements by wastewater treatment plant, sampling point, and MeOH eluate fraction.

Facility	Elution Fraction (MeOH)	Influent/ Filterable (M)	Influent/ non-filterable (M)	Effluent (M)	Sludge (centrate) (mol/kg)	Sludge (solids) (mol/kg)
Ina Road	0.2	2.74×10^{-12}	ND	ND	1.22×10^{-11}	2.54×10^{-4}
	0.5	7.02×10^{-10}	5.41×10^{-12}	8.80×10^{-11}	5.46×10^{-12}	5.07×10^{-4}
	0.8	1.76×10^{-10}	1.08×10^{-11}	1.76×10^{-10}	2.44×10^{-11}	2.54×10^{-4}
	Σ	8.81×10^{-10}	1.62×10^{-11}	2.63×10^{-10}	4.20×10^{-11}	1.01×10^{-3}
	ΣΣ	8.97×10^{-10}		2.63×10^{-10}	1.01×10^{-3}	
Randolph	0.2	3.29×10^{-11}	9.24×10^{-12}	ND	ND	4.11×10^{-8}
	0.5	1.32×10^{-10}	ND	ND	3.29×10^{-11}	ND
	0.8	6.58×10^{-11}	ND	4.12×10^{-12}	6.58×10^{-11}	ND
	Σ	2.31×10^{-10}	9.24×10^{-12}	4.12×10^{-12}	9.88×10^{-11}	4.11×10^{-8}
	ΣΣ	2.40×10^{-10}		4.12×10^{-12}	4.12×10^{-8}	

Notes: Σ, sum of contributions from 0.2, 0.5 and 0.8 (volume fraction methanol) eluates. ΣΣ, sum of both solid and liquid contributions to sample.

The Ina Road mass balance was complicated by the influx of digested sludge from the Roger Road facility, which is dewatered via centrifugation with the plant's own digested sludge. Unfortunately, the solids sampling location was beyond the dewatering station, so that the contributions of the Roger Road and Ina Road sludges to the effluxes total estrogenic activity in dewatered solids cannot be separated. Instead, the balance is based on the combined

contaminant efflux in dewatered sludge. Centrifuge centrate, which is recycled internally, was ignored in the analysis. The removals of total estrogenic activity were 70% and 69% in the influent-to-effluent and overall plant balances, respectively (Figure 3). Despite the transfer of digested sludge from Roger Road to the Ina Road facility, the total effluxes of total estrogenic activity at Ina Road were dominated by the plant effluent.

The performance at the Randolph Park facility was excellent (Figure 4). Total estrogenic activity was attenuated by $\geq$ 98% and 97% in the influent-to-effluent and overall plant balances, respectively.

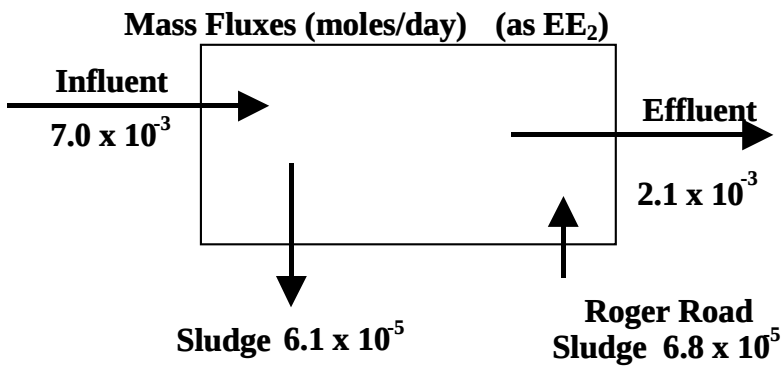


Figure 3. Ina Road mass balance for total estrogenic activity.

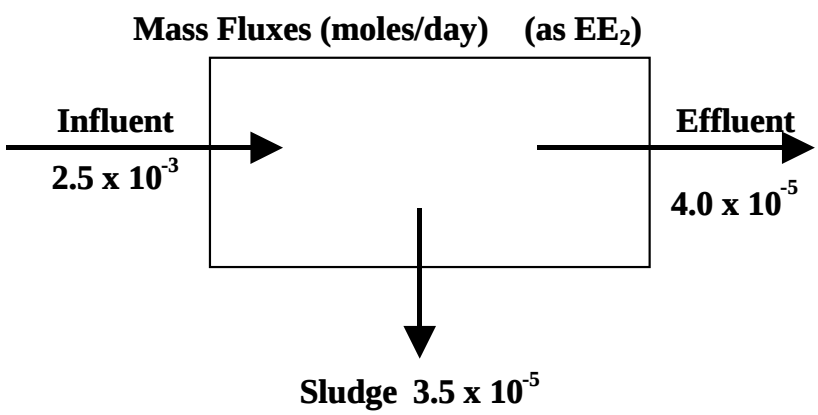


Figure 4. Randolph Park mass balance for total estrogenic activity.

Discussion

There are a number of encouraging consistencies in the total estrogenic activity data. The consistency of these results seems acceptable in light of the chemical complexity of extracts derived from municipal wastewater, expected analytical error, potential toxicity (YES bioassay only) and unknown contribution of influent non-filterable solids to total estrogenic activity at three of the two plants sampled due to problems with sample handling. The contributions of filterable liquids to influent levels of total estrogenic activity was significantly greater than that of non-filterable solids. The result is mildly surprising in light of the hydrophobicities of wastewater contaminants with known estrogenic properties.

Removal efficiencies for total estrogenic activity paralleled expectations based on general plant performance indices. That is, the plant that best removed biochemical oxygen demand and suspended solids also removed more total estrogenic activity (Tables 2 and 4). Nitrogen transformation efficiency was also correlated with loss of estrogenic activity. It has been suggested that nitrifying bacteria play a disproportionate role in the transformation of estrogenic compounds, in part because of the partial aromatic character of known estrogens. Further investigation is also necessary in this area.

Table 4. Summary of fractional removals of total estrogenic activity. .

Facility	**Influent-to-Effluent**	**Overall**
Ina Road	0.70	0.69
Randolph Park	0.98	0.97

Total estrogenic activity increased during anaerobic sludge digestion. It is possible that anaerobic treatment converted ethoxylated alkylphenols to more estrogenic compounds (octylphenol and nonylphenol), as observed by others. Alkylphenols and alkyphenol precursors may escape aerobic treatment via adsorption on primary sludges. Further investigation is warranted in this area.

The measurement of total estrogenic activity in wastewater and sludge extracts remains inexact. Measurement at part-per-trillion levels presents a challenge in most environmental settings. Potential losses during sample preparation are worrisome. Measurements of total estrogenic activities can reflect antagonisms among estrogenic and anti-estrogenic contaminants. Matrix effects are likely to be important when organics are concentrated from wastewater or sludge samples. Finally, toxicity effects can trouble the YES bioassay. Additional groundwork in sample preparation and analytical steps is warranted to minimize potential sources of analytical error.

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Information Transfer Program Introduction

The WRRC has established itself as a primary link among people in the academic community, local, state and federal government, and the private sector on water−related issues. Drawing on its 44 years of experience, the WRRC provides timely and relevant information on water and resource management issues statewide through its publications, functions, and targeted research projects. Water news and information are provided to the academic community, water professionals, elected and appointed officials, students and the public. WRRC staff reaches out to the community through presentations and lectures, service on boards, committees and panels, written articles and research activities.

Information Transfer

Basic Information

Title:	Information Transfer
Project Number:	2007AZ236B
Start Date:	3/1/2007
End Date:	2/28/2008
Funding Source:	104B
Congressional District:	5
Research Category:	Not Applicable
Focus Category:	Law, Institutions, and Policy, Management and Planning, Education
Descriptors:	
Principal Investigators:	Sharon Megdal, Susanna Eden

Publication

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WRRC STAFF ACTIVITIES

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

In addition to serving as WRRC Director, **Dr. Sharon Megdal** is Professor and Specialist in the Departments of Agricultural and Resource Economics and Soil, Water and Environmental Science. She holds courtesy appointments in the Departments of Public Administration & Policy and Geography & Regional Development and an adjunct appointment to the Planning Degree Program, and she is a member of the Arid Lands Resource Sciences Graduate Interdisciplinary Program. This year Dr. Megdal was named the first recipient of the C.W. and Modene Neely Endowed Professorship for Excellence in the College of Agriculture and Life Sciences. She also serves as Director of The University of Arizona Water Sustainability Program, funded by the Technology Research Initiative Fund (TRIF). Dr. Megdal teaches a popular multi-disciplinary graduate course on Arizona water policy and writes a regular column on water policy for the WRRC's newsletter, *Arizona Water Resource*.

Dr. Megdal conducted policy research; wrote articles, reports and commentary; and gave numerous presentations on the topic of water management and planning. She has appeared on public television and written on water issues of current interest for local newspapers. She completed two studies of special interest to state and regional water planners. The first was an Evaluation of the Active Management Area Management Plans that have been carried out by the staff of the Arizona Department of Water Resources since the passage of the 1980 Groundwater Management Act. The project report contains an assessment of the effectiveness of the management plans relative to legislative goals and recommendations for ADWR as it moves forward with the Fourth Management Plans. The second study focused on the Tucson metropolitan region, where there is growing public concern about water. Dr. Megdal was instrumental in bringing about the Tucson Community Conversation on Water on October 26, 2007, in which information and ideas were freely exchanged among the diverse participants. She analyzed the answers to questions collected from all who attended and reported her conclusions in an Op Ed opinion piece in the Arizona Daily Star on January 13, 2008. To test and extend these conclusions, she carried out a study that developed an understanding of similarities, as well as differences, in what different segments of the community would like to see emerge from a regional water resource planning process. The report is being used to inform the joint city-county talks currently underway. Since the release of these reports, Dr. Megdal has presented results to various audiences.

Carl Bauer, the WRRC's Associate Director, was awarded tenure as an associate professor in the Department of Geography and Regional Development in Spring 2007. Since the spring of 2007, Carl Bauer has been responsible for implementing the UA's new Graduate Certificate in Water Policy. As faculty coordinator for the program, he designed the new website (http://gcwp.arizona.edu), with technical aspects handled by Scott Moomaw. Students began applying to the program in Fall 2007 and there are currently about six enrolled. During the three semesters from Spring 2007 through Spring 2008, Dr. Bauer taught four new courses in the Geography Department: two undergraduate courses (Water and Sustainability; Water, Environment, and Society) and two graduate seminars (Comparative and International Water Policy; Law, Geography, and Property).

Dr. Bauer has also continued his international outreach, giving an invited talk about drought and water rights at the International Forum on Drought in Sevilla, Spain, in June 2007. He spent two weeks in Chile in July, studying hydropower development, water governance, and energy policy in Patagonia and gave two talks about this research at UA in Spring 2008. Dr. Bauer helped organize an international conference on environmental flows held in Australia in September 2007. He brought four experts to UA as visiting speakers on water policy, from South America, Spain, and Oregon. He is also the academic contact for Visiting Scholar Graciela Schneier Madanes, who directs an international research network on urban water governance for the French Government's National Center of Scientific Research.

As the Director of the Arizona Project WET Water Education for Teachers Program, **Kerry Schwartz** runs a comprehensive statewide water education program reaching in the tens of thousands of individuals each year. Arizona Project WET (APW) is a multi-faceted water education program that under Ms Schwartz's leadership is expanding each year to reach more school districts, teachers, students and encompass a growing variety of activities. As an Associate Specialist with the Department of Agricultural Education, she combines her knowledge of water resource management and hydrogeology with an ability to engage adults and students in learning. Ms Schwartz administers grants from federal, state, county, city and public/private entities and supervises two full time staff, four part-time staff and seven UA students. In addition, she meets with an advisory council bi-monthly to guide the APW program. Ms. Schwartz participates in water education assessment and research projects and presented on them at the North American Association of Environmental Education Research Symposium in November 2007. She is co-author of the new Arizona Conserve Water Educators' Guide, published May 2007. She also was on the steering committee and a contributing author of three educational student booklets: Waters of Arizona, Drought, and Discover a Watershed: the Colorado Educators Guide.

As an Assistant Area Agent with Cooperative Extension, **Kristine Uhlman** is working with several Arizona Counties on projects addressing water resources. She continues her role as the Arizona NEMO (Non-point Education for Municipal Officials ww.ArizonaNEMO.org) Program Coordinator and is responsible for the development of watershed-based planning documents and educational outreach to land-use decision makers on non-point source pollution issues. Other projects include developing volunteer watershed and river monitoring programs for watershed partnerships across the state (NEMO Wet/Dry); development of a predictive MODFLOW ground water model of ground water resources in the central part of the State; and, a series of county-based water resource fact sheets for the domestic well owner. In addition, Ms. Uhlman is Principal Investigator on a series of Rapid Watershed Assessments with the Natural Resources Conservation Service (NRCS). NEMO and the Water Resources Research Center (WRRC) have contracted with the Natural Resources Conservation Service (NRCS) to develop a series of Rapid Watershed Assessments for ten of Arizona's seventeen watersheds.

Jackie Moxley, Coordinator for the Water Sustainability Program (WSP), manages the major components of WSP that include: a competitive grants program, student fellowship program, recruitment and research initiative, center directed initiatives, center support and an education and outreach program. Five water centers now form the hubs for WSP campus research and activities with the addition of the Superfund Basic Research Program in early January. Ms. Moxley is also now the coordinator of the new campus Water and Environmental Sustainability Program, which combines WSP and the Translational Environmental Research initiative into one reporting unit for the Arizona Board of Regents. She was instrumental in planning four fall 2007 collaborative events on campus: a water-energy forum, the Community Sustainability Forum, the Arizona Association for Environmental Education's Sustainability Conference, and UA Campus Sustainability Day. Ms. Moxley also organized a workshop on reclaimed water use in collaboration with Cooperative Extension, with support from USDA and Global Water, as part of the series of WSP Education and Outreach workshops she organizes. In addition, she was involved in three UA web sites over the course of the year: development of the Campus Sustainability site, revisions to the WSP site, and re-design of the WRRC site.

In addition to participating on grant funded research projects, **Susanna Eden**, Coordinator, Applied Research, had a substantial role in developing publications, public information, and community outreach activities. She led the WRRC's collaborative effort with the Water Education Foundation that resulted in publication last fall of the *Layperson's Guide to Arizona Water*. She was lead author on the well received Arroyo issue "Artificial Recharge: A Multi-Purpose Management Tool," published Winter 2007, and the 2008 issue, "River Restoration: Arizona's Oft Neglected Waterways Get Overdue Attention." She led the effort to develop a competition and summer internship at the WRRC to encourage and develop new talent in writing about water science for the general public. Dr. Eden assists in organization of the WRRC Annual Conferences and was a member of the

organizing committee for the Community Conversation on Water for the Tucson region. This year she assumed responsibility for the 104(b) Information Transfer project and 104 Program reporting.

Terry Sprouse, senior research specialist, continues his work with Project NEMO, coordinating activities in the Santa Cruz watershed, and helping to produce Rapid Watershed Assessment Reports and Watershed Based Plans for watersheds in Arizona. He produced a water quality report for Tumacacori National Historical Park. Dr. Sprouse is also coordinating an update of the popular Arizona Water Map Poster. He was one of the producers of the NEMO wet-dry video that won the Bronze Award for Excellence from the Association of Natural Resource Extension Professionals.

Joe Gelt has a major role in the production of the two WRRC newsletters. He writes and edits the *Arizona Water Resource* and he is a co-author on the Winter 2008 *Arroyo* "River Restoration: Arizona's Oft Neglected Waterways Get Overdue Attention," which he also edited. Joe Gelt prepared special text for two editions of the AWR: a four-page supplement reporting on WRRC's annual conference commemorating the 20th anniversary of the Arizona Department of Environmental Quality, and a special edition of the AWR noting the 50th anniversary of the University of Arizona's Water Resources Research Center. He collaborated on development of the summer writing internship and a statewide contest for student writers planned for fall 2008. In Spring 2008, Mr. Gelt received the UA College of Agriculture and Life Sciences Outstanding Staff Award.

WRRC PUBLICATIONS

Arizona Water Resource Newsletter

The Arizona Water Resource, edited by Joe Gelt, is a 12-page newsletter focusing on state and regional water issues. It is published six times per year and is sent free of charge to more than 2,440 people on the mailing list. In an effort to delete "dead wood" from the list, we required readers wanting to continue receiving the publication to respond by returning a form. The large response we got indicated strong interest in and support of the publication.

The newsletter has wide distribution; the majority of its readers are from Arizona, but it also is mailed to 42 states and 14 foreign countries. The publication regularly includes a feature article, a guest view, news briefs, sections on special projects and on legislation and law, and public policy column written by the WRRC Director, as well as announcement and publication notices. Most issues of the newsletter include a four-page special supplement inserted as a center fold. This mutually beneficial arrangement permits sponsoring organizations to disseminate information about their activities at the same time it assists the WRRC in covering newsletter costs. Organizations sponsoring a supplement this year were U.S. Geological Survey, Global Water the UA Water Sustainability Program.

Mr. Gelt writes most sections of the newsletter including Water Vapors, News Briefs, Legislation and Law, Publications, Special Projects and Announcements along with the main feature.
The 2007-2008 features published were:

- Study Says Northern Arizona's Water Supplies Unsustainable (Jan – Feb)
- U.S. Supreme Court to Hear Arizona Case Challenging ESA Primacy (March – April)
- Arizona to Nevada Water Export Plan Proposed, Contested (May – June)
- Plan to Protect San Pedro River Offers Option for Rural Water Management (July – August)
- Conservation Easements, A Strategy to Check Development, Preserve River Flow (Sept – Oct)
- Wanted: A Viable Bio-fuel Crop to Grow in Semi-arid Arizona (Nov – Dec)
- Prescott Valley's Effluent Water-Rights Auction is Innovative, Profitable (Jan – Feb)
- Special 50th Anniversary Issue (March – April)

Arroyo Newsletter

An edition of the Arroyo, a newsletter focusing on a single topic, was published in Winter 2007 for the first time since May 2002. Titled "Artificial Recharge: A Multi−Purpose Water Management Tool," it summarized in

understandable language the uses of artificial groundwater recharge and its applications in Arizona. The publication filled a major gap in information as evidenced by the requests from various agencies for multiple copies for their staffs. WRRC also has received numerous unsolicited letters commending the importance and quality of the publication. The Winter 2008 issue on the subject of river restoration and environmental enhancement projects in Arizona , "River Restoration: Arizona's Oft Neglected Waterways Get Overdue Attention," drew on research for the U.S. Bureau of Reclamation carried out by Sharon Megdal and then graduate students, Kelly Mott Lacroix and Andrew Schwartz.

Laypersons Guide to Arizona Water

Fall 2007 saw the publication of the *Laypersons Guide to Arizona Water*. It was immediately in demand as a basic source of comprehensive, easily understandable information about water in Arizona. Developed in collaboration with the Water Education Foundation (WEF), the Laypersons Guide to Arizona Water is the third in a series of guides published by WEF. Aimed at a general audience, the Guide describes Arizona's water resources and their uses, the history of water development, water law and the management framework, and discusses the major water issues confronting the State. The Guide can be downloaded free of charge from the WRRC website or purchased in hardcopy form from WEF.

WRRC PRODUCTS

Arizona Water Map

The Arizona Water Map is being completely revised with up to date information. This full sized (31.5" X 41") color poster is suitable for framing and classroom use. Printed in high quality, the new Arizona Water Map is designed to be attractive and informative, to please the eye and engage the mind. Through color and form, the map displays Arizona's surface water and groundwater resources, riparian areas, areas with water quality concerns and much more. Text capsules discuss the Colorado River, the Central Arizona Project, water quality, water uses, water conservation, groundwater, surface water, riparian areas, and climate. Revisions to the water map will include updating all figures, photos and text.

Arizona Know Your Water

The publication, *Arizona Know Your Water* has proved very popular, and in 2007 it was reprinted and its translation and printing of the Spanish version was completed. Downloadable web−based versions are offered on the WRRC web site through a link to the WSP web site at www.uawater.arizona.edu.

WRRC WEB PRESENCE AND ELECTRONIC COMMUNICATIONS

The Internet is an effective outreach vehicle and the WRRC endeavors to make effective and extensive use of its web site. The site has recently undergone redesign to update its look and improve its navigability. The new website takes advantage of software improvements to be more attractive, user-friendly, and easier to manage. In addition to the WRRC publications, we post papers, presentations and links to many other water sites. Staff profiles, a calendar of events, and information about WRRC products are also easily accessible. Viewership has grown steadily since the redesigned website appeared, with the *Laypersons Guide to Water in Arizona* and an older *Water Harvesting Guide* pages receiving the most hits in the 2007-2008 period.

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

WRRC SEMINAR PROGRAM

The WRRC's brown bag seminar series provides information on water issues of timely interest and offers opportunities for community - university interaction. Topics vary widely, as the list below demonstrates, and the number of people attending from the university and from the wider community varies with the topic. An

average of 26 people attended each brown bag and slightly more than half of all who attended were from the community.

Brown Bag Seminars 2007 - 2008

• Mark Howden, Senior Principal Research Scientist, CSIRO (Commonwealth Scientific and Industrial Research Organization) Sustainable Ecosystems in Australia (August 13, 2007)
Title: Climate Change Issues and How We Are Reacting Both Environmentally and In Policymaking
• Kathy Chavez, Water Policy Manager, Pima County Regional Flood Control District
Title: Pima County Comprehensive Plan Amendment to the Water Resources Regional Plan Policies Integrating Water Resources and Land Use (Sept. 20, 2007)
• James J. Riley, Associate Professor, SWES, Member of Surface Water Working Group (SWWG), Grant McCormick, Campus Facilities Design and Planning, Member of SWWG, Leona Davis, PARASOL, Project Leader, Visitors Center Greening, Renee Johns, Project Leader, Developing GIS Layer on Water Harvesting on UA campus, Richard Rushforth, SWES Club/PARASOL
Title: Student Rainwater Harvesting on the UA Campus (Oct. 22, 2007)
• Brad Hill, Water Resources Manager, City of Peoria
Title: Principles of Sound Water Management (Nov. 7, 2007)
• Terry Sprouse, Water Resources Research Center, UA and George Frisvold, AREC, UA
Title: Valuing Bi-national Effluent in Ambos Nogales (Nov. 28, 2007)
• Teresa Makinen and Doug Toy, East Valley Water Forum
Title: East Valley Water Forum Management Plan (Jan. 18, 2008)
• Pedro Arrojo, Univ. of Zaragoza, Spain, Dept. of Economic Analysis
Title: Water banks, markets and policy reform in Spain (Jan. 29, 2008)
• Brent Cain, Brown & Caldwell
Title: Groundwater Model Visualization (Feb. 13, 2008)
• Sharon Medgal, WRRC, and Joanna Bate, GRA, WRRC
Title: Conserve to Enhance: Voluntary Municipal Water Conservation to Support Environmental Restoration (April 3, 2008)
• Dr. Pam McRae-Williams, Water in Drylands Collaborative Research Centre (WIDCORP), University of Ballarat, Australia
Title: Water in drylands: Changes brought about by major water reform in Australia (April 14, 2008)

Co-sponsored lectures and seminars

The WRRC co-sponsored a special colloquium lecture by Israeli water resources expert, Itay Fishhendler at UA on September 7, 2007, attended by graduate students and other members of the university community.

Steve Schneider of Stanford University present a lecture co-sponsored by WRRC, titled “Global Warming: Is the Science Settled Enough for Policy?" at the Gallagher Theater on the UA campus on March 27, 2008.

The WRRC co-sponsored a public lecture by Peter Gleick of the Pacific Institute on the topic of national and global water issues on August 30, 2007.

ANNUAL WRRC CONFERENCES

2007 Conference

Titled "The 20th anniversary of the Environmental Quality Act and ADEQ: Assessing and Protecting the State's Water Quality," the June 5 event was cosponsored by the Arizona Department of Environmental Quality and the Arizona Water Institute. It was held at the Hyatt Regency, Phoenix at Civic Plaza. The one-day conference featured panels on the genesis and history of the Environmental Quality Act and the Arizona Department of Environmental Quality (ADEQ), the water quality assurance revolving fund (WQARF), emerged and emerging contaminants, emerging policy challenges, and the future of ADEQ. Also included was a luncheon presentation on the state of ADEQ by Director Steve Owens and insights from former directors.

2008 Conference

The year 2008 is the 40th anniversary of the Colorado River Basin Project Act, which authorized construction of the Central Arizona Project and the 80th anniversary of the Boulder Canyon Project Act authorized Arizona's 2.8 million acre foot allocation of Colorado River water. Casting an eye forward 40 years, the conference, "The Importance of the Colorado River for Arizona's Future," will consider Arizona's future utilization of Colorado River water. Planning for the conference, scheduled for June 24, 2008, has been a collaboration with the Central Arizona Project.

SPECIAL EVENTS

Water Expo 2007 at the Arizona State Capitol

In what has become an annual event, this year's expo was held on February 27. Cosponsored by UA's Water Sustainability Program, Central Arizona Project (CAP), Salt River Project (SRP) and the U.S. Bureau of Reclamation, this was an opportunity to bring water information and education to Arizona lawmakers about ongoing projects across the state. Eighteen senators and 37 legislators attended the event featuring 40 exhibits and a luncheon program. Other guests included 19 legislative committee members, and board members from the Arizona Water Institute, SRP, and CAP. Conducted on the Senate lawn of the Arizona State Capitol, exhibitors represented state agencies and associations, state universities and colleges, small and large municipalities, rural county and watershed partnerships, and federal organizations working locally. Planning is now underway for 2008.

Community Conversation on Water

On October 26, 2007, along with several state and local partners, the WRRC co-sponsored a community forum where a common set of facts were presented and interested citizens discussed the major water resource issues facing the Tucson region. Attended by approximately 300 people including a cross-section of the community, from civic leaders and water professionals to environmentalists and community advocates, the Conversation was envisioned as an important step toward identifying and working for common water resource management goals.

Chocolatefest and program to honor Dr. Sharon Megdal

The WRRC hosts an annual campus community get-together in February. In 2008 Dr. Sharon Megdal was honored with announcement by Dean Kaltenbach and Provost Sander of her award as the first recipient of the new C.W. and Modene Neely Endowed Professorship for Excellence in the College of Agriculture and Life Sciences.

ASSOCIATED PROGRAMS

The WRRC houses several programs with important university and statewide missions in water research, education and information transfer. WRRC staff members have major responsibility for directing and coordinating these programs and the WRRC provides them administrative support. The association of these programs has a synergistic effect, greatly enhancing the reach and impact of each.

Transboundary Aquifer Assessment Program

The United States-México Transboundary Aquifer Assessment Act, which became law in December 2006, mandates the assessment of priority aquifers along the U.S. – Mexico border through the appropriation of up to $50 million over 2007 – 2016. The United States Geological Survey (USGS) and the Water Resources Research Institutes of Arizona, New Mexico, and Texas, in partnership with the International Boundary and Water Commission (IBWC) in 2007 began developing binational collaboration with Mexican federal, state, and local agencies to undertake hydrogeologic characterization, mapping, modeling, and institutional assessment of priority aquifers. The two priority aquifers is Arizona are the Santa Cruz aquifer and San Pedro aquifer – shared by Arizona and the Mexican state of Sonora. Historically, there has been little official dialogue between the water management agencies on either side of the border concerning use of the Santa Cruz aquifer. TAAP activities there have included the formation of a binational technical committee focused on hydrogeologic

modeling, and field visits to both U.S. and Mexican sides of the shared aquifer by a diverse range of stakeholders including water management agencies, researchers, IBWC/CILA, and civil society organizations. For the San Pedro aquifer, program activities to date have focused on integrating TAAP objectives in the ongoing basin management planning of the U.S. Upper San Pedro Partnership and the Mexican Comisión de Cuenca del Alto Río San Pedro.

The UA Water Sustainability Program

WRRC is one of five UA water centers comprising the Water Sustainability Program (WSP). Completing its seventh year, this campus-wide collaboration of scientists and educators has made significant contributions to the body of research, education and outreach applied to Arizona water resources issues. Funded through the state Technology and Research Initiative Fund (TRIF) the WSP will allocate approximately $3.6 million/year over the next three years to campus water projects and programs. WRRC continues to play a pivotal role in implementing, developing, and managing program components that include a competitive grants program, recruitment and research initiative, student fellowships, center activities and directed initiatives, and an education and outreach program. WSP has created and maintains a separate web site and in addition is responsible for the new web site for the campus sustainability program. The $5,000 internship Jackie Moxley received from the Arizona Water Institute in January 2007 paid for a graduate student through September to assist with that web site's content development and community contacts.

Co-Sponsored Forums and Workshops

WSP actively seeks out partners and cooperates on organization and implementation of informational events, including the Water Expo 2007 at the Arizona State Capitol described above. WSP hosted a water-energy forum in conjunction with the College of Engineering and the College of Science, with a special keynote speaker, Vince Tidwell from Sandia National Labs. This was a first effort to address linkages between water and energy and some of the new research on campus in this area. The forum also included a student poster competition. The Community Sustainability Forum, held at UA, was a combined effort of the City of Tucson, Pima County and UA-WSP. Water was one of eight thematic areas for community discussion. The Arizona Association for Environmental Education held a Sustainability Conference at UA; water was one of the session tracks. Campus Sustainability Day, a nation-wide college/university event, was a mix of speakers and displays highlighting campus and community efforts on sustainability. In the spring, a joint workshop on reclaimed water use was held by WSP and Cooperative Extension, with support from USDA and Global Water, as part of a series of workshops to inform water managers and decision makers. Jackie Moxley organizes these workshops, which address the WSP Education and Outreach Committee objectives. Accredited continuing education units are offered to participants. Reclaimed water is Arizona's last available water source to be utilized and interest in this topic is high.

Competitive Grants

A key component of the WSP is the competitive grants program. Each year approximately $1 million is allocated to UA faculty and staff to fund projects relevant to critical Arizona water issues. In spring 2008, 16 new projects were selected through a panel review process and four projects were granted continuation of funding for the next cycle beginning July 1, 2008. More information on the grants can be found at www.uawater.arizona.edu. New projects selected in the review process this spring that involve WRRC staff and/or are hosted by the WRRC for 2008/09 include the following:

1. Ground Water Age Dating for Water Budget Development in the Show Low Watershed, Navajo County, AZ. Kristine Uhlman, Water Resources Research Center, CALS and Chris Eastoe, Geosciences, COS, and Steve Campbell, Navajo County, Cooperative Extension. 1 year; Award: $4,800. Partners: Arizona NEMO (Nonpoint Education for Municipal Officials), Arizona Department of Water Resources and Show Low Creek Watershed Enhancement Partnership.
2. Science Education That Makes a Difference - through Inspired Teacher Leaders. Kerry Schwartz, Water Resources Research Center, CALS; 1 year; Award: $34,479.

Partners: ASU Polytechnic Science Education Program, and Arizona Foundation for Resource Education.
3. Yuma Desalting Operations, Water Quality and Vegetation Distribution in the Cienega de Santa Clara. Karl Flessa, Geosciences, COS; 1 year; Award: $30,895.
Partners: Central Arizona Project and Centro de Investigación en Alimentación y Desarollo (CIAD).
4. Optimum and Minimum Irrigation Requirements of Landscape Trees. Ursula Schuch, Plant Science, Ed Martin, Maricopa Ag Center and Rick Gibson, Pinal County, Cooperative Extension, CALS; 1 year; Award: $20,959. Partners: Arizona Landscape Contractor's Association, Pinal County Master Gardeners and the City of Maricopa.

One multi-year project involving WRRC staff received continued funding and will finish up in the next fiscal year: Estimating Water Use: Monitoring Rural Domestic Wells with Low-cost, Near-real Time Water Metering. $58,970 (2 years) Susan Pater, Kim McReynolds, Cado Daily, Cochise County Cooperative Extension, Gary Woodard and Ramon Vazquez, SAHRA, Hydrology &Water Resources, Sharon Megdal and Susanna Eden, Water Resources Research Center. Partners: Cochise County and Badger Meters.

WSP Funded WRRC Directed Initiatives

In addition to the WSP projects conducted in-house or hosted by the WRRC, WSP funding has provided opportunities for the WRRC to strengthen educational programs, support new and continuing projects, and expand ties to other departments and colleges in the area of water policy and management. In 2007/08 WRRC provided support to David Adelman, Associate Professor in Roger's College of Law, with a focus on environmental law and for Chris Scott (Geography/Udall Center) for research on urban warming and residential water demand, complementing a USGS 104(b) grant he was awarded in 2007. WRRC-WSP money is funding half of two Translational Science Fellows awards sponsored by the Institute for the Study of Planet Earth (ISPE) Janick Artiola and Eric Betterton. In addition, Dr. Graciela Schneier-Madanes, chairman of "rés-EAU-ville" / CNRS (Centre National de la Recherche Scientifique), Paris, France has spent the 2007-2008 academic year at UA, hosted by WRRC and the Udall Center, as part of a new collaborative agreement with the French Government.

WRRC provided funding for a number of research and outreach projects, including rainwater harvesting projects and development of a drought reporting system. The WRRC continued its support of projects associated with enhanced drought preparedness planning for the Colorado River; and climate change adaptation for water managers. Directed Initiative funds also supported exploratory work in preparation for U.S.-Mexico Transboundary Aquifer Assessment Act implementation. Arizona Project WET education programs continued to receive support as well. The WRRC funding made it possible to publish a Spanish translation of the popular booklet, *Arizona Know Your Water*. The booklet was originally published as the product of a Water Sustainability Program grant. The WRRC also directed funds to help support Kristine Uhlman's video projects for NEMO that have won multiple awards. The WRRC provided support for the Symposium on Water History of the Southwestern United States held on Wednesday March 19, 2008. The symposium showcased research on a range of water history topics including U.S.-Mexico water issues, the Colorado River, northern Mexican water governance, and American Indian water rights. In addition, the WRRC was an institutional sponsor for the celebratory events marking the 50th Anniversary of the first graduations from Department of Geography and Regional Development; a public lecture in Tucson by Peter Gleick, of the Pacific Institute; and contributed to the Desert Horticulture 2008 Conference.

Arizona Project WET

Arizona Project WET Water Education Program

Arizona Project WET is a comprehensive water resource education program with a twelve-year history of successful teacher training. The Arizona Project WET program uses nationally recognized educator guides to deliver water education programs that meet Arizona Academic Standards Water Education Workshops, developed with local education and water specialist partners, meet grade level specific instructional goals and bring relevancy to the subject of water education for each audience. Water resource materials used to develop

workshops cover all water topics from the physical and chemical properties of water to something as specific as CAP's junior priority status for Colorado River water. Workshops designed specifically for pre-service teachers are taught through UA, ASU and NAU. Through intensive train-the-trainer workshops, volunteer facilitators are also equipped to offer teacher/educator workshops that focus on water issues in their particular areas of the state. The Arizona Project WET program is guided by an advisory council, which meets bi-monthly. The Council members are water specialists and stakeholders from statewide government agencies and private entities.

Teacher workshops and other Arizona Project WET activities are funded by grants from federal, state, county, city and public/private entities, and grant funds are supporting an on-going program evaluation to assess impact and expand appropriately. During the reporting period 805 teachers participated in at least one of 54 six to sixteen-hour water education workshops held in 13 cities across Arizona. These teachers report reaching 86,544 students each year with water education. To the statement "The workshop was excellent - one of the best I have ever attended" 86% agree or strongly agree. To the statement, 'The workshop was relevant and improved my knowledge 85% agree or strongly agree. Finally to the statement, "I intent to become a better water steward as a result of this workshop," 86% agree or strongly agree. A new standards-based interactive computer module is being evaluated based on input from 1,445 6th grade students over the 2007-08 school year.

Arizona Makes a Splash with Project WET Water Festivals Program
Arizona Project WET developed the Arizona Make a Splash with Project WET Water Festival Program. These 4th grade standards-based water education events have engaged and instructed 21,380 students and 800 teachers across Arizona. This reporting period water festivals reached 4,523 students, 388 teachers and 268 parents. Lessons were conducted by 341 trained volunteers. Over 94% of participating teachers agree that water festival participation increases student understanding of the standards based concepts covered. This project attracts about $85,000 annually in event funding from statewide partners. Festivals held regularly include Flagstaff, Phoenix metro area, Tucson, Yuma, Sierra Vista, and Safford and additionally this year serving the Gila River Indian Community.

Arizona Nemo - Nonpoint Education for Municipal Officials
Arizona NEMO is a program to provide technical support and outreach to communities and land use decision makers in Arizona. With a strong focus on water quality concerns, Arizona NEMO watershed based planning documents characterizes each watershed with GIS mapping and includes predictive numeric modeling to simulate watershed response and to predict nonpoint source transport modeling. The Arizona NEMO program has developed watershed based planning documents for nine of the twelve large watersheds of the state, and a contract is in place to continue the effort until the entire state has been completed in June 2010. Funding is provided under Federal Clean Water Act 319, under the direction of the Arizona Department of Environmental Quality. Planning documents, maps, and a manual of Best Management Practices (BMPs) can be found at the NEMO website (www.AirzonaNEMO.org).

2007-2008 NOTABLE INFORMATION TRANSFER ACHIEVEMENTS

Adoption and Use of Arizona Water Resource
Evidence of the impact of the WRRC newsletter, Arizona Water Resource, went beyond praise of its many loyal readers in 2007-2008. The UA Hydrology and Water Resources Department is including copies of the AWR as part of their recruitment package to attract applicants. A national agricultural publication will be reprinting the AWR feature "Wanted: A Viable Bio-fuel Crop to Grow in Semi-arid Arizona." Material from the newsletter has been reprinted in the *Arizona Capitol Times*, the major source of information for and about state government.

Community Conversations on Water
The Tucson Community Conversation on Water, held on October 26, 2007, provided a forum for approximately 300 participants to discuss important water supply issues facing the region. Water experts presented basic facts

about the area's water supply and water management framework in the first session of the day. Subsequent presentations and panel discussions explored many perspectives on the issues. The audience was encouraged to ask questions and provide their input. Dr. Sharon Megdal, Director of the WRRC, and Dr. Susanna Eden, Coordinator – Applied Research helped to organize the meeting and Dr. Megdal served a moderator for the morning session. Written feedback from audience on questions discussed in the Conversation was compiled and summarized by the WRRC. Following on this effort, an project was undertaken with funding from The University of Arizona Technology and Research Initiative Fund (TRIF) to gain an understanding of similarities, as well as differences, in what different segments of the community would like to see emerge from regional water resource planning process. In-depth interviews were carried out with representatives of a cross section of the community. Study results have been presented to various audiences in the region and the study report made available on the WRRC web site. Key results and recommendations also appeared as an Op Ed opinion piece by Dr. Megdal that appeared in the Arizona Daily Star on January 13, 2008. Interest in these issues remains high in the community (a separate city-county dialogue involving community meetings and workshops is ongoing) and it is generally acknowledged that the efforts of the WRRC to inform stakeholders and the public is making positive contributions to the conversation.

Sustainability through Rainwater Harvesting

Work that began with 104(b) funded grant project 2006AZ131B has continued and expanded with additional funding for the WRRC, WSP and others. Awards and commendations resulting from the work continue to pile up.

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

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

• The student group PARASOL went on to win second prize in the WSP annual poster contest on the theme sustainability at the water and energy nexus, for their poster titled "The UA Visitor Center: Demonstrating Sustainable Campus Facilities."

• A 1st Place - Student Showcase Award in the Architecture, Planning and Landscape Architecture undergraduate category was awarded to Leona Davis, Richard Rushforth, and Lincoln Perino in 2007 for "The UA Visitor Center: Demonstrating Sustainable Campus Facilities" by the Graduate & Professional Student Council (GPSC).

• The students won a Sustainable Solutions Award from Cummings Publishing.

• In the spring and summer of 2007, UA students designed and implemented a "green retrofit" for the UA Visitor Center. Improvements emphasize water harvesting and solar energy, featuring working systems which double as educational models. This project was partially funded through WRRC support.

Informational Videos on Western Rivers and Watersheds

As reported last year, Kristine Uhlman, of the WRRC, was associate producer of the video, "Stormwater Management from a Watershed Perspective: Extreme Western Climates" in 2006-2007, which was broadcast nationwide on satellite television and at numerous conferences and meetings in Arizona. In 2007-2008, Ms. Ulhman produced the "Arizona NEMO Wet/Dry" video with the help of Terry Sprouse. Both videos won Awards of Distinction for the Communicator Awards group, an international competition that recognizes excellence in communication. In addition, the video won the Bronze Award for Excellence from the Association of Natural Resource Extension Professionals.

Arizona Make a Splash with Project WET Water Festival

Arizona Project WET organizes Water Festivals for school districts throughout Arizona. Water Festivals are intensive and interactive learning experiences for 4th grade students and their teachers. Content is in accordance with the state mandated learning objectives for the students and includes the water cycle, watersheds and water

supply, riparian systems, groundwater and water conservation. At the festival, structured hands-on lessons are used to engage students in understanding natural systems and water resources while having fun. This reporting period water festivals reached 4,523 students, 388 teachers and 268 parents. Lessons were conducted by 341 trained volunteers. Over 94% of participating teachers agree that water festival participation increases student understanding of the standards based concepts covered.

Other notable achievements and awards

• Sharon Megdal was named the first recipient of the C.W. and Modene Neely Endowed Professorship for Excellence in the College of Agriculture and Life Sciences.
• In late 2007, Carl Bauer was the only American named to the Experts' Committee on Water Markets of the Spanish Government's Environment Ministry. He helped write the report that the Committee presented to the Ministry in early 2008.
• Joe Gelt received the UA College of Agriculture and Life Sciences Outstanding Staff Award.
• Kristine Uhlman was reappointed by the Governor for another 3−year term on the Water Protection Fund Commission.
• Jackie Moxley received an Arizona Water Institute Internship Grant in January 2007, to hire a graduate student to assist with coordination of campus sustainability efforts and serve as liaison among campus student groups, faculty, staff and community organizations.
• A Water Policy Certificate Program was created at the University of Arizona under leadership of Carl Bauer.
• The *Laypersons Guide to Arizona Water* was published and posted for download on the WRRC website

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 NCGP Award**	**NIWR−USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	3	6	0	0	9
Masters	3	4	0	0	7
Ph.D.	3	4	0	0	7
Post−Doc.	0	0	0	0	0
Total	9	14	0	0	23

Notable Awards and Achievements

Matt Tomanek, MS student, won a Thunderbird scholarship in 2006 awarded by the Environmental Professionals of Arizona, a nongovernmental organization.

Otakuye Conroy, Ph.D. student, won the University of Arizona Centennial Achievement Award in 2005. This award is to recognize outstanding achievement and contributions of minority graduate students at the University of Arizona. Awards are given to one male and one female student per academic year working at the doctoral level.

Kris Kuhlman (graduate student funded by grant 2004AZ68G) received the Errol Montgomery Prize for best presentation at the workshop for his presentation, based on project research, at the annual Dia del Agua workshop of the University of Arizona Department of Hydrology and Water Resources in March 2007.

Work that began with 104(b) funded grant project 2006AZ131B has continued and expanded with additional funding for the WRRC, WSP and others. Awards and commendations resulting from the work: • Jim Riley, the project PI, was awarded the Community Xeriscape Leader Award for 2007 by the Arizona Department of Water Resources and Tohono Chul Park for work on this project. The award came with a special recognition by the Governor of Arizona, Janet Napolitano. • Ms. Emily Brill Duisberg, past President of the student group, PARASOL, which implemented the project, was awarded the Student Sustainability Award at the national conference of the Association for the Advancement of Sustainability in Higher Education, AASHE. • The student group PARASOL went on to win second prize in the WSP annual poster contest on the theme sustainability at the water and energy nexus, for their poster titled “The UA Visitor Center: Demonstrating Sustainable Campus Facilities.” • A 1st Place − Student Showcase Award in the Architecture, Planning and Landscape Architecture undergraduate category was awarded to Leona Davis, Richard Rushforth, and Lincoln Perino in 2007 for “The UA Visitor Center: Demonstrating Sustainable Campus Facilities” by the Graduate &Professional Student Council (GPSC). • The students won a Sustainable Solutions Award from Cummings Publishing.

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