Water Resources Research Center Annual Technical Report FY 2002

Introduction

The Florida Water Resources Research Center (WRRC) was re-established as a separate entity from the combined Center for Wetlands and Water Resources Research in 1995. Historically, since 1964, the WRRC as a separate or combined center has been a university-wide focus for water-resources research and has served as the Water Resources Center for the state of Florida. The mission of the WRRC is to serve as a center of expertise in the water resources field, assist public and private interests in the conservation, development, and use of water resources, provide opportunities for professional training, assist local, state, regional, and federal agencies in planning and regulation, and communicate research findings to interested users. The WRRC administers funding received from the federal Water Resources Research Act of 1964 and coordinates water-resources research and technology transfer as authorized by the funding, acts as a liaison for Florida agencies and water management districts, promotes water-resources research by seeking external support, and seeks to enhance the state and national image of the University of Florida (UF) as a focal point for water resources research. The WRRC is funded in part by Section 104 of Public Law 98-242 and Public Law 104-99, which are administered by the U.S. Geological Survey, Department of the Interior. Additional funding and support are provided by UF and research sponsors that include state agencies such as the water management districts.

Research Program

During FY2002, the Florida Water Resources Research Center (WRRC) supported projects that investigated taste and odor problems in drinking water, applied multi-scale and multi-process hydrologic models to a natural watershed in south Florida, and studied the flux of ammonia at the air-water interface of Tampa Bay. Also, partial support was provided toward the development of two numerical groundwater flow models of north-central Florida.

Biological Transformation of 2-Methylisoborneol (MIB) for Improved Water Quality

Basic Information

| Title: | Biological Transformation of 2-Methylisoborneol (MIB) for Improved Water Quality | |
|-----------------------------|-------------------------------------------------------------------------------------|--|
| Project Number: | 2002FL2B | |
| Start Date: | 3/1/2002 | |
| End Date: | 2/28/2003 | |
| Funding Source: | 104B | |
| Congressional District: | 5 | |
| Research Category: | Biological Sciences | |
| Focus Category: | Water Quality, Treatment, Surface Water | |
| Descriptors: | Activated Carbon, Adsorption and Exchange, Algae, Anaerobic Treatment, Bacteria | |
| Principal Investigators: | Angela S Lindner, David William Mazyck | |

Publication

- Lauderdale, C., D. Mazyck, P. Chadik, and A. Lindner. 2003. Microbial Transformation Potential of 2-Methylisoborneol: Potential Drinking Water Applications. 5th Annual Environmental Research Poster Symposium, Department of Environmental Engineering Sciences, April 17, 2003.
- Lauderdale, C., D. Mazyck, P. Chadik, and A. Lindner. 2002. Microbial Transformation Potential of 2-Methylisoborneol: Potential Drinking Water Applications. 5th Annual Environmental Research Poster Symposium, Department of Environmental Engineering Sciences, April 14, 2002.

Title: Biological Transformation of 2-Methylisoborneol (MIB): Investigation of Remediation for Improved Water Quality

Investigators: Angela Lindner, Univ. of Florida, Gainesville, Florida Water Resources Research Center,

> David Mazyck, Univ. of Florida, Gainesville, Florida Water Resources Research Center

Congressional District: 5

Focus Categories: WQL, TRT, SW

Descriptors: Activated carbon, Adsorption and Exchange, Algae, Anaerobic Treatment, Bacteria

Problem and Research Objectives: One of the most problematic taste and odor molecules in drinking water is 2-methylisoborneol (MIB), a product of cyanobacteria, microorganisms that exist in natural waters. MIB has been detected in drinking waters in Australia, England, the U.S. and Japan (Ashitani et al., 1988; Juttner, 1995; Suffet et al., 1996; Zimmerman et al., 1995). While not harmful to human health, this chemical confers a musty taste and odor to the water at a very low odor threshold concentration (OTC) of less than 10 ng/l, and, because consumers value the aesthetic qualities of drinking water, current research has focused on the development of cost- and performance-effective methods for MIB removal (Pirbazari et al., 1992). Conventional treatment methods, including chlorination and flocculation-sedimentation, have not been shown to be capable of consistently removing MIB below its OTC; therefore, alternative methods are being sought. One such approach is biological removal of MIB. Previous studies have shown that depletion of MIB by pure cultures is possible; however, no single study has shown that complete removal (*<*OTC) is possible by either pure or mixed populations (Izaguirre et al., 1988; Kim et al., 1997; Namkung and Rittmann, 1987; Tanaka et al., 1996). The overall objective of this study was to examine the effectiveness of microbial cultures isolated from a variety of natural sources to remove MIB. The results reported herein involve first-year experiments focusing on the isolation and characterization of MIB-degrading populations and the development of a protocol for MIB analysis.

Objectives: The overall hypothesis guiding this work is that MIB-degrading populations can be isolated from a variety of sources, including from raw surface water and activated sludge. To this end, the broad objectives of this work are as follows:

- 1. Isolate microbial cultures from various water sources (Lake Manatee raw water and return activated sludge obtained from the University of Florida waste water treatment facility) capable of utilizing MIB as their sole carbon and energy source.
- 2. Conduct phenotypic characterization of all isolated cultures and compare these characteristics to those of known degraders.
- 3. Develop and test a protocol using Solid Phase Micro Extraction (SPME) and GC/MS analysis to determine MIB depletion in microbial microcosms.

Methodology: Isolation, Characterization, and Growth Measurement of MIB-degrading Microorganisms. Mixed cultures of MIB degraders were isolated from water obtained from the Manatee County Water Treatment Facility and the University of Florida Wastewater Treatment Facility. Samples from each water source were used to inoculate nutrient broth containing 8 mg/l MIB. This solution was then recycled through a filter packed with anthracite until a biological film was formed. The filter effluent was then used to inoculate a minimal medium (See Appendix I for recipe) that contained 8 mg/l of MIB as the sole substrate. Positive growth was verified by observing an increase in turbidity of the effluent using UV/V is spectrophotometry ($\lambda = 600$ nm). Known degraders of MIB, Pseudomonas putida (ATCC # 12633) and Bacillus subtilis (ATCC # 6051), were obtained from the American Type Culture Collection and cultured in a liquid mineral medium that contained MIB as the sole substrate. Solid culturing was performed by streaking from the liquid cultures onto mineral medium agar plates that were subsequently incubated in a 4-liter dessicator containing an open beaker of 5 ml of 100 mg/l MIB solution. The contents of the dessicator were incubated at 30° C for 96 hours before colony development was observed. Each isolated mixed culture was tested for the presence of the catalase enzyme and peptidoglycan in the cell wall, while the cellular morphologies were determined using light microscopic techniques.

Protocol Development of MIB Analysis. The protocol for the analysis of MIB depletion was developed using the Solid Phase Micro Extraction (SPME) procedures described in Standard Method 6040D. For each microcosm, 9 g of NaCl were added to a clean 40 ml glass vial with a screw top septum cap. 30 ml of the liquid culture were then added to the vial, and immediately capped. Sufficient internal standard (2-isopropyl-3-methyoxy pyrazine and 2-isobutyl-3-methyoxy pyrazine) was then injected into the septum to make the concentration of each standard 20 ng/l. The solution was then mixed to dissolve as much NaCl as possible (~15 seconds). Each vial was then placed into a water bath heated to 65 degrees. The SPME needle was then inserted through the septum into the sample headspace while ensuring that the fiber is fully retracted. The fiber was left extended over each sample for 30 to 35 minutes to ensure equilibrium had been reached. The fiber was then removed and blotted dry to avoid getting water into the injector during sample desorption. The SPME needle was subsequently inserted into the injector of the GC and was left in the injector for 10 minutes. The needle was cooled before taking the next sample.

Principal Findings and Significance: *Isolation, Characterization, and Growth Measurement of MIB-degrading Microorganisms.* The initial phase of this project entailed the isolation of mixed cultures capable of growth on MIB as a sole substrate. The previously published optimal initial conditions for the isolation of MIB degraders proved to be ineffective for the isolation of cultures from Manatee County Water Treatment Facility and the University of Florida Wastewater Treatment Facility ((Izaguirre et al., 1988; Tanaka et al., 1996). After several months of unsuccessful isolation attempts using previously described methods, alternative isolation techniques were employed. Successful isolation occurred by concentrating the source water microbial populations in a biofilm on anthracite columns. Samples taken from the effluent of these columns were capable of displaying positive signs of growth on MIB in liquid culture as shown by an increase in turbidity. Growth rates for each culture were determined using side-arm flasks and UV/VIS spectrophotometry at 600 nm. Figure I illustrates the growth of each mixed culture isolated from the biological columns.

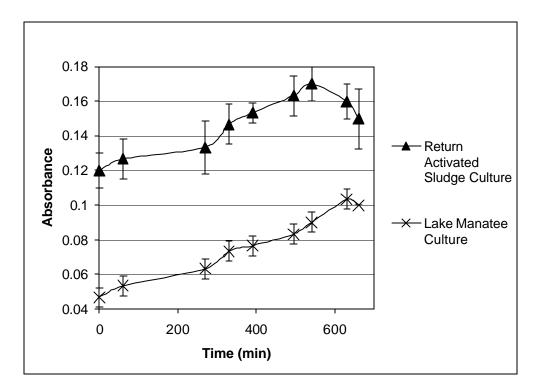


Figure I: Mixed Culture Growth Curves (Each data point represents an average of three measurements, and the error bars represent the 95% standard deviation of these points.)

The growth rates calculated for the Lake Manatee mixed culture and return activated sludge mixed culture were 0.0012 min⁻¹ and 0.0006 min⁻¹, respectively. This illustrates that both isolated mixed cultures are capable of growth on MIB, albeit slowly. The growth of the two known degraders was also assessed for comparative purposes. Table I summarizes the growth rate and doubling time for each culture investigated.

Table I: Growth Characteristics of Isolated Mixed Cultures and Known Degraders

| | Doubling | |
|---------------------------------|----------|-------------------|
| Culture | Time, | Growth Rate, |
| Name | min | min ⁻¹ |
| Bacillus subtilis | 630 | 0.0012 |
| Pseudomonas putida | 693 | 0.001 |
| Mixed (Return Activated Sludge) | 1155 | 0.0006 |
| Mixed (Lake Manatee) | 578 | 0.0013 |

As shown in Table I, the mixed culture obtained from Lake Manatee has growth characteristics similar to those of the known degraders. The difference in the growth characteristics between the two mixed cultures is perhaps due to previous acclimation of the Lake Manatee cultures to MIB, which is prevalent in their natural environment.

A comparison of the colony and cell characteristics of each culture studied may provide further insight into their relative potentials to degrade MIB. Table II provides the limited colony and cell characteristics of isolates grown on minimal medium agar in the presence of MIB.

| | Characteristic | | | |
|-------------------------|------------------------|--------|-----------|------------|
| Culture | | Colony | Colony | Cell |
| Name | Colony Shape | Color | Elevation | Morphology |
| Return Activated Sludge | | | | |
| Colony 1 | amorphous | mucoid | flat | rod-shaped |
| Colony 2 | round w/ defined edges | yellow | raised | coccus |
| Lake Manatee Raw Water | round w/ defined edges | white | flat | rod-shaped |
| Bacillus subtilis | round w/ defined edges | white | flat | rod-shaped |
| Pseudomonas putida | round w/ defined edges | mucoid | flat | rod-shaped |

 Table II: Colony Characteristics of Isolated Mixed Cultures and Known Degraders

Two dominant MIB-using colonies were isolated from the return activated sludge. The first colony isolated possessed an amorphous shape, a mucoid-like color, and was composed of bacillus-shaped cells. The second colony type isolated from the return activated sludge possessed round and defined edges, a yellow color, and cells that are coccus in shape. The Lake Manatee raw water yielded only one colony type that was round in shape, white in color, and possessing cells that are bacillus in shape. Consistent full growth for all colonies was observed in approximately 3 days. Comparison of these isolated microorganisms with the well-studied *B. subtilis* and *P. putida* shows similar cell and colony characteristics.

The remaining phenotypic characterization of the isolated cultures included a gram stain and catalase test. Table III summarizes these results for each culture.

| Culture | Characteristic | | |
|-------------------------|----------------|----------|--|
| Name | Gram Stain | Catalase | |
| Return Activated Sludge | | | |
| Colony 1 | + | + | |
| Colony 2 | - | + | |
| Lake Manatee Raw Water | + | + | |

Table III: Gram Stain and Catalase Test Results

The results from the gram stain test show that both mixed cultures have populations that are Gram positive; however, there is one colony in the activated sludge mixed culture that has an outer cell wall that is Gram negative. Both isolated cultures also showed the presence of populations capable of expressing the catalase enzyme as a means of protection when exposed to hydrogen peroxide.

Protocol Development of MIB Analysis. The initial protocol development for a method to measure the MIB depletion of a microbial culture was conducted by Mr. Roy Sirengo in his Master's Project in the department of Environmental Engineering at the University of Florida, entitled "Quantification and Removal of Taste- and Odor-Causing Compounds in Drinking Water: A Study of MIB and Geosmin." In this study, growth measurements were taken of a P. putida liquid culture, and headspace samples were collected for SPME analysis. The preliminary results provided in this study show a correlation between MIB depletion with population growth. Figure II shows the data collected from this experiment.

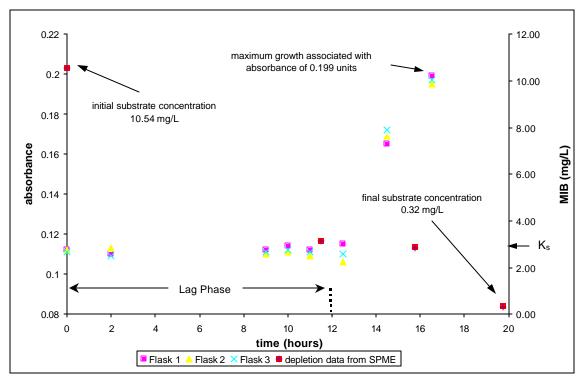


Figure II: Cell Growth and MIB Depletion Using UV/VIS Spectrophotometry and Solid Phase Micro Extraction Analysis

The initial MIB concentration of 10.54 mg/l was reduced to 0.32 mg/l after 19 $\frac{3}{4}$ hours. These results corroborate those collected in the growth studies showing *P. putida is* capable of using MIB as a sole carbon source; however, as described below, future work will focus on continued development of the SPME-based analytical method for more precision.

Future Work: Current and future work on this project include all of the following tasks:

- 1. Complete the microbial characterization by performing phylogenetic studies on each isolated culture using PCR-based methods.
- 2. Determine the MIB-transformation potential of both known MIB-degraders and the isolated mixed cultures using solid phase microextraction (SPME) coupled with GC/MS.
- 3. Identify any intermediate compounds formed as a result of pure- and mixedculture transformation activity using GC/MS methods and assess their odor characteristics.
- 4. Summarize all results by assessing the overall biodegradation potential of isolated cultures.

The anticipated completion of this project is August 2003 and the primary deliverables of this work will be a thesis report and a publication targeted for the journal of *Water Research*.

References:

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- Izaguirre, R.,L. Wolfe, and E.G. Means. (1988) Bacterial Degradation of 2-Methylisoborneol. *Water Science and Technology* 20(8/9): 205-210.
- Juttner, F. (1995) Physiology and biochemistry of odorous compounds from freshwater cyanobacteria and algae. *Water Science and Technology* 31(11): 69-78.
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| Species | Concentration (mg/l) |
|---------------------------------|-------------------------|
| NH ₄ Cl | 50 |
| K ₂ HPO ₄ | 100 |
| MgSO ₄ | 50 |
| CaCl ₂ | 20 |
| FeCl ₃ | 1 |
| MIB | 8 |

Appendix I: Components of Mineral Medium

Student Assistants: Chance Lauderdale, Master's of Engineering, Environmental Engineering Sciences. Anticipated Date of Graduation: Fall 2003

> Roy Sirengo, Master's of Engineering, Environmental Engineering Sciences. Graduation Date: September, 2002

Application of a Multi-Scale, Multi-Process Hydrologic Model to the C-111 Basin in South Florida

Basic Information

| Title: | Application of a Multi-Scale, Multi-Process Hydrologic Model to the C-111 Basin in South Florida | |
|-----------------------------|-----------------------------------------------------------------------------------------------------|--|
| Project Number: | 2002FL4B | |
| Start Date: | 3/1/2002 | |
| End Date: | 2/28/2003 | |
| Funding Source: | 104B | |
| Congressional District: | 5 | |
| Research Category: | Not Applicable | |
| Focus Category: | Hydrology, Models, Water Supply | |
| Descriptors: | Hydrologic Models, Groundwater Hydrology, Watershed Management | |
| Principal Investigators: | Andrew L James, Wendy D Graham, John J Warwick | |

Publication

- 1. Siqing Liu, S., Graham, W.D., and James, A. A hydrologic model coupling overland flow with flow in the unsaturated and saturated zones. American Geophysical Union 2002 Spring Meeting, 2002.
- 2. Liu, S., Graham, W.D., and Jacobs, J. The value of diurnal vs. daily climate forcings to capture soil water dynamics and actual evapotranspiration. In preparation.
- 3. Liu, S., Graham, W.D., and James, A. Monte Carlo simulation of coupled atmospheric, overland, and vadose zone flow processes. In preparation.
- 4. Liu, S., Graham, W.D., and James, A. Stochastic modeling of coupled overland and vadose zone flow. In preparation.

Title: Application of a Multi-Scale, Multi-Process Hydrologic Model to the C-111 Basin in south Florida

Focus categories: HYDROL, MOD, WS

Keywords: Hydrologic models, ground water hydrology, watershed management.

Duration: 3/1/2002-2/28/2003

Principal investigators: Andrew L. James, Wendy D. Graham, John J. Warwick.

Congressional district: 5

Problems and Research Objectives:

Natural watersheds exhibit large degrees of spatial heterogeneity in topography, surface roughness, vegetation, and soil infiltration characteristics. This variability has significant influence on surface runoff, pollutant transport and soil erosion. Most existing studies of combined overland flow/infiltration studies have relied on coupling a simple one-dimensional kinematic wave model for overland flow with a simple infiltration model such as Green-Ampt infiltration equation, Phillip infiltration equation or the Smith-Parlange equation. In order to study coupled overland flow and infiltration processes, it was necessary to develop a physically based multidimensional model for the stochastic analysis of coupled surface and subsurface water flow.

Methodology:

As part of this study, a model was developed to couple overland flow with subsurface flow. The model includes three components to model hydrologic processes in different physical domains and two components that link flow between domains. The three physical domains in which flow is modeled are surficial, or overland, flow, subsurface (vadose and groundwater) flow, and evapotranspiration/precipitation. The linkages between domains incorporated into the model are transfer from overland flow and the unsaturated zone into the atmosphere, and infiltration from overland flow or precipitation into the subsurface. Monte Carlo and stochastic simulations were performed to determine how the variability of surface topography, surface roughness (through Manning's coefficient), and subsurface hydraulic conductivity affects runoff and infiltration.

Principal Findings and Significance:

Of the three parameters, variability in the saturated hydraulic conductivity has the most pronounced effect on runoff and infiltration, followed by surface roughness, and lastly surface topography.

High variability in subsurface conductivity, when compared to a uniform conductivity field, is manifested in the resulting surface runoff hydrograph in the following ways:

- Water begins to pond on the surface earlier as the degree of variability increases, and consequently runoff begins earlier.
- Runoff continues for a longer period of time as variability increases.

- The mean overland flow depth increases, particularly in the early stages of runoff.
- Total runoff volume increases as variability increases.
- The peak discharge of the hydrograph is lower compared with the uniform case.

Note that the earlier surface ponding time and the increase in total runoff volume imply that recharge to the saturated zone is lessened. This was confirmed during the simulations. The lower peak flow and increased total runoff volume were demonstrated in previous studies, and are reconfirmed here.

Variability in the Manning coefficient, affects the runoff hydrograph in the following ways:

- Surface runoff begins later for the random field.
- The mean ponding time is not significantly different between the random and uniform case.
- Runoff continues for a longer period of time as variability increases.
- The mean overland flow depth for the random field is not significantly different from the uniform case at early times (i.e., on the rising limb of the hydrograph), but depths are greater for the random field with increasing time. It was also found that the variability in water depth was higher as the degree of variability in Manning's coefficient increased.
- The peak discharge of the hydrograph is lower compared with the uniform case.
- Total runoff volume decreases as variability increases.

The lower total runoff volume indicated that recharge to the saturated zone increases as the surface roughness increases. The increase in mean overland flow depth indicates an increase in surface storage during a rainfall event, which in turn allows a greater period of time for infiltration to occur.

Variability in surface topography has the same effect on the hydrograph as variations in surface roughness. This result is not surprising, since variability in surface topography can be thought of as a larger scale expression of surface roughness.

Student Involvement:

One Ph.D. student was involved with this project for both 2001 - 2002 and 2002 - 2003.

The Flux of Ammonia at the Air/Water Interface of Tampa Bay

Basic Information

| Title: | The Flux of Ammonia at the Air/Water Interface of Tampa Bay |
|--------------------------|-------------------------------------------------------------------------|
| Project Number: | 2002FL5B |
| Start Date: | 3/1/2002 |
| End Date: | 2/28/2003 |
| Funding Source: | 104B |
| Congressional District: | 11 |
| Research Category: | Water Quality |
| Focus Category: | Hydrology, Nutrients, Non Point Pollution |
| Descriptors: | Ammonia, Flux, Dry Deposition, Eutrophication, Tampa bay, Water Quality |
| Principal Investigators: | Noreen D Poor, Scott W Campbell |

Publication

- Mizak, C.A., Poor, N.D., 2002. Ammonia Flux at the Air/Water Interface of Tampa Bay. Proceedings of the 95th Annual Air & Waste Management Conference and Exhibition, June 23-27, Baltimore, MD, A&WMA, Pittsburgh, PA.
- 2. Mizak, C.A., Poor, N.D., 2002. Ammonia Flux at the Air/Water Interface of Tampa Bay. The Florida Air & Waste Management Association Annual Meeting, September 15-17, Jupiter, FL.
- 3. USF Health Science Center Research Day on February 13, 2003 and awarded a prize for superior presentation: http://www.hsc.usf.edu/PUBHEALTH/GRANTS/HSCResearchDay2003.html

Title: The Flux of Ammonia at the Air/Water Interface of Tampa Bay

Investigators: Noreen D. Poor, Ph.D. P.E., Scott W. Campbell, Ph.D., Connie A. Mizak, M.S., University of South Florida, Tampa, Florida

Congressional District: #11

Focus Categories: WQL, NU, NPP

Descriptors: Ammonia, flux, dry deposition, eutrophication, Tampa Bay, water quality

Problem and Research Objectives:

Tampa Bay is one of the largest and most diverse estuaries on the West Coast of Florida and contributes over \$5-billion annually to the region from trade, tourism, development and fishing. Over the past fifty years, unchecked pollution destroyed more than half of the bay's sea grass meadows and contributed to a decline in the number of important species native to the region. Since the Tampa Bay Estuary Program (TBEP) was established in 1991, several key action initiatives were defined to improve conditions in the bay and return it to a viable state. Atmospheric deposition of nitrogen was identified as a key action initiative in the program because it is expected to increase with population, power consumption, and traffic growth. To better quantify nitrogen deposition to the bay, the Florida Department of Environmental Protection, in conjunction with the TBEP, developed the BRACE (Bay Regional Atmospheric Chemistry Experiment) program. The goals of BRACE are to estimate the direct deposition of biologically active nitrogen to Tampa Bay, to apportion the regional source contributions to this deposition, and to assess Tampa Bay's air quality before and after the Gannon station re-powering. Understanding the mechanisms that contribute to atmospheric ammonia deposition to the bay is an important component of this study.

Recent nitrogen deposition research in the estuary indicates that ammonia deposition dominates the total dry nitrogen flux to the bay. Gaseous plus aerosol ammonia contribute approximately 450 tons per year or 60% of the total nitrogen deposition of 760 tons per year to the estuary. Research data also indicate that during the summer months, Tampa Bay may act as a source for atmospheric ammonia as the water temperature increases and ammoniam concentrations become elevated. To better quantify the contribution of ammonia to the annual inputs of new nitrogen, the daily flux of ammonia will be calculated at the air/water interface to quantify the seasonal and temporal patterns of atmospheric ammonia deposition to Tampa Bay.

Objectives:

- 1. Describe the direction and magnitude of the ammonia flux at the air/water interface;
- 2. Determine if estuarine meteorological conditions and bay salinity cause a bidirectional ammonia flux;

- 3. Accurately estimate the temporal patterns of atmospheric ammonia deposition;
- 4. Utilize analysis of ambient measurement data to test and improve algorithms that calculate the flux of ammonia at the air/water interface; and
- 1. Explore the variation between measured data and modeled fluxes to reduce or explain any observed error.

Methodology:

Flux measurements were derived from one year of seasonal integrated daily monitoring data collected over Tampa Bay. Intensive data collection occurred daily over three, 2week sampling periods to discern the effects of temporal variability on the dry deposition of ammonia to the bay. The Gandy Bridge monitoring site was utilized for the April 2002 sampling and the Picnic Island Pier site was utilized during the November 2002 and January 2003 sampling events. Gaseous and aerosol ammonia were collected using a URG Inc. annular denuder system (ADS). The ADS operated at an airflow of 10 L/min for 12 hours and consisted of a 2.5 um particle cutpoint cyclone inlet, 150 mm gas denuder and a filter pack containing a 47 mm diameter/1um pore size nylon filter. The denuders and filters were extracted with DI water and analyzed for ammonia with an ion chromatograph (IC). Water grab samples were analyzed in the laboratory by automated colorimetry for ammonium concentrations. The net ammonia flux was calculated as the product of the difference of the average daily and equilibrium ammonia air concentrations and the average daily deposition velocity. The ammonia equilibrium concentration was calculated based on Henry's Law through measurements of bay salinity, temperature, pH and ammonium concentrations. The NOAA inferential buoy model was used to calculate the average daily gaseous and aerosol ammonia deposition velocities.

Measurements taken during each sampling event included:

- Hourly wind speed and direction NOAA CO-OPS (8726607 Old Port Tampa, Fl)
- Hourly air temperature and relative humidity Omega RHTEMP 1000 probe
- Hourly bay water temperature, pH, and salinity HYDROLAB minisonde
- Diurnal collection of bay water samples analyzed for NH3-N by automated colorimetry
- Diurnal NHx measurements URG Annular Denuder System

Principal Findings and Significance:

• Describe the direction and magnitude of the ammonia flux at the air/water interface;

Ammonia flux calculations were made using ambient monitoring data that included atmospheric and bay water ammonia and ammonium concentrations and meteorological measurements. The measurements were used as inputs to the NOAA Buoy model to calculate the deposition velocities of gaseous ammonia. Monitoring and subsequent flux

calculations occurred over three sampling periods: April 2002, November 2002, and January 2003. During April 2002, the 24-hour average flux was 2.57 g/ha and the daily and nightly average fluxes were 1.35 and 3.79 g/ha, respectively. The November 2002 24-hour, daily, and nightly average fluxes were 0.72, 0.68, and 0.75 g/ha, respectively. The January 2003 24-hour, daily, and nightly average fluxes were 0.62, 0.52, and 0.70 g/ha, respectively. It is important to note that the April 2002 average fluxes were considerably greater than the fall and winter average flux calculations. It is likely that this seasonal trend is due to the dependence of ammonia emission strength on local climate. Based on U.S. EPA data, it is estimated that the agricultural sector contributes approximately 85% of U.S. ammonia emissions. An ammonia emission inventory completed for Hillsborough County, Florida indicated that approximately 62% of county ammonia emissions originated from livestock and fertilizer applications, with only approximately 8% from point sources. Since the majority of emissions originate from agricultural sources, it is possible that the higher average temperature and relative humidity in the spring season would cause greater volatilization of ammonia from the land. Because ammonia has a short residence time in the atmosphere and is highly soluble in water, the increased volatilization and ambient concentrations would contribute to an increase in ammonia flux to Tampa Bay.

During the three monitoring periods, the direction of ammonia flux was from the air to the water, with few exceptions. The direction of flux is dependent on the ambient air concentrations of gaseous ammonia, bay water concentrations of ammonium, and the Henry's Law equilibrium theory. The majority of the time, the atmospheric ammonia concentrations are high enough that the ammonia flux is positive and ammonia is deposited to the bay. However, when bay water concentrations become elevated, the ammonium ion dissociates to ammonia gas and hydrogen ion, which drives the flux from the water to the air. There were several times during the sampling when this occurred.

• Determine if estuarine meteorological conditions cause a bi-directional ammonia flux;

During the November 2002 and January 2003 sampling events, there were three times when a large negative flux (from water to air) was calculated. The negative fluxes were due to a simultaneous decrease in measured ambient concentrations and an increase in bay water concentrations of ammonia. Upon further analysis, it was discovered that these events followed significant rainstorms that contributed greater than 0.2 inches of precipitation. Our hypothesis is that the precipitation directly and indirectly transferred ammonia to the bay and substantially increased the bay water concentration of ammonium while decreasing the ambient air concentrations of ammonia. This in turn triggered an ammonia flux from the bay back to the airshed.

• Accurately estimate the temporal patterns of atmospheric ammonia deposition;

The two air monitoring sites, Gandy Bridge and Picnic Island Pier, are located adjacent to Tampa Bay along the western edge of Hillsborough County. The majority of local ammonia sources, including the agricultural and industrial sources, are located in eastern Hillsborough County. Therefore, one would expect to find increased ammonia fluxes when the winds were coming from the east/southeast direction. Comparing daily and nightly fluxes with wind speed and direction for the three monitoring periods, reasonable correlations were discovered. During the April 2002 period, daily fluxes increased for winds between 7 and 9 m/s and 120 to 180 degrees (SE of the monitoring site). Nightly fluxes were greater than daytime fluxes and increased substantially with winds between 6 and 7 m/s and 100 to 180 degrees (E/SE of the site). Although the November 2002 and January 2003 monitoring periods did not show strong correlations with wind direction, wind speed correlations did remain strong with increased fluxes occurring at moderate wind speeds for both daily and nightly comparisons. In general, increases in ammonia flux only occurred with wind speeds less than 6 m/s. One reason for the absence of a wind direction correlation during these periods may be the low ambient concentrations of gaseous ammonia during the fall and winter seasons. The decrease in ammonia volatilization from agricultural sources at cooler temperatures coupled with a strong thermal buoyancy is most likely causing increased mixing at higher atmospheric elevations, thereby diluting the already low ambient ammonia concentrations. However, the consistent trend with moderate wind speeds can be explained by the short atmospheric residence time for ammonia. Local source emissions are remaining in the area under these wind speed conditions.

- Utilize analysis of ambient measurement data to test and improve algorithms that calculate the flux of ammonia at the air/water interface; and
- Explore the variation between measured data and modeled fluxes to reduce or explain any observed error;

The NOAA Buoy model was utilized to estimate the air/water exchange rates of ammonia over Tampa Bay. In the model, the standard bulk transfer coefficient equations for mass, heat, and momentum were used to derive expressions for temperature and wind speed gradients. The model was developed to use over-water meteorological parameters as inputs, which include wind speed, air and water temperature, and relative humidity. Iteration was performed until measured temperature and wind speed gradients equaled the calculated values. Model outputs include gas and particle deposition velocity, sensible and latent heat flux, and friction velocity.

The NOAA Buoy model was tested with data recorded at an offshore meteorological tower. Meteorological and bay water measurements recorded at the Port Manatee Turn meteorological tower, which is located in the middle of Tampa Bay, were used as inputs to the model, and the model outputs were compared with direct measurements of sensible heat flux and friction velocity taken at the tower. Differences between the modeled and the measured sensible heat flux and friction velocity were less than 4% and 2%, respectively, indicating that the model accurately predicts these parameters when measurements are recorded offshore.

A study was then conducted to determine if turbulent flux parameters are accurately predicted with near-shore measurements as inputs to the NOAA Buoy model. Meteorological and bay water measurements recorded at the Picnic Island Pier over the same time period were then used as inputs to the NOAA Buoy model, and the model outputs were also compared with the direct measurements of sensible heat flux and friction velocity taken at the tower.

Although a consistent trend between modeled and measured sensible heat flux and friction velocity can be seen over the 2-week period, the modeled results are consistently lower than the measured parameters. For the November 2002 data, on average, the modeled and measured sensible heat fluxes were 23.3 W/m2 and 39.2 W/m2, respectively, indicating that over this time period the model underestimated the sensible heat flux by approximately 40%. Likewise, the average modeled and measured friction velocities were 0.18 m/s and 0.24 m/s, respectively, indicating the model underestimated the friction velocity by approximately 25%.

During January 2003, average modeled and measured sensible heat fluxes were 15.1 W/m2 and 22.2 W/m2, respectively, indicating that the model underestimated the sensible heat flux by approximately 32%. The average modeled and measured friction velocities were 0.13 m/s and 0.17 m/s, respectively, again indicating the model underestimated the friction velocity by approximately 24%.

It is apparent that there is a consistent trend with the NOAA Buoy model underestimating direct over water measurements of sensible heat flux and friction velocity when meteorological input parameters are recorded near-shore. This may be due to the fact that the model was developed with meteorological parameters recorded from a buoy located offshore in coastal waters. For this study, the meteorological measurements were taken at sites located adjacent to Tampa Bay. The effects of land elements on wind speed and air and water temperatures may have skewed the model results causing an underestimation of the flux parameters. Based on the results of this study, the NOAA Buoy model, when using input data recorded near land, may be underestimating the deposition velocity by between 30 and 40%.

Numerical Groundwater Flow Models of North-Central Florida

Basic Information

| Title: | Numerical Groundwater Flow Models of North-Central Florida |
|-----------------------------|--------------------------------------------------------------------------------|
| Project Number: | 2002FL20B |
| Start Date: | 10/1/2002 |
| End Date: | 2/28/2003 |
| Funding Source: | 104B |
| Congressional District: | 5 |
| Research Category: | Ground-water Flow and Transport |
| Focus Category: | Groundwater, Models, Water Supply |
| Descriptors: | Groundwater Flow, Groundwater Recharge/Water Budget, Karst, Numerical Modeling |
| Principal Investigators: | Louis H. Motz |

Publication

 Dogan, A., and Motz, L. H. 2002. Regional Steady-State Groundwater Flow Model With an Active Water Table. 2002 Annual Water Resources Conference, American Water Resources Association, Philadelphia, Pennsylvania, November 3-7, 2002 (Poster presentation). Title: Numerical Groundwater Flow Models of North-Central Florida

Duration: 10/01/2002 – 02/28/2003

Congressional District: 5

Focus Categories: GW, MOD, WS

Descriptors: Groundwater Flow, Groundwater Recharge/Water Budget, Karst, Numerical Modeling

Principal Investigators: Louis H. Motz

Problem and Research Objectives

Groundwater is the major source of fresh water used in Florida. In 1995, approximately 7,200 million gallons per day (mgd) of fresh water was withdrawn for use, and groundwater accounted for 4,300 mgd, or 60 percent of these withdrawals (Marella 1999). More than 90 percent of the municipal water supply was obtained from groundwater, and nearly half of the 3,200 mgd used for agricultural irrigation was obtained from groundwater. In the future, agricultural demand for groundwater may become constant or even decrease due to more efficient irrigation practices and land-use changes, but public-supply demand for groundwater is expected to continue to increase. The population of Florida is projected to increase by 40 percent from 14 million people in 1995 to more than 20 million people by 2020. Groundwater usage for public supply likely will increase proportionally if fresh groundwater resources are determined to be available.

New fresh groundwater is the preferred public water-supply source in Florida because it is generally a relatively inexpensive source of good quality. However, this must be balanced against the potential for causing unacceptable environmental impacts. Groundwater pumping already has adversely impacted groundwater levels, wetlands, and lakes in some areas of Florida, and it has caused saltwater intrusion in some coastal areas. Long-term planning for public water-supply sources now includes consideration of alternative water-supply sources and management options such as system interconnections, surface water, brackish groundwater, artificial groundwater recharge, reuse and water conservation, wetlands augmentation, and aquifer storage and recovery (PBSJ 2001). For Florida's five water management districts, determining the regional impacts that groundwater pumping will have on aquifer water levels and adjacent and/or overlying lakes and wetlands has become a major priority. Alternatives to using fresh groundwater can be planned for and developed if groundwater pumping rates that meet environmental as well as hydrologic constraints can be quantified.

This research supplements and enhances an ongoing research project being conducted for the St. Johns River Water Management District (SJRWMD) in which the objective is to develop two numerical groundwater flow models of north-central Florida.

These models, which build on a previously developed model of north-central Florida (Motz and Dogan 2002), will represent the surficial aquifer system and the Floridan aquifer system, which consists of the upper and lower Floridan aquifers. A steady-state model will be developed first, and then a transient model will be developed utilizing the results of the first model. The impacts that groundwater pumping will have on aquifer water levels will be determined for present (1995) conditions and for projected conditions in 2020 and 2025. In these models, the surficial aquifer will be an active layer, and thus it will be possible to determine the impacts that pumping (most of which is from the upper Floridan aquifer) will have on the water table as well as on upper Floridan aquifer water levels. The two groundwater flow models will be used for resource planning and management and for making regulatory decisions.

Methodology

The steady-state model will be calibrated for average 1995 hydrologic conditions, and then the transient model will be calibrated for monthly stress periods for 1995-1999. Hydrologic and hydrogeologic data have been acquired in electronic and paper formats from SJRWMD, USGS, and other sources such as the Florida Geological Survey and the Soil Conservation Service. Input files for MODFLOW (McDonald and Harbaugh 1988) have been prepared representing aquifer parameters, boundary heads, and pumping rates for municipal, agricultural, commercial and industrial, and self-supplied domestic pumpage. Input data are being assembled and processed using ArcView, ArcGIS, FORTRAN, and Excel software. Processing MODFLOW (Chiang and Kinzelbach 2001) is being used as a pre- and post-processor for MODFLOW, and output files as required are being prepared for graphical output and publication.

Principal Findings and Significance

To date, a preliminary calibration has been obtained for the steady-state groundwater model, which has been used to make projections for 2025 utilizing a wateruse database provided by SJRWMD. This database includes pumpage from municipal, agricultural, commercial and industrial, and domestic self-supply wells, and recharge due to drainage wells, municipal and domestic self-supply irrigation, agricultural irrigation, and land application of wastewater in rapid infiltration basins and by means of spray irrigation. It is estimated that a 29 percent increase in pumpage from 1995 to 2025 will cause maximum drawdowns of 2.5 ft in the water table in the surficial aquifer and 16.5 ft in the upper Floridan aquifer in the northwestern part of the study area. Also, it is estimated that spring discharges will decrease approximately 1 percent in the study area due to the projected increase in pumpage.

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- Motz, L.H., and A. Dogan. 2002. *Revised North-central Florida regional groundwater flow model.* St. Johns River Water Management District. Palatka, Florida, 107 pp.
- PBSJ. 2001. Volusia Water Alliance Water Supply Plan. Draft Report for Volusia Water Alliance.

Information Transfer Program

Information Transfer

Basic Information

| Title: | Information Transfer | |
|--------------------------|----------------------|--|
| Project Number: | 2002FL6B | |
| Start Date: | 3/1/2002 | |
| End Date: | 2/8/2003 | |
| Funding Source: | 104B | |
| Congressional District: | 5 | |
| Research Category: | Not Applicable | |
| Focus Category: | , None, None | |
| Descriptors: | | |
| Principal Investigators: | Louis H. Motz | |

Publication

- Motz, L. H. 2002. Leaky One-Dimensional Flow with Storage and Skin Effect in a Finite-Width Sink. Journal of Irrigation and Drainage Engineering, American Society of Civil Engineers (ASCE), 128(5): pp. 298-304.
- Motz, L. H., and Dogan, A. 2002. Calibration of the North-Central Florida Steady- State Groundwater Flow Model. ModelCARE 2002: Proceedings of the 4th International Conference on Calibration and Reliability in Groundwater Modelling, Prague, Czech Republic, 17-20 June: pp. 253-256.

Information Transfer

During FY2002, the Florida WRRC actively promoted the transfer of the results of water-resources research to water-resource groups in Florida. The target audience was the scientific and technical community who address Florida's water problems on a professional basis. Specific activities that were part of this task included maintaining an updated mailing list with email addresses and a web-based home page. The email list and home page were used to provide timely information about research proposal deadlines, conference announcements and calls for papers, and other water-related activities. The home page describes ongoing research at the WRRC and lists research reports and publications that are available. Also, the home page is used to list research reports and publications that are available through the WRRC and elsewhere, and it provides links to other water-resource organizations and agencies, including the five water management districts in Florida and the USGS. The WRRC continues to maintain a library of technical reports that have been published in past years by the WRRC. Copies of these reports can be checked out by researchers, and also they are distributed upon request with a nominal charge made to cover the cost of reproduction and mailing. As newer reports become available, electronic versions of these reports will be made available for distribution by downloading from the WRRC home page. Financial support was provided for publishing research results in refereed scientific and technical journals and conference proceedings. Also, the WRRC hosted a seminar given by Dr. K. A. Narayan from CSIRO's Davies Laboratory, Townsville, Queensland, Australia on "Modelling Saltwater Intrusion in the Lower Burdekin Delta, North Queensland, Australia". Dr. Louis H. Motz, who is Director of the WRRC, was the Principal Investigator for the Information Transfer task.

USGS Summer Intern Program

Student Support

| Student Support | | | | | |
|-----------------|---------------------------|---------------------------|-------------------------|------------------------|-------|
| Category | Section 104 Base Grant | Section 104 RCGP Award | NIWR-USGS Internship | Supplemental Awards | Total |
| Undergraduate | 0 | 0 | 0 | 0 | 0 |
| Masters | 2 | 0 | 0 | 0 | 2 |
| Ph.D. | 2 | 0 | 0 | 0 | 2 |
| Post-Doc. | 1 | 0 | 0 | 0 | 1 |
| Total | 5 | 0 | 0 | 0 | 5 |

Notable Awards and Achievements

Research was presented at the USF Health Science Center Research Day on February 13, 2003 and awarded a prize for superior presentation: http://www.hsc.usf.edu/PUBHEALTH/GRANTS/HSCResearchDay2003.html

Publications from Prior Projects

- 2001FL4341 ("Flow Duration Curves to Advance Ecologically Sustainable Water Management") -Other Publications - Jacobs, J.M., G.R. Ripo, J.C. Good, S.R. Satti, Sustainable Watershed Ecohydrology And Optimized Water Management Using A Flow Duration Curve Framework, Eos Trans. AGU, Spring Meet. Suppl., Abstract EAE03-A-04385;HS29-1TU1P-0464, 2003.
- 2001FL4341 ("Flow Duration Curves to Advance Ecologically Sustainable Water Management") -Dissertations - Ripo, G.C., 2003, Framework to Assess Streamflow Withdrawal Availability and Impacts of Ecological Conditions, ME Thesis, Department of Civil and Coastal Engineering, College of Engineering, University of Florida, Gainesville, Florida, 59 pages.