INVESTIGATIONS OF BRACKISH WATER AQUACULTURE IN THE BLACKLAND PRAIRIE REGION OF WESTERN ALABAMA

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INVESTIGATIONS OF BRACKISH WATER AQUACULTURE IN THE BLACKLAND PRAIRIE REGION OF WESTERN ALABAMA

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DISSERTATION ABSTRACT

INVESTIGATIONS OF BRACKISH WATER AQUACULUTURE IN THE BLACKLAND PRAIRIE REGION OF WESTERN ALABAMA

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Three investigations were performed related to brackish water aquaculture in the Blackland Prairie region of western Alabama. Two of these investigations were related to pond fertilization with magnesium fertilizers needed to supplement water deficient in this cation, and the subsequent adsorption of these cations by pond bottom soils. The third investigation was performed to address the concern of salinization of local streams as the result of utilization of brackish water for culture purposes.

A magnesium budget was prepared for a commercial inland brackish water shrimp farm for one production cycle. Fertilization with sulfate of potash magnesia ($K_2SO_4 \cdot 2MgSO_4$ or K-Mag®) was applied to three ponds. Two of the ponds had four previous production cycles and corresponding exposure to magnesium fertilizers, and the third pond had only one previous production cycle prior to the current study. Losses of magnesium that resulted from outflows of water failed to account for all of the magnesium applied, indicating that unaccounted magnesium inputs may have been adsorbed by the pond bottom soils. Increases of exchangeable magnesium in the upper 15-cm layer of pond bottom soils could not account for total inputs of magnesium. Magnesium unaccounted for may have been adsorbed on soil exchange sites at depths greater than 15-cm, analytical errors could have contributed to some magnesium being unaccounted for as well. Differences between the newer pond and two older ponds may indicate that the soils previously exposed to magnesium fertilizers have a diminishing affinity for the magnesium or an equilibrium concentration was being established.

A study conducted in laboratory soil-water systems revealed that soils from an inland brackish water shrimp facility strongly adsorbed magnesium applied as fertilizer — magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$). The rate of adsorption declined over time, indicating the systems were reaching equilibrium. Repeated exposures of soils to solutions of 40 mg Mg^{2+}/L failed to saturate exchange sites, but rather maintained equilibrium with other base cations on soil adsorption sites. Dissolved sulfate resulting from additions of magnesium with magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) was also monitored over the trial. Though difficulties of analysis occurred, it appears the sulfate is not adsorbed by the pond bottom soils.

Investigation into stream salinization resulting from low-salinity aquaculture in was initiated in June 2006. Eight streams were sampled bimonthly for salinity, conductivity, and chloride concentrations. Four of the eight streams were associated with aquaculture production facilities, and received effluents from these operations. The remaining four streams were located in the area near the aquaculture facilities, but did not receive any effluents or runoff from any aquaculture facility. The streams associated with the aquaculture production facilities were sampled at sites both upstream and downstream of the facility. Sampling through November 2007 revealed that the streams associated with the aquaculture facilities had chloride concentrations that exceeded 230 mg Cl^-/L — upper standard set by the Alabama Department of Environmental Management for freshwater streams — at various times throughout the year. Results reveal that these facilities contributed to stream salinization.

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Style manual or journal used: Journal of the World Aquaculture Society

Computer software used: Microsoft Excel 2003, Microsoft Word 2003, and SigmaPlot

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I. INTRODUCTION

Commercial aquaculture is performed in several regions of Alabama, with much of the production concentrated in the Blackland Prairie region. Portions of this region have access to aquifers containing brackish water with salinities ranging from 1 to 10 g/L, which are currently being utilized to supply water to several pond based aquaculture facilities. The use of low-saline water has been beneficial for the production of Channel catfish, Ictalarus punctatus, and has been found suitable for the culture of marine species such as the Pacific white shrimp, Litopeneaus vannamei.

The development of brackish water aquaculture of euryhaline species in Alabama is still in its early stages. Progress has been made, but further research is needed for this sector to realize its potential. Understanding of ionic deficiencies, particularly of potassium and magnesium, in waters from groundwater sources in the region and amendment of those deficiencies has aided progress. However, further understanding of aquatic and soil chemistry of these culture environments is needed to provide further insight, leading to improved culture conditions and management.

Improved understanding the pond dynamics of inland brackish water aquaculture will increase opportunities to diversify aquaculture practices in the Blackland Prairie region, leading to greater sustainability of the aquaculture sector. It would also provide greater economic opportunity for the region. The use of brackish groundwater also has environmental implications that must be considered, mainly related to the possibility of salinization of the local environment. The sustainability of brackish water aquaculture is contingent upon recognition and management of possibly deleterious environmental affects of the culture practices. This study was initiated to investigate some of these aspects, including water quality, soil chemistry, and potential salinization of local streams resulting from inland brackish water aquaculture. The goal is to improve management of culture systems, particularly in terms of the application of high cost magnesium fertilizers. Understanding the pathways in which magnesium is lost to the environment provides insight into the development of better management practices and leads to greater efficiencies. Furthermore, realization of potential impacts on the environment, such as stream salinization, will require additional management practices that will enhance the sustainability of inland brackish water culture in Alabama.

The first investigation is concerned with the application of magnesium fertilizers and identifying pathways in which it is lost to the environment. The hydrologic equation was applied to three inland brackish water culture ponds for this purpose. Chapter 1 provides a magnesium budget used to account for magnesium inputs and outputs based on the hydrologic equation.

Based upon the results of the magnesium budget and previous work utilizing a potassium budget, the uptake of magnesium by soils was investigated in Chapter 2. A laboratory study was designed to monitor the uptake of dissolved magnesium, and sulfate, from the water column. The goal was to further understand how magnesium was adsorbed by soils common to the Blackland Prairie region of western Alabama. As cations may be adsorbed by both exchangeable and non-exchangeable process, the laboratory study provided an opportunity to determine which process dominate the adsorption of magnesium. Further study was performed to examine the rate of magnesium uptake, as well as whether or not magnesium adsorption reached equilibrium in these systems.

Chapter 3 investigates the possibility that inland brackish water culture practices result in salinization of local streams. Utilizing the maximum permissible chloride concentration (230 mg/L) for freshwater streams set by the Alabama Department of Environmental Management, streams associated with inland brackish water culture facilities were monitored for chloride concentrations. The goal was to identify whether or not these brackish water facilities cause or contribute to stream salinization, and provide insight into possible strategies to manage losses of salt to the environment.

II. REVIEW OF LITERATURE

Fisheries and Aquaculture Production

According to the Food and Agriculture Organization (FAO) of the United Nations statistics, growth of global fisheries products have occurred through the early part of this century despite declines in capture fisheries production (FAO 2007). Aquaculture is responsible for this growth, as it continues to make up a larger portion of total fisheries production. Since 2000, aquaculture production has grown from 35.5 million mt to 49.8 million mt in 2005, while capture fisheries has remained consistent averaging 93.6 million mt over the same period (FAO 2007). It is apparent that if demand for fisheries products continues to grow, additional demand will need to be met through aquaculture production.

Fishery production in the United States does not follow the same overall global trend. While capture fisheries appears to have become maximized with a 7-year average production of 4.96 million mt, aquaculture production has fallen 23% between 2004 and 2006 (NMFS 2007). This decline in production has occurred despite a nearly 21% increase in consumption of fisheries products in the US from 2000 to 2007 (NMFS 2007). Therefore, increased consumption has not been met by greater domestic production, and the US has relied on imports to meet demand.

Alabama's fishery production has followed the overall trend for the US with capture fisheries averaging 12.2 thousand mt and aquaculture production (catfish) dropping 17.1% from 2003 to 2006 to 59.5 thousand mt (ACES 2007, NMFS 2007). Reasons for the decline in aquaculture production vary, but many observers and most producers have attributed them to competition from imports and rising production costs. As this decline has occurred, ongoing research has been investigating opportunities to diversify aquaculture in Alabama mainly focusing on higher valued species such as marine shrimp, Litopenaeus vannamei. The focus has been aimed at utilizing inland brackish groundwater sources to culture euryhaline species in the Blackland Prairie region of the state.

Inland Brackish Water Aquaculture

Inland culture of euryhaline species in mineralized waters has been, and continues to be, performed throughout the world including; Australia, China, Ecuador, India, Thailand, United States, as well as others (Boyd and Thunjai 2003, Partridge *et al.* 2008). Several different species are cultured under inland brackish, or low salinity, conditions and include: shrimp; Peneaus monodon and L. vannamei; fish; Barramundi, Lates calcifer; red tilapia, Orechromis mossambicus; gilthead seabream, Sparus aurata; and others either experimentally or commercially (Boyd and Thunjai 2003, Flaherty *et al.* 1999, Partridge et al. 2008, Samocha *et al.* 2002, Chervinski 1984, Romana-Eguia and Eguia 1999).

Motivation for culturing euryhaline species in inland areas is the exploitation of under-utilized resources such as mineralized water, which often has little practical use. Furthermore, presence of saline waters may indicate lands are salt affected – limiting beneficial use. Examples include semi-arid and arid regions such as portions of the Murray-Darling Basin in Australia and the Rio Grande Valley in the United States (Ghassemi *et al.* 1995). Introducing aquaculture represents an adaptive use of these areas, and could make them more productive (Barson and Barrett-Lennard 1995, Smith and Lawrence 1990, Stickney and Davis 1981). Further, advantages of moving aquaculture operations inland from the coast are: removal from sensitive environments, limited contact with common pathogens, avoidance of extreme weather events, and reduced property costs (Atwood *et al.* 2003, Flaherty et al. 1999).

Brackish Water Sources and Composition

Natural waters contain various amounts of total dissolved solids (TDS), and are commonly described as fresh, brackish, or saline waters and brines. In this paper designation of these descriptions will have the following ranges of TDS: fresh waters, 0 to 1.0 g/L; brackish waters, 1.0 to 20.0 g/L; saline waters, 20.0 to 50.0 g/L, and brines, > 50.0 g/L (Drever 1997). The term mineralized will be used to refer generally to brackish and saline waters.

Sources of water utilized for the culture of euryhaline species, though all mineralized, vary considerably in origin, degree of mineralization and ionic composition. Mineralized waters can originate from seawater (or brine) that is transported inland and diluted to desired concentrations (Boyd and Thunjai 2003, Flaherty and Vandergeest

1998). Mineralized groundwater sources are commonly exploited and can originate from either primary or secondary processes. Groundwater that is mineralized through primary processes is recovered from geologic formations, and results from mixtures of formation and infiltrated meteoric water (Drever 1997). Secondary mineralization is anthropogenic in nature, often resulting from rising water tables (shallow groundwater) because of irrigation, which puts groundwater in contact with either historic salt deposits or salts that have accumulated overtime (Hillel 1992).

The degree of mineralization of water sources ranges from brackish to hypersaline. All sources can be found within a wide range of salinities. Seawater and brines that have been transported inland can be diluted to nearly any desirable salinity. Water that has been mineralized by primary processes is highly variable in salinity, and is strongly influenced by the proportions of formation and meteoric waters (White 1965, Feth 1970, Hitchon and Friedman 1969). The degree of mineralization by secondary salinization processes is dependant upon the concentrations of salt deposits encountered.

More important than the degree of mineralization of source water is the ionic composition. Though euryhaline organisms are capable of tolerating wide ranges of salinity, they do require certain ions for physiological processes, and the presence of others could be toxic. Diluted seawaters and brines will contain all of the ions present in the source water in proportion to the dilution factor (Boyd *et al.* 2002a). Groundwater will have highly variable ionic compositions resulting from several processes. Groundwater extracted from geologic formations will undergo processes that alter the ionic composition of the water. Drever (1997) summarized these processes:

-*Membrane filtration.* The combination of ion exclusion and pressure causes clays to behave as semi-permeable membranes allowing water to pass through with varying concentrations of ions.

-*Dissolution of halite.* The increase sodium and chloride concentrations attributed to dissolution of marine evaporites.

-*Dolomitization*. The process of calcite ($CaCO_3$) reacting with magnesium to form dolomite ($MgCa(CO_3)_2$) in the presence of magnesium-rich solutions, decreasing Mg^{2+} in solution.

-*Bacterial sulfate reduction.* The reduction of sulfate to hydrogen sulfide through microbial activity.

-*Gypsum (anhydrite) precipitation.* Precipitation of $CaSO_4$, removing both calcium and sulfate from solution.

-*Diagenetic reactions of silicates.* Increased temperatures cause the conversion of smectite minerals to illite and chlorite, resulting in net removal of Mg^{2+} from solution.

-*Cation exchange.* Redistribution of ions between solution and exchange sites on clay minerals affects the concentrations of ions in solution.

Different combinations and the extent of these processes will produce waters with considerable differences in ionic composition. The ionic composition of shallow groundwater mineralized by secondary processes will mainly be influenced by the source of salts: oceanic, irrigation water residue, fertilizers or plant accumulates. Some of the processes listed for formation waters may also alter the ionic composition of these waters, especially cation exchange with soils and microbial activity (Stumm and Morgan 1996).

Brackish Water Utilization and Amendment in the United States

In the United States, all of the previously described water sources are available, however, the cost of handling and transporting seawater or brine for aquaculture production is likely prohibitive. Within the conterminous US, roughly two-thirds of the land is underlain with mineralized groundwater from geologic formations, the composition of which varies due to processes explained above (Feth 1970). Utilization of this groundwater for channel catfish Ictalurus puntatus aquaculture has occurred in Alabama and Mississippi since at least the early 1980s (Boyd and Brown 1984). Though not exploited for the expressed benefit of raising catfish, brackish water has therapeutic value to fish and its elevated chloride concentrations aids in preventing nitrite-toxicity (Schwedler and Tucker 1983). Early direct exploitation of mineralized groundwater for aquaculture was performed by Smith and Lawrence (1990), in an attempt to raise Pacific white shrimp, L. vannamei, in inland Texas. Since then, inland culture, either experimental or commercial, of euryhaline species has expanded to Alabama, Arkansas, Arizona, Florida, as well as others (Samocha et al. 2002, Saoud *et al.* 2003).

The suitability of groundwater sources located in four states; Alabama, Florida, Mississippi, and Texas were investigated by Saoud *et al.* (2003). Findings revealed that the salinity and ionic composition of brackish well waters varied among states and over relatively small areas. Groundwater sources from Alabama investigated in this study were located in the Blackland Prairie region of western Alabama. Many of these sources are known to have anomalous hydrogeochemical composition, with elevated concentrations of chloride (in excess of 3,000 mg/L) and high total dissolved solids, these waters are found mainly within the Tuscaloosa aquifer system, which includes the Coker, Eutaw, and Gordo formations (Cook 1997). Water from these sources are a mixture of saline formation waters and meteoric recharge water, which have undergone several geochemical processes such as membrane filtration, dissolution of halite, dolomitization, and cation exchange (Robinson and Journey 2004, Cook 1993). The analysis of well waters from Alabama by Saoud et al. (2003) revealed and that potassium, magnesium, manganese, and sulfate concentrations were below concentrations expected in seawater diluted to similar salinities. Similar results have been obtained for groundwater sources utilized for brackish water aquaculture in other regions (Boyd and Thunjai 2003, McGraw and Scarpa 2003).

Several ions are essential for osmoregulation and other physiological processes in euryhaline species. Deficiencies of ions — particularly potassium and magnesium — have been shown to lead to poor growth and survival of L. vannamei (Boyd *et al.* 2002b, Davis *et al.* 2005, Roy *et al.* 2007). As a result ionic supplementation with potassium (muriate of potash) and magnesium (sulfate of potash magnesia) fertilizers was investigated, and because of positive results, has become a crucial part of water quality management for inland shrimp farms in Alabama (McNevin *et al.* 2004).

The practice of amending waters to suitable ionic compositions has been confounded by losses of potassium, magnesium, and other ions to the environment. Boyd (2006) revealed that major loss (>50%) of potassium was the result of soil adsorption by bottom soil. Loss of magnesium is believed to be lost by similar soil processes, but the extent of which is not known.

Soils of the Blackland Prairie regions are generally 2:1 expansible clays with smectite mineralogy, high cation exchange capacities, and high concentrations of exchangeable calcium (Boyd 2006, Dixon and Nash 1968). These soils may have a high affinity for magnesium in the soil solution, which could remove the cation from the water column (Bohn *et al.* 1985). Soil adsorption processes likely contribute to the low concentration of magnesium in the groundwater. Possible losses of sulfate are less straightforward, and losses to the environment may be through several pathways, including adsorption by bottom soil and volatilization following reduction of sulfate to hydrogen sulfide under anaerobic conditions.

Salt Losses to the Environment

Though the beneficial use for channel catfish aquaculture and the success of a few operations raising L. vannamei using brackish water in inland areas of Alabama is promising, there are concerns with bringing mineralized water into a freshwater environment. Salinization of pond soils is inevitable, and the potential exists to salinize streams and the surrounding land. Inland brackish water shrimp aquaculture in Thailand resulted in elevated salinity of irrigation canals to a level that would negatively impact the main crops of the region — rice and fruit trees — and lead to the subsequent ban of the practice in areas with freshwater designations (Braaten and Flaherty 2001).

Effluent salinity, conductivity, and TDS criteria or standards currently do not exist in the Alabama, however, the Alabama Department of Environmental Management (ADEM) regulations specify the in-stream chloride concentrations must not exceed 230 mg/L (Benoit 1984). Recent investigations into salt discharges by a marine shrimp farm in the Blackland Prairie region of Alabama revealed chloride concentration in excess of the ADEM standard, with in-stream chloride concentrations as high as 918 mg/L downstream of the operation (Boyd *et al.* 2006). The impacts of these discharges into surrounding streams are not well known, but may result in reduced aquatic species diversity, changes in flora and fauna, direct toxicity, alterations in chemical processes, and loss of habitat (James *et al.* 2003, Horrigan *et al.* 2005, Hart *et al.* 1991).

As a result of releases of salts into the environment, best management practices (BMPs) have been developed to reduce the potential for stream salinization associated with brackish water aquaculture. Recommended BMPs developed include: preparation and evaluation of management plans, avoidance of placing sites on soils with high infiltration rates, minimization of overflow events, conservation and reuse of mineralized water, release of effluents when streams have the capacity to dilute chloride concentrations below 230 mg/L, and monitoring of associated streams (Boyd 2004). Though BMPs were developed for inland shrimp culture, they should apply to any culture activity, such as channel catfish, that could potentially expose the surrounding environment to mineralized waters.

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III. MAGNESIUM BUDGET FOR INLAND BRACKISH WATER SHRIMP PONDS IN ALABAMA

Abstract

A magnesium budget was prepared for a commercial inland brackish water shrimp farm located in the Blackland Prairie region of Alabama for one production cylce. All ponds had previously been used for production and fertilized with magnesium; two ponds (S-5 and S-6) for four previous years, and one pond (N-9) for one previous season. Fertilization with sulfate of potash magnesia ($K_2SO_4 \cdot 2MgSO_4$ or K-Mag®) was applied to these three ponds to obtain a magnesium concentration of 20 mg/L, averaging 1,274 kg Mg^{2+}/ha. Additional inputs of magnesium from sources including groundwater, rainfall, and runoff averaged 441.5 kg/ha. Analysis of a water budget for the ponds using the hydrologic equation suggested losses of magnesium with water outflows totaling 292.6 kg/ha. The remainders of the magnesium inputs were potentially adsorbed by the pond bottom soils. However, increases of exchangeable magnesium in the upper 15-cm layer of pond bottom soils could not account for total inputs of magnesium. The differences in unaccounted magnesium for the ponds are as follows: N-9, 17.9%; S-5, 9.2%; S-6, 4.3%. The decreased uptake of magnesium by older ponds, S-5 and S-6, may indicate that the soils had a diminishing affinity for the cation or an equilibrium concentration was becoming established.

Introduction

The inland culture of marine shrimp utilizing brackish water originated in Thailand and expanded to several countries including the United States (Boyd and Thunjai 2003; Flaherty and Vandergeest 1998). In the United States, Pacific white shrimp, Litopenaeus vannamei, are grown either experimentally or commercially in several states (Saoud *et al.* 2003). The greatest effort has been in the Blackland Prairie region in west-central Alabama. Unlike in Thailand where brine solution from coastal seawater evaporation ponds and freshwater are mixed to obtain brackish waters with ionic proportions similar to seawater, inland culture of marine shrimp in Alabama relies on brackish groundwater with salinities ranging from 2.0 to 9.0 g/L. The brackish water available in Alabama is typically deficient, in relation to seawater at similar salinities, in potassium, magnesium, and sulfate (Boyd and Thunjai 2003; Saoud et al. 2003).

Ionic deficiencies in brackish water have lead to poor growth and survival of marine shrimp (Boyd *et al.* 2002; Atwood *et al*. 2003). Both potassium and magnesium are necessary for several physiological processes (Roy *et al.* 2007). Potassium is crucial to both growth and survival, while magnesium increases survival (Roy *et al*. 2007; Saoud *et al*. 2003; Davis *et al*. 2005; Sowers *et al*. 2005). Ionic supplementation of brackish groundwaters with potassium and magnesium fertilizers such as muriate of potash (KCl) and sulfate of potash magnesia ($K_2SO_4 \cdot 2MgSO_4$ or K-Mag®, IMC Global Inc., Lake Forest, Illinois, USA) has improved both growth and survival of L. vannamei in commercial ponds utilizing brackish groundwater (McNevin *et al*. 2004).

Amending the water quality of brackish water ponds in Alabama with potassium and magnesium fertilizers has been successful, but it has been confounded by losses of applied cations from the water over time. Boyd et al. (2007a,b) made a potassium budget and investigated the fate of potassium fertilizers used in brackish water shrimp culture. They found that over half of the potassium inputs were lost to exchangeable and non-exchangeable soil adsorption processes. The common soils of the Blackland Prairie region of Alabama are 2:1 expansible clays with smectitic mineralogy, typically with cation exchange capacities (CEC) of 15-30 cmol/kg, and capable of adsorbing a large quantity of cations from solution (Dixon and Nash 1968). Thus, these soils also should be capable of removing large amounts of added magnesium from pond waters. The current study was designed to investigate the fate of magnesium inputs to inland brackish water shrimp ponds.

Materials and Methods

This study was conducted in ponds at a commercial, inland shrimp farm located on Alabama Highway 43 about 6 km north of Forkland in the Blackland Prairie region of west-central Alabama. Soils used in constructing the ponds were mainly represented by three official series – Leeper, Sumter, and Trinity. The Leeper (inceptisol) and Trinity (vertisol) series represented on this farm are clay soils with smectitic mineralogy, the Sumter series is a carbonatic (>40% carbonate), inceptisol also containing smectite clay (United States Department of Agriculture, Natural Resources Conservation Service, Soil Survey Staff website). Three embankment ponds were selected: Ponds S-5 and S-6 are 0.97 and 1.42 ha, respectively, were constructed in 2003, and they had been in production for 4 years. Pond N-9 was 1.62 ha, built in 2006, and it had only been in production for 1 year. Average depths, referenced from the top of the standing overflow pipes, for Ponds N-9, S-5, and S-6 were 1.25 m, 1.23 m, and 1.31 m, respectively. The watershed for each pond extended from the waterlines to the centers of the tops of the embankments. When measured with water surfaces 10 cm below the overflow level, watershed areas were as follows: N-9, 3240 m^2; S-5, 2037 m^2; S-6, 3266 m^2.

Ponds were drained for the previous year's harvest and re-filling with brackish groundwater began in late March 2007. Before filling ponds with water, soil samples were collected at nine places in an S-shaped pattern along the length of the bottom of each pond. Samples were collected with a shovel at 5-cm increments to a depth of 15 cm. The nine samples for each depth were combined and thoroughly homogenized to provide a representative, composite sample. The bottom of Pond S-6 was wet, making it impossible to dig to an exact depth with a shovel. In this pond, cores were taken with 5-cm diameter core sample tubes (Wildco Supply Company, Buffalo, New York, USA). The core tube could not be forced more than 10 cm into the heavy clay soil, and only samples of the 0 to 5-cm and 5 to 10-cm layers were obtained for Pond S-6.

Ponds were filled leaving approximately 10 cm of depth from the waterline to the top of overflow pipe to provide storage capacity for rainfall and runoff into the ponds. After initial filling, additional inputs of well water only were added as needed to replace water lost to seepage and evaporation. Ponds were completely drained for harvest in late September and early October. Once ponds bottoms were suitably dry (cracked appearance), another 27 soil samples were gathered as described above – except that it was possible to sample the 10 to 15-cm layer in Pond S-6.

Sampling of the well and pond water began on 6 April and continued monthly until 28 September. On 9 April ponds were treated with K-Mag® to increase magnesium and potassium concentration (Table 1). Ponds were stocked from mid to late May with post larval shrimp at the rate of 30 /m^2. Shrimp were fed a 35% crude protein diet throughout the production cycle, with feed inputs to ponds recorded and feed samples collected for analysis (Table 1).

Water Budget

A method proposed by Boyd (1982) was used to make water budgets for the ponds. This procedure relies upon the basic hydrologic equation:

$$\text{Inflows} = \text{outflows} \pm \Delta \text{ Storage.} \tag{1}$$

Inflows were well water, precipitation, and runoff. Outflows were evaporation, seepage, overflow, and draining for harvest.

Precipitation was measured on the farm using a National Weather Service approved RAINEW 111 tipping bucket rain gauge (Rainwise Inc., Bar Harbor, Maine, USA) fitted with a datalogger. Runoff was calculated using the curve number method (Yoo and Boyd 1994), which estimated that 67% of rain falling on the watersheds would enter the ponds in runoff. Runoff (R) was calculated using the following equation:

$$R = 0.67\,(a/A)P \tag{2}$$

where a = watershed area (m^2), A = pond surface area (m^2), and P = precipitation (cm). Well discharge into ponds could not be directly measured, and was calculated using the following equation:

$$W = (E + S + O + H) - (P + R) \tag{3}$$

where W = water from well, E = evaporation, S = Seepage, O = overflow, H = water depth (measured using USGS style M staff gages).

Evaporation was measured with a class A evaporation pan located on the farm. Evaporation measured in the pan was related to pond evaporation by multiplying it by a factor of 0.81 as determined by Boyd (1985). Seepage was determined during dry periods when there were no inflows of water into the ponds. The difference in the decline in water level and pond evaporation is seepage:

$$S = \Delta H - E. \tag{4}$$

Maintaining water levels 10 cm below overflow pipes limited overflow events, however, if overflows were expected, staff gages were read within a few hours after the storm event to ascertain if the water level exceeded the top of the drain pipe. Overflow was then estimated as:

$$O = H - T \tag{5}$$

where T = elevation of top of drain pipe.

Magnesium Determinations

Feed samples were collected during the production cycle and shrimp samples were collected at harvest. Samples were dried at 60° C, pulverized with mortar and pestle, and ignited in a muffle furnace at 500° C for 8 hr. The ash was taken up in 1N solutions of both nitric and hydrochloric acids (Anonymous 1974). Solutions were filtered through Whatman Number 41 filter paper and brought to 100 mL volume. Magnesium concentrations were determined by flame atomic absorption spectrophotometry using a Varian Model AA240FS (Varian Incorporated, Palo Alto, California, USA).

Rainwater samples were collected from a standard rain gauge twice over the production cycle. Well water and pond water samples were collected monthly. Additional pond water samples were collected as ponds were draining for harvest. Magnesium concentrations in rain, well, and pond water were determined by a method outlined by Boyd and Tucker (1992). An aliquot of each sample was titrated for calcium plus magnesium using 0.01 M ethyelenediamine tetraacetic acid (EDTA) and erichrome black-T indicator. Another aliquot was titrated for calcium using EDTA and muroxide indicator. The difference in the two titrations provided the magnesium concentration.

Soil samples were dried at 60°C in a mechanical convection oven and pulverized with a mechanical soil crusher (Custom Laboratory Equipment, Orange City, Florida, USA) to pass a number 40 US standard sieve. Extraction and determination of magnesium and other basic cations and cation exchange capacity (CEC) were performed using a method designed for soils containing salts, carbonates, or zeolites, as all pond bottom soils had previously been exposed to brackish water and possessed free calcium carbonate (Amrhein and Suarez 1990; Sumner and Miller 1996).

Results and Discussion

Precipitation and class A pan evaporation data collected at the shrimp farm and obtained from a National Weather Service (NWS) gauging station at Demopolis Lock and Dam 30 km southeast of the farm are provided in Table 2. Total rainfall for April through September was slightly higher at the NWS station than at the farm site, and evaporation was higher at the farm site. Rainfall at the NWS station was 12.2 cm below average rainfall for the period, indicating that the period was drier on average than typical years.

Seepage was measured at least twice for each pond during the study. Seepage could be calculated only during periods when no water was being added to the ponds from the well or rainfall. Because weather was drier than normal during the study, ponds required frequent inputs of well water to maintain water levels, limiting the opportunity for seepage determinations. Pond N-9 had the highest seepage rate at 0.72 ± 0.4 cm/d. The seepage rate declined from a high of 1.37 cm/d in early May to 0.401 cm/d in August. The diminished seepage is the result of the discovery and repair of leaks around the drain pipe. Ponds S-5 and S-6 had seepage rates of 0.053 ± 0.02 cm/d and 0.09 ± 0.01 cm/d, respectively.

Well water was the major inflow during the budget cycle (Table 3). Precipitation and runoff recuperated a little more than half of the water lost to evaporation and seepage, except in Pond N-9 were it only accounted for 28 % of evaporation and seepage. The smaller replacement of water losses in Pond N-9 by rainfall and evaporation resulted from the leak around the drain pipe. Harvest effluent was the largest loss of water for Ponds S-5 (57.4%) and S-6 (53.8%) followed by evaporation at 37.9% and 40.2%, respectively. Seepage only accounted for approximately 5% of water loss for Ponds S-5 and S-6. In contrast, Pond N-9 had the greatest loss of water through seepage (38%); losses to harvest effluent and evaporation were 35% and 27%, respectively. Overflow events were not recorded during the water budget cycle because of the paucity of rainfall and especially the lack of large storm events.

Inputs of magnesium are summarized in Tables 1 and 5. As with the water budget, well water was the largest component of the magnesium budget for the ponds. The mean magnesium concentration of the well water was 14.4 mg/L, and with a mean per hectare water input of nearly 19,000 m^3, well input accounted for approximately 62% of magnesium entering ponds. The ponds were fertilized with K-Mag® to obtain a magnesium concentration of 20 mg/L. This is not a large increase over the magnesium concentration in the well water, and therefore, input of magnesium from fertilizer only accounted for about 32% of magnesium input to ponds. The other sources of magnesium — feed, rainfall, and runoff — made up 6% of the total magnesium input.

The greatest loss of magnesium from Ponds S-5 and S-6 was harvest effluents (Mg^{2+} concentration at harvest × the volume of harvest effluent) – it accounted for 92% and 88% of magnesium losses, respectively (Tables 4 and 5). Again, Pond N-9 differed from other ponds because of excessive seepage around the drain pipe. Seepage loss (mean Mg^{2+} concentration × volume of seepage) from Pond N-9 accounted for 55% of the magnesium lost to the environment, while harvest effluent made up 43% of the loss. Shrimp harvested from ponds were the only other accounted loss, and comprised less than 5% of total magnesium loss.

Despite accounting for the different inflows and outflows of water and associated magnesium, the amount of magnesium added to the ponds was considerably higher than the amount lost with outflowing water. On average, 148.9 kg/ha more magnesium was applied to the system than accounted for in outflows. The discrepancy was mainly the result of magnesium adsorption by the bottom soils. The magnesium concentration in the 15-cm layer increased, on average, 99.6 kg/ha during the budget cycle (Table 6).

However, increases in exchangeable magnesium in soils differed between the ponds. The newest pond (N-9) had been in production for one cycle, and it had the largest amount of magnesium unaccounted (95.2 kg/ha). Ponds S-5 and S-6 had four previous production cycles and had 35.5 and 17.5 kg Mg^{2+}/ha unaccounted, respectively. The differences in unaccounted magnesium for the ponds are as follows: N-9, 17.9%; S-5, 9.2%; S-6, 4.3%.

Boyd *et al.* (2007a) performed a potassium budget on ponds at the same farm. In contrast to that study, it is likely that the additional magnesium unaccounted for in the 0 to 15-cm layer of soil may be the result of soil adsorption taking place at depths beyond 15 cm. A large portion of the potassium uptake by bottom soil (Boyd et al. 2007b) was explained by non-exchangeable adsorption of potassium by fixation within the interlayers of the 2:1 layer silicates (1 octahedral sheet between 2 tetrahedral sheets). As the soils are hydrated they expand, and potassium is small enough, hydrated radius 0.330 nm, to fit within the space (> 1.0 nm) between the layered silicates. Theoretically, upon drying the interlayers collapse and retain potassium, dehydrated radius 0.133 nm, against exchange by various extraction solutions (Bohn *et al*. 1985). It is less likely that magnesium follows this same process, as its dehydrated radius of 0.066 nm is much smaller than that of potassium, decreasing the retention capacity of collapsed interlayers for magnesium. Therefore, nearly all of the magnesium should be exchangeable and able to be accounted.

The uptake of magnesium by soil adsorption processes accounted for different proportions of the magnesium budget for each of the ponds. Soil adsorption of magnesium accounted for 21.9%, 15.6%, and 30.5% for ponds N9, S5, and S6 respectively. This may indicate that previous exposures of the pond bottom soils to magnesium does not affect soil adsorption processes. Ponds N9 amd S6 had the highest amounts of magnesium adsorbed by the pond bottom soils (116.5 and 119.8 kg/ha respectively), with N9 in production of one previous production cycle and S6 for four production cycles. The increase uptake of magnesium by these two ponds may result from increased KMag® application to these ponds (Table 5). KMag® though soluble in water takes a considerable amount of time to dissolve completely under typical pond conditions. As KMag® is denser than water; the fertilizer sinks to the bottom, and is in direct contact with the pond bottom soils, which may facilitate the adsorption of magnesium.

The uptake of magnesium through adsorption and cation exchange processes will likely never cease altogether, and could possibly increase under certain circumstances. It has been reported that shifts in cation preferences by vermiculite, a 2:1 moderately expansible clay, can shift from selective retention of calcium to greater selectivity for magnesium under conditions in which calcium carbonate is precipitating and where former marine sediments are contributing soluble salts (Bohn *et al.* 1985). These conditions are met by the pond bottom soils at this site, but the exchangeable calcium to magnesium ratio in the soils is greater than 200:1, limiting the chances of this occurrence.

Seepage and soil adsorption processes are not easily controlled in earthen ponds. Eliminating seepage is possible, but it requires installation of impermeable liners, which are cost prohibitive at the production levels sought by inland shrimp farmers in Alabama. The greatest control that can be exercised to reduce losses of magnesium to the environment would be to recycle harvest effluents as described by Boyd *et al.* (2006). Maintaining adequate magnesium concentrations throughout the production cycle requires routine analysis and re-fertilization as needed. Pre-mixing magnesium fertilizers into a slurry may also help to reduce losses of magnesium directly to the pond bottom soils by keeping the cation in solution, and minimizing direct contact with the soils.

Conclusion

The greatest losses of magnesium from shrimp pond aquaculture are through harvest effluents discharge and soil adsorption processes. The adsorption of magnesium occurs through exchangeable processes, and is not fixed by the soils encountered in this study. Previous exposure to culture conditions and magnesium fertilizers does not seem to limit the amount of magnesium adsorption. Farmer intervention to reduce or eliminate losses of magnesium through effluent discharges is currently the best method for maintaining magnesium concentrations and minimizing the need for further inputs.

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Table 1. Amounts and magnesium concentrations of fertilizer input, feed added and shrimp harvested for three ponds (N-9, S-5, and S-6) at an inland shrimp farm in Alabama.

Variable	Magnesium (%)	N-9 (kg)	S-5 (kg)	S-6 (kg)	Mean ± SD* (kg/ha)
Kmag®	11.0	2,295	1,912	1,092	1,274 ± 128
Feed	0.25	9,178	5.117	10,793	6,092 ± 1,308
Shrimp	0.15	7,376	1,079	6,750	4,019 ± 3,112

*SD = Standard Deviation

Table 2. Precipitation and class A pan evaporation data for the period 1 April to 28 September 2007 at an inland shrimp farm in Alabama and a National Weather Service (NWS) gauging station.*

Month	Precipitation (cm)			Class A pan evaporation (cm)	
	Farm	NWS	Normal	Farm	NWS
April	5.94	8.48	12.49	13.0	14.6
May	0.91	1.55	11.68	20.0	19.3
June	3.99	5.79	9.22	21.7	18.4
July	22.63	17.22	12.65	19.1	20.6
August	8.1	13.49	8.92	21.0	21.3
1-28 September	6.32	5.82	9.63	17.6	14.5
Total	47.89	52.35	64.59	112.4	108.7

*NWS gauging station located approximately 30 km southeast of farm, at Demopolis Lock and Dam.

Table 3. Water budgets for Ponds N-9 S-5, and S-6 at an inland shrimp farm in Alabama.

Variable	N-9		S-5		S-6		Mean Volume ± SD (m^3/ha)
	Depth (cm)	Volume (m^3)	Depth (cm)	Volume (m^3)	Depth (cm)	Volume (m^3)	
Inflows:							
Well	246.7	39,941	168.1	16,323	158.3	22,415	19,103 ± 4846
Precipitation	45.6	7,383	47.9	4,651	47.9	6,783	4,713 ± 133
Runoff	6.4	1,039	6.7	651	7.4	1,048	684 ± 51
Outflows:							
Evaporation	77.9	12,612	85.2	8,273	85.2	12,064	8,277 ± 421
Seepage	108	17,485	8.5	825	14.4	2,039	4,363 ± 5,582
Harvest effluent	100	16,190	129	12,526	114	16,142	11,433 ± 1,450

Table 4. Mean concentrations and standard deviations for magnesium in rainfall, well water, and pond water in Ponds N-9, S-5, and S-6 at an inland shrimp farm in Alabama.

Variable	N-9 (mg/L)	S-5 (mg/L)	S-6 (mg/L)
Rainfall	1.21 ± 0.2	1.21 ± 0.2	1.21 ± 0.2
Well Water	14.4 ± 0.8	14.4 ± 0.8	14.4 ± 0.8
Pond Water			
Mean for crop	16.4 ± 2.4	19.7 ± 2.0	20.7 ± 2.0
At harvest	13.6	20.3	21.1

Table 5. Magnesium budgets for Ponds N-9, S-5, and S-6 at an inland shrimp farm in Alabama.

Variable	N-9 (kg/ha)	S-5 (kg/ha)	S-6 (kg/ha)	Mean ± SD (kg/ha)
Inputs				
Kmag®	156.1	123.9	148.7	142.9 ± 16.8
Well Water	355.2	242.0	228.0	275.1 ± 69.7
Feed	14.1	9.0	27.8	17.0 ± 9.7
Rainfall and Runoff	6.3	6.6	6.7	6.5 ± 0.2
Sum	531.7	381.5	411.2	441.5 ± 78.2
Outputs				
Harvest effluent	136.0	261.9	240.5	212.8 ± 67.4
Seepage	177.1	20.5	26.1	74.6 ± 88.9
Shrimp	6.9	1.6	7.3	5.3 ± 3.1
Sum	320.0	284.0	273.9	292.6 ± 24.2

Table 6. Means and standard deviations for cation exchange capacity, soil magnesium and calcium concentrations in March and November 2008, magnesium uptake by upper 15-cm layer of bottom soil of ponds N-9, S-5, and S-6 at an inland shrimp farm in Alabama.

Variable	N-9	S-5	S-6
Cation Exchange Capacity			
(cmol$_c$/kg)	24.8 ± 6.5	24.0 ± 8.4	23.8 ± 6.8
Exchangeable magnesium (mg/kg):			
March 2007			
Depth: 0 to 5 cm	134.5 ± 57.6	249.4 ± 67.7	223.4 ± 49.6
5 to 10 cm	58.5 ± 10.1	170.0 ± 58.6	124.4± 69.9
10 to 15 cm*	45.0 ± 3.1	112.4 ± 25.7	–
November 2007			
Depth: 0 to 5 cm	172.8 ± 58.0	283.6 ± 14.9	242.7 ± 57.6
5 to 10 cm	80.1 ± 27.1	144.5 ± 16.5	166.4 ± 82.2
10 to 15 cm	44.72 ± 6.5	135.7 ± 84.4	131.6 ± 73.3
Exchangeable calcium (mg/kg):			
March 2007	5,572 ± 1536	6,431.2 ± 1077	4,794 ± 1805
November 2007	4,698 ± 870.1	3,837.9 ± 918.6	5,137 ± 1049
Magnesium uptake by soil:			
(mg/kg)	59.6	32	61.3
(kg/pond)[†]	188.6	60.7	169.7
(kg/ha)	116.5	62.5	119.8

*Calculated using mean bulk density value of 1,303 kg/m^3 obtained from previous research conducted on this farm (Boyd et al. 2007a).

IV. ADSORPTION OF MAGNESIUM BY BOTTOM SOILS IN INLAND, BRACKISH WATER SHRIMP PONDS IN ALABAMA

Abstract

Inland, low-salinity (2.0 - 9.0 g L^{-1}) aquaculture in Alabama faces many challenges. The well waters used are adequate for marine shrimp culture in terms of salinity, but they are imbalanced with respect to ionic composition — especially potassium and magnesium. Inputs of potassium (muriate of potash) and potassium-magnesium sulfate (Kmag®) fertilizers are used to correct these imbalances. Concentrations of potassium and magnesium decline over time following treatment with fertilizers. Potassium is lost from water through adsorption by bottom soils by exchangeable and non-exchangeable processes. The present study was initiated to determine if bottom soils removed magnesium in the same manner as potassium.

A study conducted in laboratory soil-water systems revealed that soils strongly adsorbed magnesium. The rate of adsorption tended to decline over time, indicating the systems were reaching equilibrium. The average loss of magnesium from the tanks was 1,568 mg/tank, with declines in magnesium increasing in tanks with soils with higher cation exchange capacity (mean 24.6 $cmol_c$/kg). Extraction of exchangeable cations from the soils averaged 1,440 mg Mg^{2+}/tank. The discrepancy between magnesium losses and exchangeable magnesium recovery is believed to be due to strong adsorption of

magnesium, as well as some analytical error. Repeated exposures of soils to solutions of 40 mg Mg^{2+}/L failed to saturate exchange sites, but rather maintained equilibrium with other base cations on soil adsorption sites.

Dissolved sulfate resulting from additions of magnesium with magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$) was also monitored over the trial. Though difficulties of analysis occurred, it appears the sulfate is not adsorbed by the pond bottom soils.

Introduction

The Pacific white shrimp, Litopenaeus vannamei, is a euryhaline speices capable of inhabiting waters of a wide range of salinities (Bray *et al.* 1994). This trait has lead to the successful culture of L. vannamei in marine, estuarine, and inland saline water areas. In the United States the inland culture of marine shrimp is performed in Alabama, Arkansas, Arizona, Florida, Texas, and possibly other states (Saoud *et al.* 2003; Samocha *et al*. 2002). The earliest attempt at inland culture of L. vannamei of which we are aware was that of Smith and Lawrence (1990). They used saline groundwater with a salinity of 28 g/L, and promoted this type of aquaculture as a possible new crop in salt-affected areas of Texas. Since then, L. vannamei have been grown successfully in inland areas for either experimental or commercial purposes at salinities as low as 2.0 g/L (Samocha *et al*. 1998, Sowers *et al*. 2005). In Alabama, inland culture of L. vannamei is conducted in the Blackland Prairie region, in earthen ponds supplied with brackish groundwater ranging in salinity from approximately 2 to 9 g/L (McNevin *et al.* 2004).

The suitability of groundwater sources in the Blackland Prairie region of Alabama for inland, shrimp culture was investigated by Saoud *et al.* (2003) and Boyd (2006). Findings revealed that salinity and ionic composition of brackish well waters varied greatly over this relatively small region, and that potassium, magnesium, and sulfate concentrations were below concentrations that would be expected in normal seawater diluted to similar salinities. Deficiencies of these ions — particularly potassium and magnesium — lead to poor growth and survival of L. vannamei (Boyd *et al.* 2002, Davis *et al*. 2005, Roy *et al*. 2007). As a result, ionic supplementation with potassium and magnesium using the fertilizers muriate of potash and sulfate of potash magnesia, respectively, was investigated. These amendments resulted in greater survival and production, and they have become a crucial part of water quality management for inland shrimp farms in Alabama (McNevin *et al*. 2004).

The practice of amending waters to suitable ionic composition has been confounded by losses of potassium and magnesium to the environment. Boyd *et al.* (2007a) revealed that more than 50% of potassium applied in fertilizer was lost from the water through soil adsorption processes. Understanding the impact of soil uptake on ion concentrations in brackish water used for shrimp culture is necessary for recommending cost-effective management procedures. This research focuses on the uptake of magnesium, and to a lesser extent sulfate, by soils representative of the Blackland Prairie region.

Materials and Methods

Three different soils were collected from an inland shrimp farm located near Forkland, Alabama, USA. The soils were visually distinctive and identified by the farmer as being the major soil types contained within the bottoms and embankments of the ponds. The soils had not been in the ponds or exposed to brackish water. Brackish groundwater from the well present on the farm was also collected. The soils and water were brought back to Auburn University, Alabama, USA. The soils were air dried and sieved using a Number 8 US Standard Sieve (2.36 mm). The soils were designated as Soils 1, 2, and 3, and each was randomly assigned to four tanks (Rubbermaid® 68-L tubs, 60.7 cm x 40.4 cm x 41.9 cm). A 5-cm layer of soil was placed in each of the tanks. Four additional tanks did not receive soils, and served as controls. All tanks were then filled with 56 L of brackish groundwater obtained from the farm. A sheet of polyethylene with perforations was placed over the soil to prevent suspension of solids during filling and then carefully removed.

One tank of the four assigned for each treatment and control was randomly chosen not to receive ion supplementation during the trial. The remaining tanks received doses of magnesium sulfate heptahydrate ($MgSO_4{\cdot}7H_2O$) to obtain an initial magnesium concentration of 40 mg/L. These tanks received two additional doses of magnesium sulfate heptahydrate during the trial to re-establish concentrations of 40 mg/L.

All tanks had tight lids to reduce evaporation and were gently and continuously mixed using airstones (suspended to prevent soil agitation) attached by polyethylene tubing to small aquarium pumps. Water samples were collected from each tank; daily for the first week, every second day for the next week, weekly for the next 6 months, and bi-weekly afterwards. The water was collected as 5-mL aliquots, and replaced each time with 5-mL of distilled water to maintain volume.

Subsamples of soils were taken from each tank before filling with water and at the termination of the trial. These samples were dried at 60 C in a mechanical convection oven and dry weights of soils were determined. After drying, soils were pulverized using a mechanical soil crusher (Custom Laboratory Equipment, Orange City, Florida, USA). The soils were then sieved using a Number 40 US Standard sieve; samples for analysis were taken from material that passed through the sieve.

The water samples were analyzed by standard protocol (Clesceri et al. 1998) as follows: magnesium and calcium (flame atomic absorption spectrophotometry using a Varian Model AA240FS, Varian Incorporated, Palo Alto, California, USA); sodium and potassium (flame emission spectrophotometry, Cole-Parmer Model 2655-00 Digital Flame Analyzer, Cole-Parmer Instrument Company, Chicago, Illinois, USA); sulfate (barium chloride turbidimetric method); total alkalinity (sulfuric acid titration to methyl orange endpoint); chloride (mercuric nitrate titration to the diphenylcarbazone endpoint). Salinity was measured using a YSI 556 multi-parameter system equipped with a conductivity-salinity probe (Yellow Springs Instrument Company, Yellow Springs, Ohio,USA). Both soil and water pH readings were measured with a glass combination electrode.

All of the soils contained free calcium carbonate (Boyd *et al*. 2007b) and were exposed to mineralized water during the trial. As a result, cation extraction and cation exchange capacity (CEC) was determined using procedures for soils containing salts and carbonates (Amrhein and Suarez 1990; Sumner and Miller 1996). After a 1:1 mixture of soil and distilled water stood for 24 hr to allow dissolved carbon dioxide to reach equilibrium, soil pH was measured with a glass electrode.

An additional experiment was conducted to measure the magnesium adsorption capacity of the soils. Dried, pulverized, sieved samples of each soil were prepared to make three, 2-g replicates that were placed into 50-mL centrifuge tubes. The tubes were exposed to 20 mL of solution containing 40 mg Mg^{2+}/L and shaken on an oscillating table shaker at 180 rpm for 1 hr. After shaking, the tubes were centrifuged for 10 min at 2,500 rpm, and the solutions decanted for analysis of magnesium concentration using flame atomic absorption spectrophotometry. The soil was retained, exposed to another 20 mL of magnesium solution, and the process repeated. A total of 19 consecutive extractions were made. The uptake of magnesium by the soil at each exposure was determined by subtracting the magnesium concentration of the decanted solution from 40 mg/L.

Results and Discussion

The initial quality of the well water was: pH, 8.1; salinity, 4.1 g/L; magnesium, 15.4 mg/L; and sulfate, 5.3 mg/L. The initial soil pH, CEC, and exchangeable, basic cation concentrations are summarized on Table 1. The soils were alkaline with a mean pH of 7.97. The CEC for the soils were 10.4, 20.9, and 42.5 $cmol_c$/kg for Soils 1, 2, and 3, respectively. Calcium was the main exchangeable cation in all of these soils. These chemical conditions are typical for brackish groundwater and soils of this region (Boyd 2006; Cook 1993; Dixon and Nash 1968).

In the tank study, there was no decline in magnesium concentration in the controls suggesting that loss of magnesium in the tanks containing soil resulted from soil uptake (Fig. 1). During the initial 3 months of the study, magnesium concentrations in the water declined from 40 mg/L to 18 mg/L in tanks containing Soil 3, but only to 27 mg/L in tanks with Soil 1. The decline in magnesium concentration clearly increased with greater soil CEC (Table 1). After 3 months, the magnesium concentrations in the water were increased to 40 mg/L again, but following retreatment, magnesium concentration declined rather slowly, and there was less difference in losses among tanks with the three soils. Six months after retreatment, concentrations in the water were 31 mg/L (Soil 1) and 28 mg/L (Soil 3). The tanks were retreated a second time, and during the following 3 months, magnesium concentration declined only slightly. The mean loss of magnesium from the water over the tanks was 1,568 ± 155 mg/tank (Table 2). The uptake of magnesium was greater for soils of higher CEC, which would be expected as these soils have more adsorption sites for cation exchange. The mean amount of magnesium recovered from the soils exposed to the brackish water containing 40 mg Mg^{2+}/L was 1,440 ± 274 mg/tank.

Magnesium is not likely to be fixed in soils by non-exchange processes as is potassium (Sparks 2000; Boyd *et al.* 2007b). Although magnesium was extracted with a calcium extracting solution 0.2 M in $CaCl_2$ and 0.0125 N in $CaSO_4$, this solution may not have displaced all of the magnesium held on ion exchange sites. This hypothesis is supported by the observation that high concentrations of calcium or other cations will not completely replace magnesium on vermiculite in environments where calcium carbonate is precipitating or where there is a high concentration of salts (Bohn *et al.* 1985). Although soils in the tanks were not vermiculites, they possessed 2:1 smectite mineralogy and high cation exchange capacity similar to vermiculites. In addition, the soils contained free calcium carbonate (Boyd *et al*. 2007b) and the water in the tanks had a high concentration of dissolved salts. A portion of the discrepancy between adsorbed and extractable magnesium, of course, was related to analytical error.

The average weight of soil in the tanks was 5.5 kg/tank. The uptake of magnesium by the soils averaged 1,568 mg/tank (12.89 $\text{cmol}_c\text{Mg}^{2+}$/tank). This is equal to 2.34 $\text{cmol}_c\text{Mg}^{2+}$/kg soil. The average CEC of the soils was 24.6 cmol_c/kg. Thus, only 9.5%, on average, of the CEC was occupied by magnesium following exposure to elevated magnesium concentrations for 12 months. The amount of calcium replaced was measured and it averaged 5.9 cmol_c/kg soil. Thus, calcium was replaced by magnesium and other base cations — sodium and potassium. Magnesium is the principal replacing cation on soils 2 and 3, 90.5% and 80.0% respectively. Only 15% of the calcium exchanged was replaced by magnesium on soil 1, leaving a remainder of the exchange sites to be occupied by sodium and potassium.

Similar trends for the adsorption of magnesium by these soils were observed when they were exposed to multiple consecutive exposures of a magnesium solution (Fig. 2). There was a trend of more rapid uptake of magnesium associated with the soils with higher CEC, but magnesium uptake declined markedly during the first eight to ten exposures. Afterwards, magnesium uptake remained fairly consistent. The same trend was noticed for the uptake of potassium in successive exposures of soil to a potassium solution (Boyd *et al.* 2007b). However, in the case of potassium, uptake was believed to be the result of non-exchange fixation processes in which potassium was held in the interlayers of the clay minerals. Magnesium is likely not fixed by the soils, and the continuous uptake is the result of a rather slow exchange of calcium for magnesium at the cation exchange sites. The soils had a very high exchangeable calcium concentration, and replacement of calcium by magnesium will continue until equilibrium is met. At aqueous concentrations of 20 to 40 mg Mg^{2+}/L, exchange of calcium with magnesium could take considerable time to achieve equilibrium.

The uptake of sulfate by the soils was measured periodically during the tank study. Each application of magnesium sulfate heptahydrate also supplied sulfate. On average, tanks received an input of 11,920 mg (213 mg/L) of sulfate. The mean ± standard deviation for the final concentration of sulfate in all tanks was within this range, 191.9 ± 27.8 mg/L (Fig. 3); therefore these soils do not appear to adsorb sulfate from the water. The sediment was only 5-cm thick in the tanks, and the water was aerated. Thus, the sediment probably remained aerobic. In aquaculture ponds, sediment below a depth of a few millimeters usually is anaerobic (Boyd and Tucker 1998). Under anoxic conditions, sulfur-reducing bacteria such as Desulfovibrio may reduce sulfate to hydrogen sulfide gas. Hydrogen sulfide may react with reduced metals such as ferrous iron or manganous manganese and precipitate as insoluble metallic sulfides. It also is volatile and could be lost to the atmosphere (Boyd 2000).

Fluctuations in sulfate concentrations over time in the tank study (Fig. 3) are likely the result of analytical errors because the barium sulfate turbidity developed in the samples was unstable leading to variability. Nevertheless, the increase in the standard error of the means after each re-application is mainly the result of tanks receiving different amounts of sulfate because of each tank's different requirement for magnesium sulfate to achieve a final concentration of 40 mg Mg^{2+}/L.

The uptake of magnesium by soils representative of the Blackland Prairie region provides insight into management of dissolved magnesium concentration. Soils in new ponds should be expected to adsorb a large amount of dissolved magnesium, and therefore magnesium concentrations should be monitored regularly to determine if additional application of magnesium fertilizers is necessary.

It is significant to notice that equilibrium was reached at a relatively low proportion of magnesium on the exchange sites. A higher concentration of magnesium in the water would favor a higher concentration of magnesium on the exchange sites at equilibrium. The proportions and concentrations of the exchangeable cations in water and on cation exchange sites in bottom soil also would affect the equilibrium magnesium concentration. Thus, pond waters should not be treated with higher concentrations of magnesium than necessary in order to reduce magnesium loss to bottom soil. The minimum, acceptable dissolved magnesium concentration for shrimp culture in low-salinity inland waters is not known.

Over time, soil adsorption will decrease resulting in the need for fewer applications of magnesium, and eventually less need for monitoring. Losses of magnesium to the environment via outflows of water will become the predominant pathway for loss of magnesium, and therefore, management strategies to conserve pond water should be employed. Loss of sulfate does not appear to be the result of soil adsorption processes. Sulfate losses experienced in ponds are the result of other pathways such as seepage, overflow, draining, precipitation as iron or manganese sulfide, or loss to atmosphere as hydrogen sulfide.

Conclusion

Exposure of pond bottom soils to magnesium concentrations of 40 mg/L for 11 months resulted in cation exchanges resulting in the net loss of magnesium from the water column leading to increases in soil magnesium. The shaker study yielded results that were consistent with the tank study, but revealed that an equilibrium of exchange between the water and soil was achieved fairly rapidly and at a low concentration of magnesium (40 mg/L). Higher concentrations of magnesium in the water would likely shift the equilibrium up, resulting in greater losses of magnesium from water to the soil. Soils with higher cation exchange capacities adsorbed more magnesium and took longer to reach equilibrium with dissolved magnesium. Sulfate did not appear to be adsorbed by the soils used in the study.

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Table 1. Composition of three soils from an inland shrimp farm in Alabama.

Variable		Soil 1	Soil 2	Soil 3	Mean ± SD
pH		7.68	8.28	7.96	7.97 ± 0.30
Cation Exchange Capacity	($cmol_c$/kg)	10.4	20.9	42.5	24.6 ± 16.4
Exchangeable calcium	(mg/kg)	2661	4754	8808	5407 ± 3125
	($cmol_c$/kg)	13.2	23.8	44.0	27 ± 15.6
Exchangeable magnesium	(mg/kg)	9.9	17.8	49.7	25.8 ± 21.1
	($cmol_c$/kg)	0.08	0.15	0.41	0.2 ± 0.2
Exchangeable sodium	(mg/kg)	180.3	40.35	58.19	92.9 ± 76.2
	($cmol_c$/kg)	0.7	0.18	0.25	0.4 ± 0.3
Exchangeable potassium	(mg/kg)	35.6	52.6	96.3	61.5 ± 31.3
	($cmol_c$/kg)	0.09	0.13	0.25	0.2 ± 0.1

Table 2. Magnesium loss from water, adsorption by soil, and change in exchangeable calcium over 11 months in laboratory soil-water systems containing 56 L of water.

Variable		Soil			Mean ± SD
		1	2	3	
Soil Weight	(kg/tank)	5.87	5.57	5.16	5.5 ± 0.4
Magnesium loss from water	(mg/Tank)	1405	1584	1713	1568 ± 155
	(mg/L)	25.1	28.3	30.6	28.0 ± 2.8
	(mg/kg)	239.4	284.4	332.6	285.5 ± 46.6
Exchangeable Magnesium adsorption by soil	(mg/tank)	1269	1296	1755	1440 ± 274
	(mg/kg)	216.1	232.6	340.2	263.0 ± 67.4
	(cmol$_c$/kg)	1.8	1.9	2.8	2.2 ± 0.6
Exchangeable calcium:					
Initial	(cmol$_c$/kg)	13.2	23.8	44	27.0 ± 15.6
Final	(cmol$_c$/kg)	1.2	21.7	40.5	21.1 ± 19.7
Difference	(cmol$_c$/kg)	12.0	2.1	3.5	5.9 ± 5.4

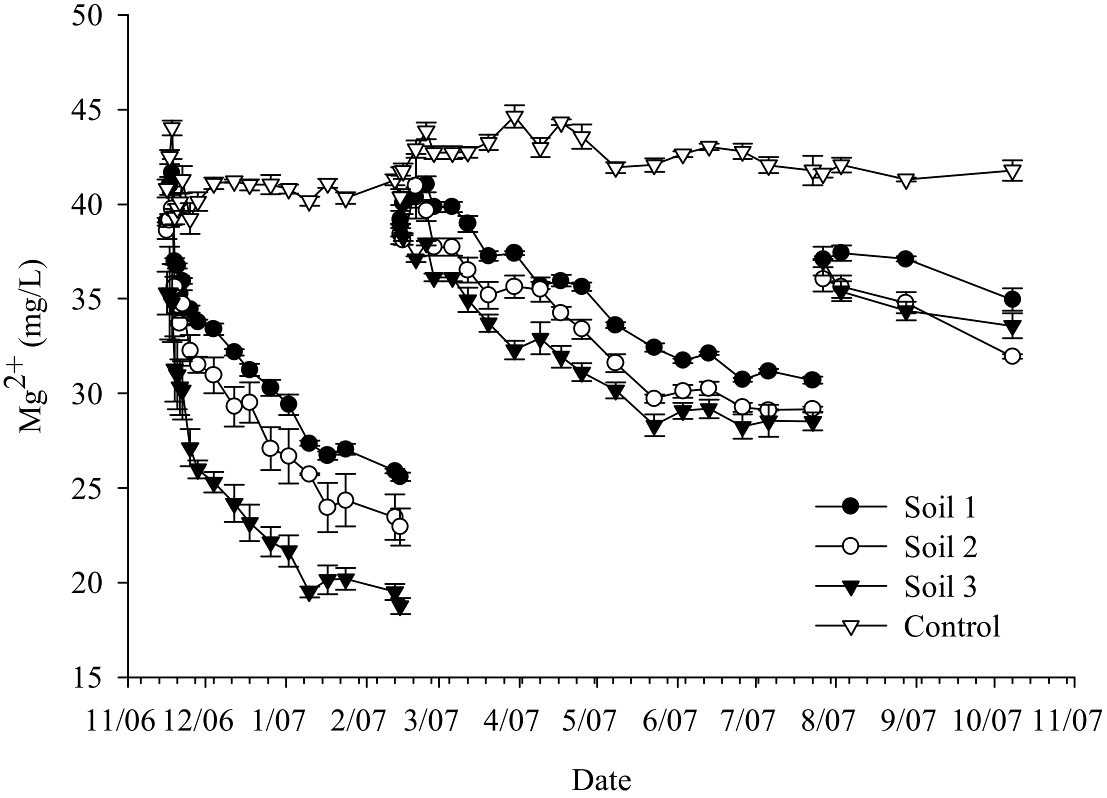

Figure 1. Means and standard errors for declines in magnesium concentrations following three magnesium additions of 40 mg/L each in laboratory systems containing 5-cm layers of original pond soil and filled with water from the source well of an inland shrimp farm in Alabama. Three replicates each of three soils were included in the trial.

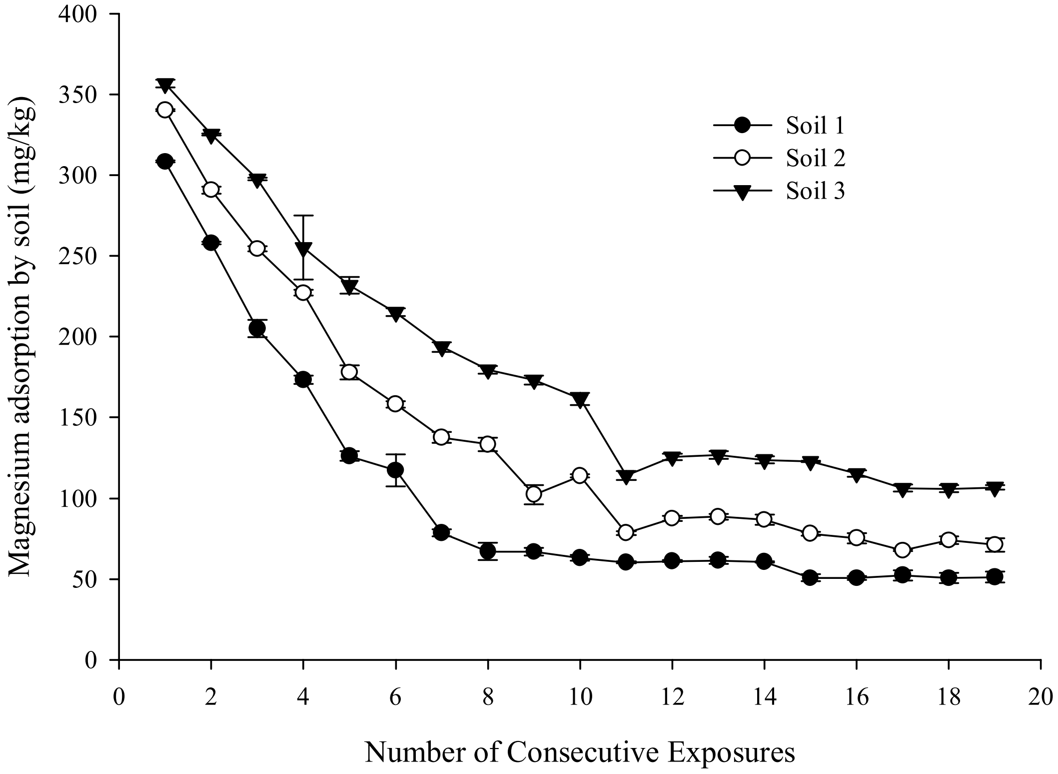

Figure 2. Averages and standard errors for magnesium uptake of three soils following 19 consecutive 1 hour exposures to 20 mL aliquouts of 40mg Mg^{2+}/L (magnesium sulfate heptahydrate and water). Three replicates of each soil were analyzed.

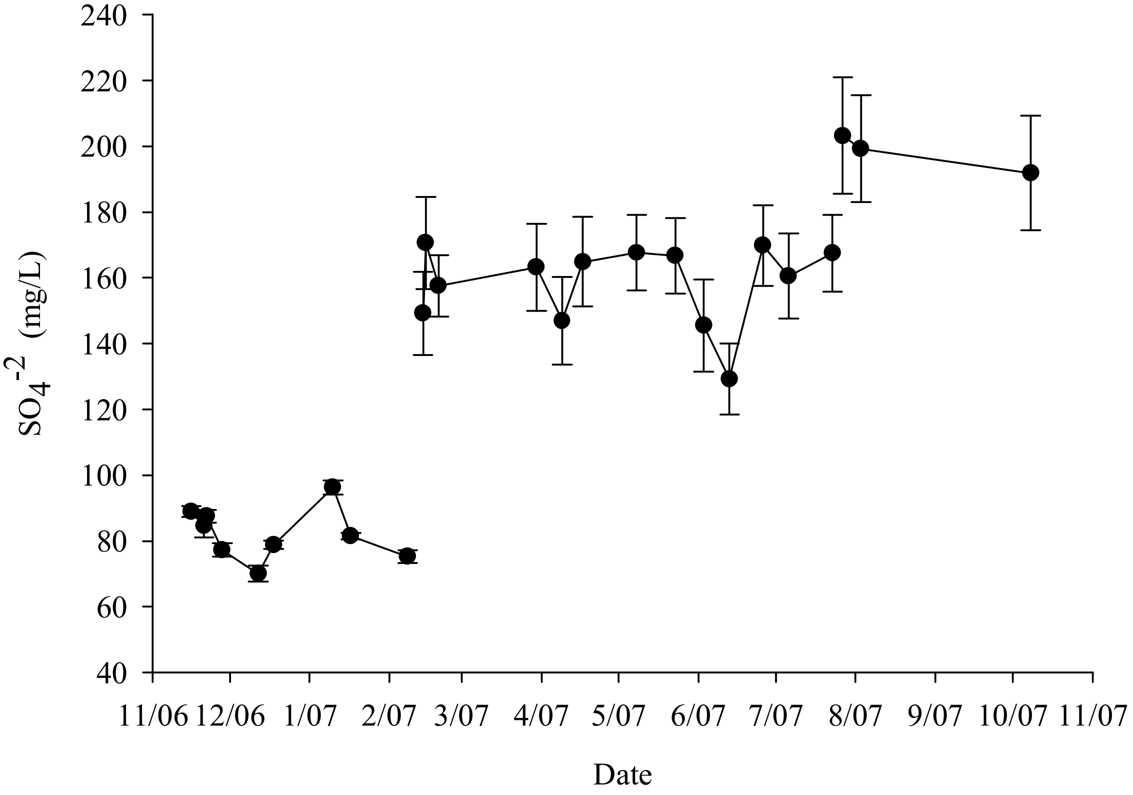

Figure 3. Means and standard errors for sulfate concentrations following three magnesium sulfate additions in laboratory systems containing 5-cm layers of original pond soil and filled with water from the source well of an inland shrimp farm in Alabama. Three replicates each of three soils were included in the trial.

V. STREAM SALINIZATION BY INLAND, BRACKISH WATER AQUACULTURE

Abstract

Commercial aquaculture is performed in several regions of Alabama, with much of the production concentrated in the Blackland Prairie region. Portions of this region have access to aquifers containing brackish water ranging from 1 to 10 g/L, which is currently being utilized to supply water to several pond based aquaculture facilities. The use of low-saline water has been beneficial for the production of Channel catfish, Ictalarus punctatus, and has been found suitable for the culture of marine species such as the Pacific white shrimp, Litopeneaus vannamei. Though beneficial use of this resource has been recognized, the potential for it to salinize local surface waters is unknown. An element of concern associated with the salinization of streams is the chloride ion. The United States Environmental Protection Agency (USEPA) has established an in-stream standard chloride concentration of 230 mg/L for freshwater, which has been adopted by the Alabama Department of Environmental Management (ADEM).

Investigation into stream salinization resulting from low-salinity aquaculture in western Alabama was initiated in June 2006. Eight streams were sampled bi-monthly for salinity, conductivity, and chloride concentrations. Four of the eight streams are

associated with aquaculture production facilities, and receive effluents from these operations. The remaining four streams are located in the area near the aquaculture facilities, but do not receive any effluents or runoff from any facility. The facilities include a catfish fingerling facility (CH), a catfish production facility (RT), a shrimp production facility (TC), and a combined catfish/shrimp production facility (AC). The streams associated with the aquaculture production facilities are sampled at sites both upstream and downstream of the facility. Sampling through April 2007 reveals that the streams associated with the aquaculture facilities have chloride concentrations exceeding 230 mg/L at various times throughout the year. Results indicate that these facilities are contributing to stream salinization.

Introduction

Aquaculture in Alabama has grown from a few hectares in the early 1960s to over 10,000 ha today (Boyd *et al.* 2000, Crews and Chappell 2007). This trend in aquacultural growth is a worldwide phenomenon, and it is the result of increasing demand for fisheries products combined with stagnant or declining natural stocks of most major fisheries species (Boyd 1999). Channel catfish, Ictalurus punctatus, farming is the main form of aquaculture in Alabama. Recent efforts to diversify Alabama aquaculture include the inland culture of Pacific white shrimp, Litopenaeus vannamei, and possibly other marine and brackish water species in brackish water from aquifers. Inland culture of marine shrimp began in Thailand in the early 1990s, and based upon its success, it spread to other countries including China, Ecuador, and the United States (Boyd and Thunjai 2003). Inland, marine shrimp culture in Alabama has utilized brackish water (2 to 10 ppt) from aquifers in the Blackland Prairie region (Saoud *et al.* 2003). Currently, there are approximately 25 ha of water area dedicated to inland, marine shrimp production in Alabama.

Before the introduction of marine shrimp culture to the Blackland Prairie region, saline groundwater has been valued by catfish farmers because of its therapeutic qualities for fish (Boyd *et al.* 2000). High chloride concentrations of these waters prevent nitrite-induced methemoglobinemia — brown-blood disease — through competitive exclusion of nitrite uptake across the gills (Boyd and Tucker 1998). The usage of saline groundwater by the catfish industry in Alabama exceeds that of marine shrimp operations.

Although utilization of brackish water sources are advantageous for catfish farmers and may lead to expansion and diversification of Alabama aquaculture, there are some concerns with bringing water containing high concentrations of total dissolved solids (TDS) to the surface. Salinization of pond soils is inevitable, and salt contamination could spread to nearby streams and surrounding land. Inland, brackish water shrimp aquaculture in Thailand elevated salinity in irrigation canals to a level that could negatively impact the main crops of the region — rice and fruits. The potential for salinization led to a ban on inland, marine shrimp farms in areas designated by provincial governments as freshwater areas (Braaten and Flaherty 2001). Effluent salinity, specific conductance, and TDS criteria or standards currently do not exist in Alabama, however, the Alabama Department of Environmental Management (ADEM) regulations specify that in-stream chloride concentrations must not exceed 230 mg/L as recommended by the United States Environmental Agency USEPA (Benoit 1984). Recent investigations into salt discharges by a marine shrimp farm in the Blackland Prairie region of Alabama revealed chloride concentration in excess of the ADEM standard with in-stream chloride concentration as high as 918 mg/L downstream of the operation (Boyd et al. 2006). The impacts of these discharges on the receiving stream were not measured, but stream salinization has been reported to cause reductions in aquatic species diversity, changes in flora and fauna, direct toxicity, alteration of chemical processes, and loss of habitat (James *et al.* 2003, Horrigan *et al.* 2005, Hart *et al.* 1991).

Stream salinization and negative impacts resulting from it are typically associated with arid climates that experience irrigation-induced salinization and rising water tables. Nevertheless, the studies by Braaten and Flaherty (2001) and Boyd *et al.* (2006) reveal that inland, brackish water aquaculture can cause stream salinization in humid regions. Boyd et al. (2006) recommended best management practices (BMPs) for reducing the risk of salinization. Ponds should be designed, constructed, and operated in a way to minimize seepage, overflow, and harvest effluent. Producers should strive to conserve water through water reuse to reduce effluent volume and salt loss. If water must be discharged, it should be discharged slowly so that a spike in stream salinity may be avoided. The current study was conducted to extend the investigation of effects of inland, brackish water aquaculture on receiving streams to additional locations.

Materials and Methods

Four farms using water from saline aquifers were located in Greene County — a county within the Blackland Prairie region of west-central Alabama. Farm AC is a combined channel catfish and marine shrimp farm, Farm CH is a channel catfish fingerling operation, Farm RT is a channel catfish farm, and Farm TC is a marine shrimp farm. Streams located near farms were identified, and sites immediately upstream and downstream of the facilities were selected for sampling. Three streams in Greene County not receiving discharge of aquaculture activities also were selected for sampling to provide background chloride concentrations in local streams.

Sampling began in June 2006 and continued every two weeks (monthly for October, November and December of 2006) until November 2007 — if water was present in streams. Additional sampling sites were added 100 m upstream of facilities TC and AC in January and March 2007, respectively, and sampled every two weeks until November of 2007. Salinity and conductivity measurements were obtained in the field using a YSI 556 multiprobe system (Yellow Springs Instrument Co., Yellow Springs, OH, USA). Water samples were collected and analyzed for chloride concentration by titration with standard mercuric nitrate to the diphenylcarbazone endpoint (Clesceri *et al.* 1998).

Results and Discussion

The existence of highly mineralized groundwater in inland areas is not an uncommon phenomenon. The salinity of this water may vary from place to place, and its ionic composition also may vary. The ionic composition of well water is dependant upon many processes including: the presence and composition of formation water, infiltration of meteoric water, dissolution and precipitation of minerals and salts, ion exchange interactions between clay minerals, as well as other biological, chemical and physical processes (Drever 1997). Different combinations of these processes and the physical geology of aquifers may lead to distinct variations in groundwater composition over relatively small areas. The area of interest (Greene County, 1,709 km^2) overlies several geologic formations containing saline water with chloride concentrations ranging form 368 to 3,700 mg/L (Boyd *et al.* 2006, Cook 1993). The four aquaculture facilities included in this study have chloride concentrations above the mean for Greene County, and range from 1,761 to 2,977 mg Cl$^-$/L (Table 1). Effluents from these facilities have the potential to increase chloride concentrations in nearby streams depending mainly upon the volume of water discharged into streams and the quantity of water present in streams to dilute high chloride concentrations.

Information on the number of samples collected at each site and the number of samples that were in excess of the ADEM stream chloride standard of 230 mg/L are provided (Table 2). Each of the four farm sites (AC, CH, RT, and TC) had downstream samples exceeding this criterion. The three control sites did not have any incidence of chloride concentrations above 230 mg Cl$^-$/L.

Farm AC, which discharges into McConnico Creek, had the highest number, as well as percentage, of both upstream and downstream samples exceeding 230 mg Cl$^-$/L (Table 2, Fig. 1). Expansion of sampling 100 m upstream confirmed that the in-stream chloride concentration upstream of site AC was often above 230 mg/L (Fig. 1). Tracing chloride concentrations upstream revealed that the source of high chloride concentration was an abandoned aquaculture facility supplied by well water of similar composition as site AC. Ponds of the abandoned facility still contained saline water and possibly contributed to the elevated concentrations of chloride at the initial upstream sampling site. However, salinization likely resulted from seepage, because pond water levels were below overflow pipe heights, and ponds were not drained. In early autumn, chloride concentrations 100 m above the initial upstream sampling site dropped below 230 mg/L, while they remained above this level at the initial site. One possible explanation for this is that rainfall diluted water seeping from ponds at the abandoned farm. Another possibility is that elevated chloride concentration at the initial upstream site originated from either seepage or backflow of effluents from Farm AC. Further expansion of sampling points within McConnico Creek was not possible as it dried up above the abandoned farm during the remainder of this study.

Farm CH is a catfish fingerling facility with embankment ponds; it is built on a slope and discharges into White Creek that enters the northern edge of the farm and exits to the south. Over half (53.6%) of the downstream samples had chloride concentrations in excess of 230 mg/L (Table 2, Fig 2). Unlike Farm AC, the upstream site remained below the acceptable chloride concentration throughout the study, indicating that elevated chloride concentrations downstream were the direct result of brackish water input from the farm. Pond effluents often were observed being discharged directly into the stream, and this occurred most frequently while the flow-through hatchery was in operation. Best management practices (BMPs) focusing on better water management and conservation could greatly reduce discharge of brackish water into the nearby creek from this facility, and therefore aide in the prevention of stream salinization (Boyd *et al.* 2006). Seepage is an additional source of mineralized water, and this was observed during periods with no effluent discharge as water collecting into the drainage canal and flowing into the creek.

Farm RT is located south of Eutaw, Alabama, in Greene County. Stephens Creek enters the northwestern edge of the facility and exits the southern edge. Results were similar to those observed at site CH; no samples above acceptable chloride levels were recorded at the upstream sampling location, while over half (70.4%) of the downstream samples were above the 230 mg Cl^-/L concentration (Table 2, Fig 3.). However, overflow and direct discharge into the stream from the facility was not observed during the study. Brackish water likely enters the stream through seepage from ponds as it flows between the northern and southern portions of the facility coming into close contact with the ponds. Implementation of BMPs would not likely reduce the salinization of the stream, and the installation of impermeable liners would be cost prohibitive. Sites such as these provide insight into a design feature for future sites. A buffer zone should be left between the ponds and the stream to limit inputs from seepage.

The fourth site, Farm TC, is located in Forkland, Alabama, and is the only operation in this study solely producing marine shrimp. The facility consists entirely of embankment ponds filled with brackish well water. Needham Creek enters the property from the north and exits the eastern edge. Samples collected during the study exceeded the in-stream standard of 230 mg Cl^-/L concentration over a majority of the sampling dates at both the upstream and downstream sites (Table 2, Fig. 4).

As with site AC, an additional upstream sampling site 100 m above the initial sampling site was established, and sampling began at this site on January 26, 2007 to assess the chloride concentration of the stream water entering the farm area. Few samples were collected at the uppermost site because drought conditions caused the stream to be dry above the initial upstream site on most sampling dates. All samples collected 100 m above the initial upstream site were below the 230 mg Cl^-/L limit, indicating that water entering the farm was not highly mineralized (Table 2, Fig. 4). Of the five samples collected from this site, four had chloride concentrations below the

ADEM standard at both the upstream and downstream sampling sites. The inflow of water from above the farm area — derived from runoff resulting from rainfall events — diluted the water and brought it within the acceptable range of chloride concentration. During dry periods when the upper portions of Needham Creek became dry, seepage from ponds were the main source of water, resulting in elevated chloride concentrations from the farm area to points down stream.

Utilization of saline groundwater for aquaculture elevated chlorides well beyond the ADEM standard of 230 mg/L over the course of the study in all receiving streams. Control streams, unassociated with aquaculture, remained well below the ADEM standard with a mean chloride concentration of 21.1 mg/L, and a maximum concentration of 36.3 mg/L (Fig. 5). The primary reason for salinization of streams by aquaculture facilities in this study tends to be seepage of saline water from ponds. A previous study (Boyd *et al.* 2006) at Farm TC found that a small stream originating on the farm and passing through the pond area had chloride concentrations above 230 mg/L because of ponds seeping into it. Although Needham Creek, the larger stream passing by the facility, exhibited elevated chloride concentration during dry weather, concentrations exceeded 230 mg/L only when effluents were discharged during shrimp harvests. The current study took place during 2 years with drought conditions classified as exceptional (United States Drought Monitor website 2008) – 50-year, return period. This resulted in reduced or no flow conditions in streams affected by discharge from facilities using saline groundwater. The lack of rain prevented dilution of mineralized water and dry conditions further increased salinities in both ponds and streams through evaporative loss of water.

Dry conditions reduced or eliminated the streams capacity to dilute inputs of brackish water. The only period with somewhat normal rainfall during this study was November 2006 to January 2007. The effects of which are noticeable at all of the farms, as chloride concentrations dropped to concentrations below the ADEM limit (Figs. 1-4). This drop indicates that the capacity of streams to dilute chloride returns rather rapidly with normal precipitation. Management and policy for these streams is complicated and may depend how these streams are classified in terms of temporal designations; perennial, intermittent, or ephemeral. Portions of many of the evaluated streams dried several times over the course of the study; however, streams appear to be perennial under average rainfall conditions. Policies regarding streams such as these may need to consider extreme conditions such as severe or exceptional droughts.

The implementation of BMPs (Boyd *et al*. 2006), to limit direct discharges of effluents into streams would not prevent salinization during periods of unusually low rainfall because of chloride input from seepage. Braaten and Flaherty (2001) made a salt budget for inland shrimp farms in Thailand and found that 38% of salt losses from ponds were from lateral seepage, and in zero discharge systems nearly half of the salt content in pond was lost to the environment. Boyd et al (2006) found that seepage accounted for nearly 24% of losses at Farm TC. The difference in seepage between the two studies is likely the result of ponds at Farm TC being constructed in an area where soils have a high concentration of expansible clay that resists infiltration of water (Yoo and Boyd 1994). The only farm in this study that would benefit from implementation of BMPs, under drought conditions, is Farm CH, where control of effluents would be effective, because the relatively large distance between the farm and the stream, and limited inputs from seepage.

Seepage in ponds typically results from: permeable soils or layers of sand or gravel, shallow soils underlain by fractured bedrock or solution cavities, soils with soluble minerals that dissolve to form voids, and sub-optimal methods of construction (Boyd 1987). Seepage may occur within all 180° from the pond surfaces down, but can be broken down into vertical and horizontal (lateral) components. The amount of seepage of embankment ponds is further influenced by the hydraulic conductivity of the construction materials. Soils used in the construction of ponds in the current area of investigation typically have low rates of hydraulic conductivity, as they have high clay content. Seepage therefore could be dominated by lateral seepage through constructed portions of ponds, and likely the result of inadequate compaction of pond banks, improper installation of drains, or the absence of anti-seep collars around drains.

However, pond seepage may not be a persistent problem, and may diminish over time. Pond seepage was not measured for the current study, but previous work has measured seepage in ponds at the TC farm site. Boyd (2006) found the seepage rate at 0.51 cm/day in 2003, recent work measured the seepage rate at 0.053 cm/day in 2007 (Chapter 1). As ponds age they may become less permeable, resulting in decreased seepage and losses of salts to the environment. This may be the result of exposure to brackish water, which with high sodium chloride concentrations may disperse once flocculated soils, thereby reducing seepage (van Olphen 1977). New ponds will not have had time to benefit from this process, but may be exposed to applications of dispersing agents such as tetrasodium pyrophosphate to help seal the ponds (Yoo and Boyd 1994). However, actively dispersing soils may not be cost effective.

Conclusions

Utilization of brackish aquifer water for aquaculture has resulted in elevated chloride concentrations in local streams. Both catfish and marine shrimp operations in the Blackland Prairie region of western Alabama lose salts to the environment throughout the year and cause chloride concentrations to exceed the USEPA standard of 230 mg Cl^-/L in streams associated with culture facilities. During the course of this study dry conditions prevailed, reaching exceptional drought status at times. The drier conditions eliminated effluent outputs from overflow events, reducing the possible pathway of salt loss from ponds to seepage. Loss due to lateral seepage is believed to dominate this pathway. Despite low permeability of the soils contained within the levees, seepage may still occur as a result of inadequate compaction of pond banks, improper installation of drains, or the absence of anti-seep collars around drains.

Current best management practices (BMPs) are not likely to mitigate the current situation. This study indicates the need for proper site selection, away from nearby streams, and a need for strict construction standards for ponds utilizing brackish water. The capacity of streams to dilute chloride concentrations to levels below the USEPA standard appears adequate during normal moisture conditions, with prolonged dry conditions reducing or eliminating this capacity.

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Table 1. Salinity, conductivity, and chloride concentrations from wells supplying water for brackish water aquaculture in Greene County, Alabama

Farm	Salinity (g/L)	Conductivity (µS)	Chloride (mg/l)	Chloride (mg/L) Brackish water*
AC	5.2	9135	2977	2783
CH	3.6	6620	2124	1927
RT	3.1	5700	2234	1659
TC	3.2	5833	1761	1713

*Expected chloride concentrations for brackish water of similar salinity

Table 2. Number of samples collected from streams associated with brackish water aquaculture, controls, and the number and percentages of samples of each exceeding 230 mg Cl^-/L.

Site	Number of samples	Number of samples exceeding 230 mg Cl^-/L	Percentage of samples exceeding 230 mg Cl^-/L
AC			
Upstream	29	23	79.3
Upstream + 100m	13	10	76.9
Downstream	27	23	85.2
CH			
Upstream	28	0	0.0
Downstream	28	15	53.6
RT			
Upstream	26	0	0.0
Downstream	27	19	70.4
TC			
Upstream	19	12	63.2
Upstream + 100m	5	0	0.0
Downstream	27	20	74.1
CONTROLS			
South Forkland	21	0	0.0
South McConnico	24	0	0.0
West Forkland	23	0	0.0

Figure 1. Upstream and downstream chloride concentrations for site AC from June 2006 through November 2007. Breaks in data indicate sampling dates when streams were dry.

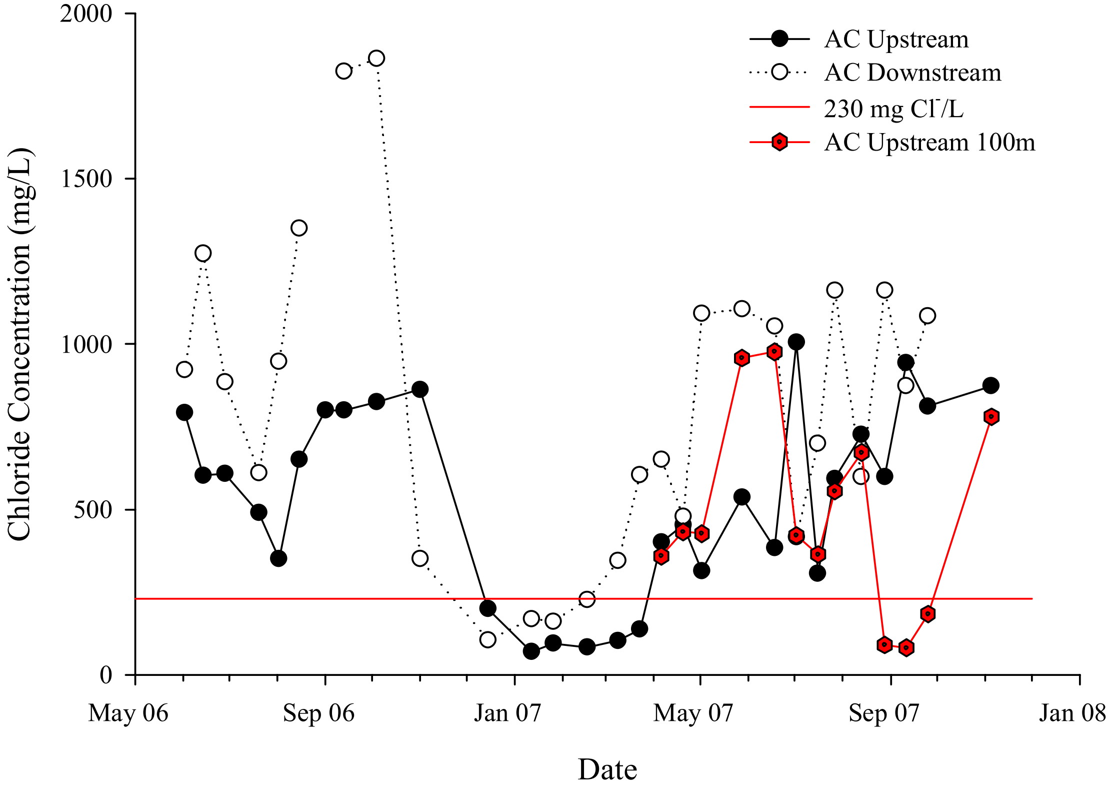


Figure 2. Upstream and downstream chloride concentrations for site CH from June 2006 through November 2007. Breaks in data indicate sampling dates when streams were dry.

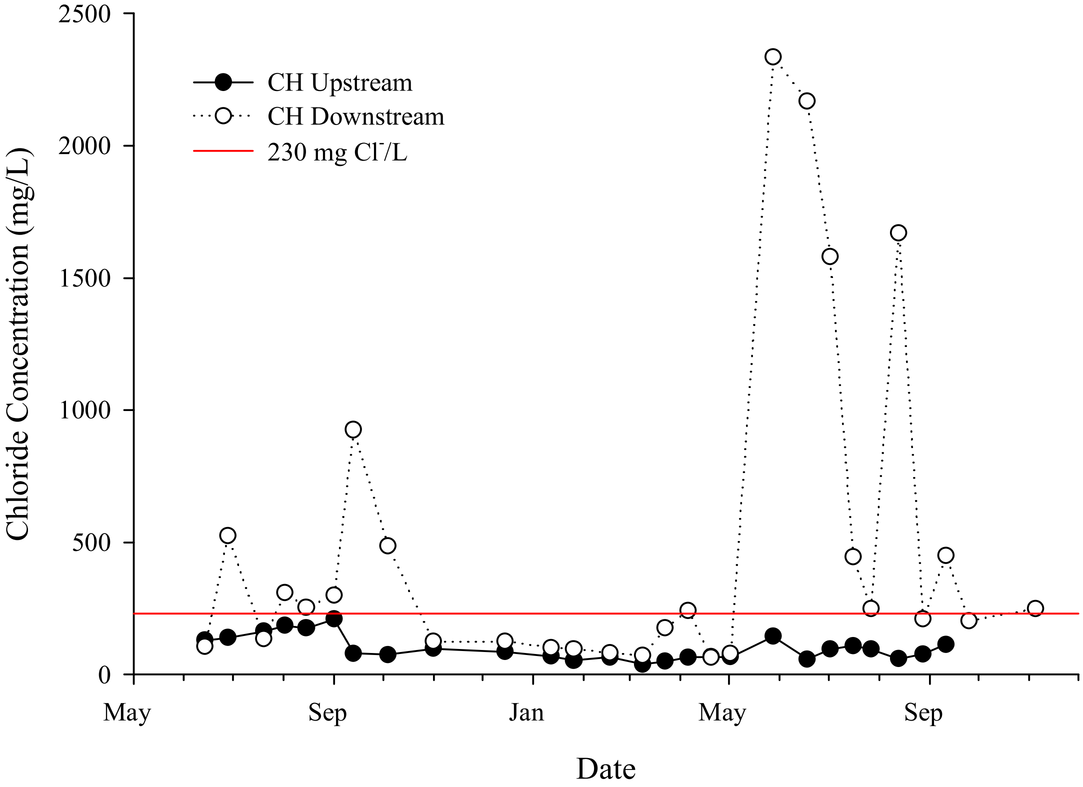


Figure 3. Upstream and downstream chloride concentrations for site RT from June 2006 through November 2007. Breaks in data indicate sampling dates when streams were dry.

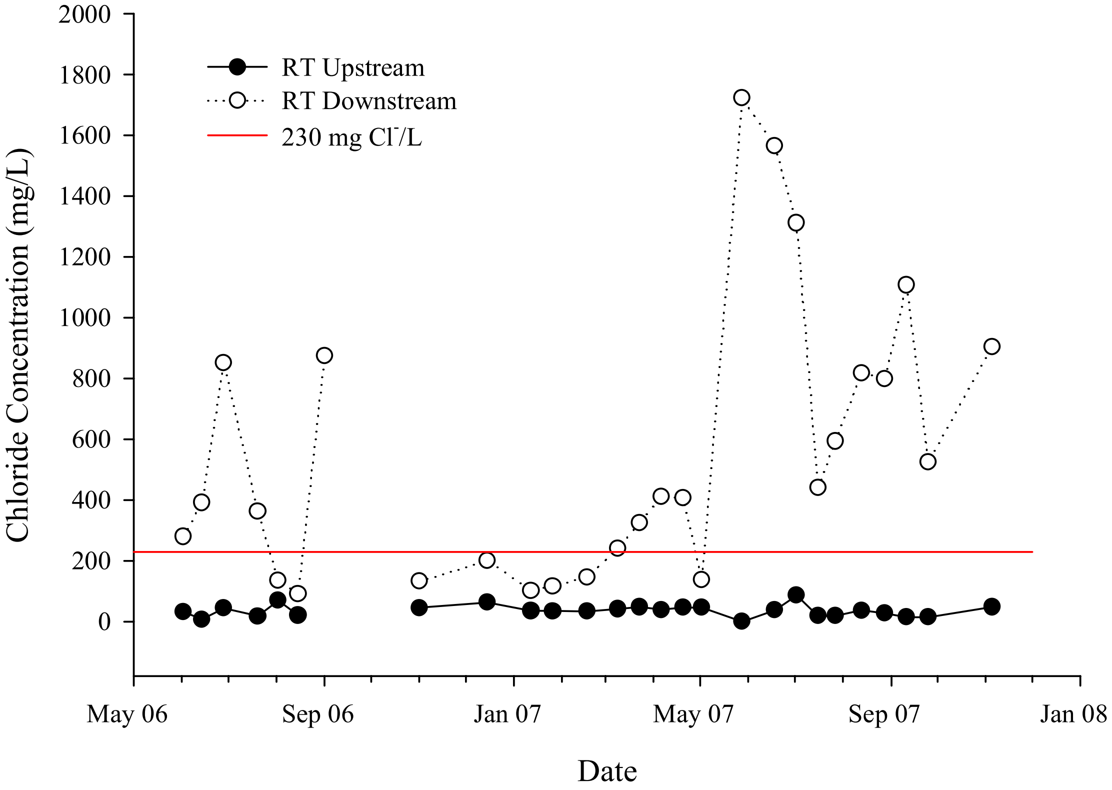


Figure 4. Upstream and downstream chloride concentrations for site TC from June 2006 through November 2007. Breaks in data indicate sampling dates when streams were dry.

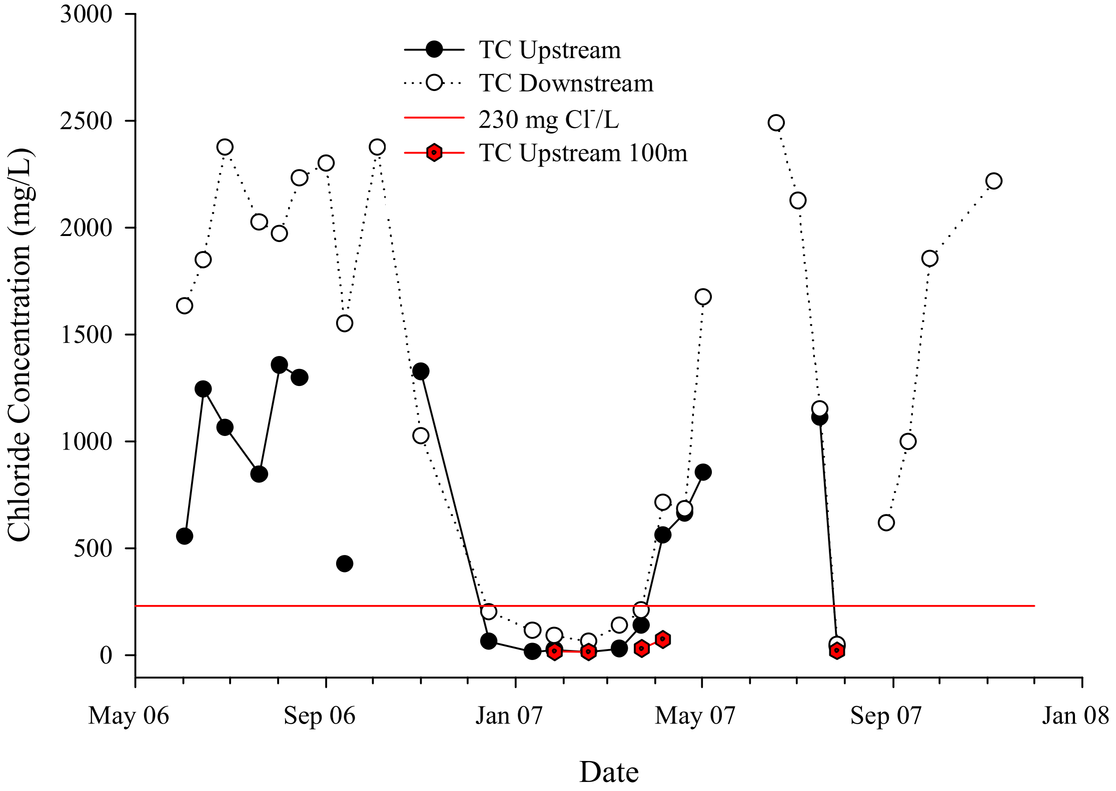
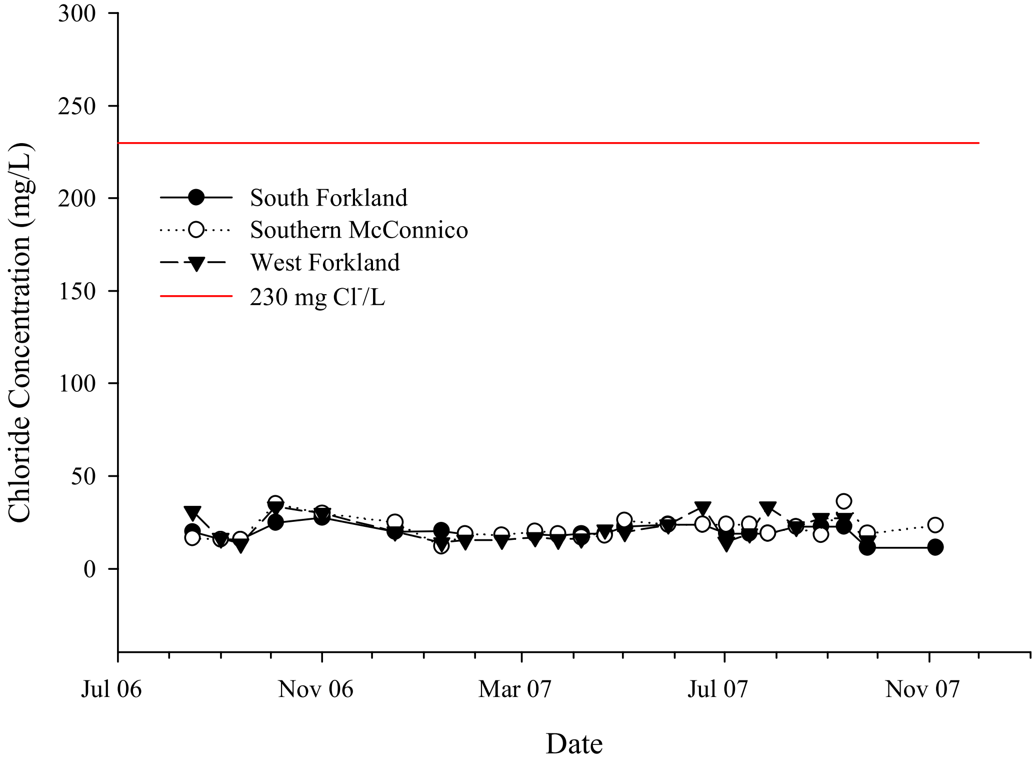


Figure 5. Chloride concentrations for control sites from August 2006 through November 2007. Breaks in data indicate sampling dates when streams were dry



VI. CONCLUSIONS

Brackish water aquaculture represents a beneficial use of water resources that are not suitable for typical exploitation. Utilization of brackish water in Blackland Prairie region of western Alabama for catfish culture provides a measure of prevention against methemoglobinemia, and offers the opportunity for diversification of the aquaculture industry in the region through the inland culture of marine species — mainly Pacific white shrimp, Litopenaeous vannamei (Boyd *et al.* 2000). However, the utilization of brackish groundwater also presents some challenges and may have some negative environmental impacts.

Present challenges to brackish water aquaculture include ionic deficiencies — in relation to diluted seawater — that are exacerbated by losses of necessary cations to the environment, including pond sediments. Ionic deficiencies in available brackish water sources have lead to poor growth and survival of marine shrimp (Boyd *et al.* 2002). Ionic supplementation of brackish groundwaters with potassium and magnesium fertilizers such as muriate of potash (KCl) and sulfate of potash magnesia ($K_2SO_4 \cdot 2MgSO_4$ or K-Mag®, IMC Global Inc., Lake Forest, Illinois, USA) has improved both growth and survival of L. vannamei in commercial ponds utilizing brackish groundwater (McNevin et al. 2004). Amending the water quality of brackish water ponds in Alabama with potassium and magnesium fertilizers has been successful, but it has been confounded by losses of applied cations from the water over time. Boyd *et al.* (2007) made a potassium budget and investigated the fate of potassium fertilizers used in brackish water shrimp culture. They found that over half of the potassium inputs were lost to exchangeable and non-exchangeable soil adsorption processes. The preceding work focused on magnesium, and to a lesser extent sulfate, uptake under similar conditions.

The main environmental impact of concern is that of salinization of streams and soils. Salinization of pond soils is inevitable, and salt contamination could spread to nearby streams and surrounding land. Inland, brackish water shrimp aquaculture in Thailand elevated salinity in irrigation canals to a level that could negatively impact the main crops of the region – rice and fruits. The potential for salinization led to a ban on inland, marine shrimp farms in areas designated by provincial governments as freshwater areas (Braaten and Flaherty 2001). The preceding work investigated the potential salinization of streams associated with brackish water aquaculture in western Alabama. Sites investigated included both marine shrimp and catfish operations utilizing brackish groundwater.

Magnesium Budget for Inland Brackish Water Shrimp Ponds in Alabama

The results of this study investigating losses of magnesium added to amend deficiencies found that the greatest losses were through the discharge of effluents during harvest. Similar to results of potassium uptake, magnesium was also adsorbed by the soils, but appears to be through exchangeable processes and accounted for mean losses of 22.7 ± 7.5%. Previous exposure of ponds to magnesium via well water and fertilizer inputs appears not to affect the amount of magnesium adsorbed. Unaccounted losses of magnesium are believed to have been adsorbed below the 15 cm depth of soil sampled for this study. Prevention of losses of magnesium to the environment through harvest effluent discharge could immediately help farmers retain magnesium in waters and lessen the need for fertilizer inputs.

Adsorption of Magnesium by Bottom Soils in Inland, Brackish Water Shrimp Ponds in Alabama

Tank and multiple exposure studies of soils representative of brackish water shrimp ponds in the Blackland Prairie region of western Alabama revealed several insights into the adsorption process of these soils. The tank study utilized soils with cation exchange capacities (CEC) of 10.4, 20.9, and 42.5 cmol_c/kg. As CEC increased the amount of magnesium lost from the water column increased. The average loss of magnesium was 1,568 mg/tank, of which 1,440 mg/tank was recovered using cation exchange techniques. Discrepancies of magnesium loss and recovery were likely the result of failure to displace all of the magnesium adsorbed by the soil with the extracting solution — 2.0 M in $CaCl_2$. Calcium was the principal cation replaced by cations present in the tank water — magnesium, potassium, and sodium. Magnesium was the principal replacing cation on two of the soils, accounting for 80 - 90.5% of calcium exchange. Magnesium only replaced 15% of exchanged calcium in the soil with the lowest CEC (10.4 cmol_c/kg). After 12 months of exposure to high concentrations of magnesium, only 9.5% of the soil CEC was occupied by magnesium on average. The rate of uptake of magnesium by the soils decreased overtime, suggesting movement towards and establishment of equilibrium.

Multiple exposures of the same soils revealed that equilibrium between magnesium concentrations in the water column and the soil is reached at a relatively low proportion of magnesium on the exchange sites. Higher concentrations of magnesium in the water would favor a higher concentration of magnesium on the exchange sites at equilibrium. Therefore it is recommended to treat ponds with the minimal concentration of magnesium to prevent unnecessary losses of magnesium; however, the minimal concentration is not yet known for marine shrimp culture. Multiple exposures also revealed that the soils with higher CECs have a greater affinity for adsorbing magnesium.

Stream Salinization by Inland, Brackish Water Aquaculture

Utilization of brackish aquifer water for aquaculture has resulted in elevated chloride concentrations in local streams. Both catfish and marine shrimp operations in the Blackland Prairie region of western Alabama lose salts to the environment throughout the year and cause chloride concentrations to exceed the USEPA standard of 230 mg Cl^-/L in streams associated with culture facilities. During the course of this study dry conditions prevailed, reaching exceptional drought status at times. The drier conditions eliminated effluent outputs from overflow events, reducing the possible pathway of salt loss from ponds to seepage. Loss due to lateral seepage is believed to dominate this pathway. Despite low permeability of the soils contained within the levees, seepage may still occur as a result of inadequate compaction of pond banks, improper installation of drains, or the absence of anti-seep collars around drains.

Current best management practices (BMPs) are not likely to mitigate the current situation. This study indicates the need for proper site selection, away from nearby streams, and a need for strict construction standards for ponds utilizing brackish water. The capacity of streams to dilute chloride concentrations to levels below the USEPA standard appears adequate during normal moisture conditions, with prolonged dry conditions reducing or eliminating this capacity.

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