CLIMATE CHANGE – GROUNDWATER INTERACTIONS IN A MIDWESTERN US AGRICULTURAL SYSTEM AND A PERI-URBAN SYSTEM IN BOTSWANA

By

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A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Integrative Biology—Doctor of Philosophy

2018

ABSTRACT

CLIMATE CHANGE-GROUNDWATER INTERACTIONS IN A MIDWESTERN US AGRICULTURAL SYSTEM AND A PERI-URBAN SYSTEM IN BOTSWANA

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Theory predicts that groundwater-fed irrigation can contribute to greenhouse gas emissions and that climate change can alter groundwater quality and quantity. But few studies have tested or documented either of these concepts, which are of global importance to food and water security. For this dissertation, I have conducted two socio-ecological investigations: one in the Midwestern US where I found that groundwater use is augmenting anthropogenic greenhouse gas emissions; and the other in Ramotswa, Botswana where I found that climate change is exacerbating threats to groundwater quality.

The first socio-ecological system is Midwestern agriculture. Midwestern corn grain sales are > $40 billion a year, which is 60% of the US corn grain sales. Maintaining such substantial crop yields depends on nitrogen fertilizer, its associated lime requirements, and, in some places, irrigation. Both lime ($CaCO_3$ or $CaMg(CO_3)_2$) and groundwater bicarbonate (HCO_3^-) alkalinity (via irrigation) are inorganic carbon (C) inputs to agricultural soils. The fate of this C and whether/how it contributes to climate change is not well understood. I conducted a field experiment at the Michigan State University Kellogg Biological Station (KBS) Long Term Ecological Research (LTER) site to investigate the fate of these inorganic C inputs in a no-till corn-soybean-wheat rotational cropping system. In Chapter 1, I show that irrigated plots had significantly less CO_2 emissions from inorganic C reactions than rainfed plots, possibly due to increased carbonic acid weathering.

I used results from Chapter 1 along with measurements of several other components to assess the global warming impact of irrigation. These irrigation impacts are important to understand, because irrigated acreage in the Midwest is expected to increase in coming decades with less rainfall and more dry days in the summer. Though irrigation can help farms adapt to climate change, I found that its associated greenhouse gas emissions put it in a pernicious positive feedback loop with climate change. In Chapter 2, I demonstrate that no-till management flips from net C storage without irrigation to net C emissions with irrigation. Irrigation increased soil organic and inorganic C storage but not by as much as it increased fossil fuel use, soil nitrous oxide emissions, and nitrous oxide and carbon dioxide emissions from the groundwater itself.

In order to minimize greenhouse gas emissions associated with irrigation or to encourage practices that induce greater C sequestration, we need to understand how producers using irrigation make decisions. In Chapter 3, I describe results from focus groups with irrigators and how their decision making process fits in a social theory context.

The second socio-ecological system is a peri-urban town in Botswana, an arid to semi-arid country in southern Africa. The town is Ramotswa, and it is undergoing rapid urbanization and population growth. In Chapter 4, I demonstrate how climate change and social systems are compounding nitrate pollution of the Ramotswa aquifer. My results suggest that human waste via pit latrines are the source of contamination and that *in situ* denitrification could be used to remediate the groundwater.

This dissertation is dedicated to Bowie-Wan Kenobi, a dog and an old friend.
Thank you for your companionship, patience, and, above all, *joie de vivre*.

ACKNOWLEDGEMENTS

I am extremely grateful for stipend support from the US National Science Foundation (NSF) through the Graduate Research Fellowship Program (DGE-1424871) and the Graduate STEM Fellows in K-12 Education award to the Kellogg Biological Station (DGE-0947896) as well as the MSU Environmental Science and Policy Program. I received generous research support from the US Agency for International Development through a US Borlaug Fellowship in Global Food Security (A1102.2), the NSF (LTER program, DEB 1027253 and 1637653), the US Department of Energy Great Lakes Bioenergy Research Center (DOE BER Office of Science DE-FC02-07ER64494 and DOE OBP Office of Energy Efficiency and Renewable Energy DE-AC05-76RL01830), a George H. Lauff Scholarship, and MSU AgBioResearch.

For my research in Michigan, I am grateful for invaluable assistance from Joe Simmons, Terry Tiley, Justin Mezo, Mir Zaman Hussain, Stacey VanderWulp, Sven Bohm, Andy Fogiel, Anika Sasinski, Carlneshia Johnson, and Julie Barrios. I also wish to thank Dave Hill at Superior Enviornmental Corp. in Marne, MI for loaning me equipment for the installation of the soil lysimeters. I thank the administrative staff at KBS and the Dept. of Integrative Biology for coordinating my funding, program requirements, and everything else they do behind the scenes.

For my research in Botswana, I thank my project mentors Yvan Altchenko, Piet Kenabatho, Steven Sylvester, and Karen Villholth. Steve Hamilton also provided critical support throughout the project. I was kindly hosted at the International Water Management Institute Southern Africa. In-kind support was graciously provided by the Botswana Dept. of Water Affairs, Water Utilities Corporation, and Botswana Geosciences Institute. The South African

Council for Scientific and Industrial Research (CSIR) in Pretoria and Basanda Pongoma provided space, materials and guidance for solid phase extraction; the KBS LTER program donated a water quality sonde; and the Dept. of Meteorological Services in Botswana provided the rainfall data used in this study. I thank the following individuals for their support: Moses Molefe, Phemelo Makoba, Phemo Moleje, Karen Gunter, Silas Ranamane, K8 Gaoagelwe, Brenda Moodley, Anita Naidoo, K. Puni Gaboutloeloe, Bakang Mpeo, Natacha Martin, Sima Baqa and Oudi Modisha.

I am cannot thank David Weed, Kevin Kahmark, Adam Reimer, and Julie Doll enough for their mentorship and expert assistance provided throughout all of my dissertation projects, near and far. I consider them unofficial committee members. It has been an honor to receive mentorship from my official committee members G. Phil Robertson, R. Jan Stevenson, and Diana Stuart. Further, I consider myself extremely fortunate to have had Stephen K. Hamilton as a Ph.D. advisor. Life has many uncertainties, but one thing I am certain of is that I chose the right Ph.D. advisor. I am most grateful for and admire his generosity. I hope Steve is proud of the scientist he has empowered me to become.

Finally, I thank my mom, Patty Moorhead, my dad, Kevin McGill, and my brother, Tim McGill. Most of the things people seem to like about me come from each of you. You taught me that despite life's difficulties a truly noble person gives kindness, respect, and empathy to others. You encouraged my curiosity and many, many questions. I will continue to learn from each of your individual wisdoms.

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ABSTRACT

Without liming and irrigation, food production would not be possible in many parts of the world. However, the carbon cycling implications of liming and irrigation are not well understood. Lime ($CaCO_3$) dissolution by nitric acid produces carbon dioxide (CO_2), but dissolution by carbonic acid sequesters additional CO_2 as bicarbonate alkalinity. Groundwater often contains high concentrations of bicarbonate alkalinity that can react with soil acidity as lime does. A field experiment established in 2005 was used to test how nitrogen fertilizer (the main source of strong acidity via nitrification), groundwater-fed irrigation, and lime affect the fate of inorganic carbon. The field experiment involved a corn (maize)-soybean-wheat rotation under no-till management across a nitrogen fertilizer gradient (eight fertilizer levels ranging from 0-246 kg N ha^{-1} in corn years) with and without groundwater-fed irrigation. The total alkalinity input from irrigation over the lifetime of the experiment was about twice the alkalinity input from liming over the same period (applied once in 2012): irrigation added 1.73 Mg alkalinity-C ha^{-1} while liming added 0.27-0.67 Mg alkalinity-C ha^{-1}. Groundwater alkalinity increased soil pH by 0.68 (at pH near 6.5), and the soil pH in the highest nitrogen fertilization treatment was 0.12 units lower than unfertilized soils. Soil pH in limed plots was significantly greater than unlimed plots even one to three years after liming. Soil leachate chemistry showed that annual CO_2 emissions from irrigated plots (at all nitrogen fertilization rates) were 5.1 g (± 1.9) CO_2 m^{-2} yr^{-1} lower than their rainfed counterparts likely due to increased carbonic acid weathering. This suggests that groundwater-fed irrigation increased bicarbonate storage

belowground resulting in less CO_2 emissions than rainfed soils.

INTRODUCTION

Human activities are increasing the amount of CO_2 in the atmosphere. Row crop agriculture can be a net source or sink of atmospheric CO_2 depending on how the land is managed (Gelfand & Robertson, 2015, Robertson *et al.*, 2000). Accounting for the net balance of CO_2 sinks and sources (i.e., the net C balance) of agricultural land management is important for projecting climate change, as well as for identifying changes in land management practices that offer the potential for climate change mitigation. Accurately estimating the net C balance of agricultural practices requires in-depth understanding of underlying and interacting C cycling mechanisms, and also must account for variability among crops, environmental settings, and farmer perceptions and behaviors.

Liming and irrigation have the potential to provide either net C storage *or* CO_2 emissions are, and for neither activities is the net C balance currently well understood. Agricultural liming most often involves mined inorganic fossil C in the form of carbonate minerals that is periodically applyied to soils to neutralize soil acidity. Liming C emissions are estimated in greenhouse gas (GHG) inventory methods used by the Intergovernmental Panel on Climate Change (IPCC), US Environmental Protection Agency (USEPA), and US Department of Agriculture (USDA); however these calculations rely on broad assumptions about lime dissolution reactions and do not account for variability among environmental settings and farming practices. Previous studies have examined the fate of C in liming materials by making inferences from patterns in surface water chemistry (Hamilton *et al.*, 2007, Oh & Raymond, 2006, Raymond *et* *al.*, 2008) that suggest that liming can act as a sink for CO_2 and from field plots (Biasi *et al.*, 2008) and laboratory soil incubations (Bertrand *et al.*, 2007) that suggest that liming can act as a source of CO_2.

As in the case of mined liming materials, alkaline groundwater when applied as irrigation, transports inorganic, and sometimes fossil, C from the subsurface to surface soils in dissolved form as CO_2 and carbonate ions. The fate of irrigation-delivered dissolved inorganic C in agricultural systems is not included in GHG inventory methods used by the IPCC, USEPA, or USDA (De Klein *et al.*, 2006, Ogle *et al.*, 2014, USEPA, 2017b). In this study I investigated the fate of inorganic C inputs from liming and irrigation across a range of eight N fertilizer rates in a Midwest US cropping system managed as a no-till, corn-soybean-wheat rotation to assess the relative effects of N fertilizer, alkaline groundwater-fed irrigation, and liming on soil pH and CO_2 emissions.

BACKGROUND

In the US, two out of every five acres are farmed or grazed (USDA NASS, 2014b). Of farmed land, 43% is used to grow crops and one third of that cropland is irrigated. In 2015 US agricultural soil management as a whole emitted 69 million metric tons (MMT) of CO_2 equivalents as carbon (CO_2e-C) or about 4% of total annual US emissions (USEPA, 2017b). For reference, 69 MMT of CO_2 is just under the total annual emissions from Spain (World Resources Insitute, 2014). Every year in the US farmers apply about 18 MMT of lime, containing ~2 MMT of C (USEPA, 2017b). The majority of this lime is in the form of calcite ($CaCO_3$) and a small amount is dolomite ($CaMg(CO_3)_2$). The USEPA (2017) estimates dissolution of lime produces a net C emission of 1 MMT of CO_2-C or about 1.5% of total emissions from agricultural soil management, but this does not include the contribution of C dissolved in groundwater used for irrigation, which could potentially be large considering the volume of water used for irrigation: US irrigation accounts for 37% of total national freshwater withdrawals and 81% of consumptive water use (Georgakakos *et al.*, 2014).

Current liming C emission estimates are based on multiplying the mass of limestone applied by the fraction of lime that is C (0.12 in the case of $CaCO_3$) and the fraction of lime assumed lost as CO_2 as it dissolves. Different methodologies use different fractions. The IPCC GHG Tier 1 inventory method assumes all lime C is converted to CO_2. In the US, a theoretical liming C budget developed by West and McBride (2005) suggests half of lime C is emitted as CO_2. The USEPA (2017) uses this assumption to estimate an emission factor of 0.059 Mg CO_2-C emissions per Mg lime-C applied as $CaCO_3$. In contrast, the USDA modifies the assumptions in West and McBride (2005) to conclude that lime C dissolution produces a net C *sink* equivalent to one third of lime C, thereby estimating an emission factor of -0.04 Mg CO_2-C emissions per Mg lime-C (Ogle *et al.*, 2014). Observational studies in the US using river water chemistry to back calculate lime C balance (see below) found lime C could represent a 12-50% C sink (Hamilton *et al.*, 2007, Oh & Raymond, 2006).

At the Long Term Ecological Research (LTER) site located at Michigan State University's Kellogg Biological Station (KBS, location of this study), the total global warming impact (GWI, in g CO_2e m^{-2} yr^{-1}) of a corn (*Zea mays*) – soybean (*Glycine max*) – wheat (*Triticum aestivum*) rotation was estimated, included all farm activities, chemical inputs (except irrigation), and biogeochemical processes for a 20-year period (Gelfand & Robertson, 2015). That estimation assumed lime dissolution is net C neutral, the fuel used for transporting and applying lime C made up about 4% of total farm GWI or 4 g CO_2 m^{-2} yr^{-1}. The main emissions were from the production of nitrogen (N) fertilizer and its subsequent microbial transformation to N_2O, a GHG with nearly 300 times the global warming potential of CO_2. Low soil pH is known to interfere with the reduction of N_2O to dinitrogen gas (inert) during denitrification, suggesting that liming can reduce N_2O emissions (Liu *et al.*, 2014). Agricultural N cycling has been studied exhaustively and practices for mitigating N_2O are relatively well understood (IPCC, 2014, Millar & Robertson, 2015, Robertson & Vitousek, 2009, Smith & Gregory, 2013). Soil organic C accretion can counteract GHG emissions: the KBS no-till system sequestered 122 g CO_2 m^{-2} yr^{-1} (Syswerda *et al.*, 2011), although this is a finite sink because soil organic C will eventually reach a dynamic equilibrium (West & Six, 2007). In contrast, lime C dissolution provides a potential C sink every time it is applied in humid regions. Lime neutralizes soil acidity generated in agricultural soils by microbial nitrification of mainly N fertilizer. N fertilizer use (and the resultant need to lime) is expected to triple by 2050 to feed the growing global population and rising per capita consumption (Tilman *et al.*, 2001).

Similar to N fertilizer and lime use, irrigation is increasing around the world to meet growing food demand and increasing rainfall variability due to climate change (Turral *et al.*, 2011). Climate projections for the US Midwest suggest that, despite increasing annual precipitation, summer rainfall will decrease over time while the number of dry days will increase (Georgakakos *et al.*, 2014, Pryor *et al.*, 2014). Groundwater is an important water supply when surface water is of low quantity or quality, although many of the aquifers that support global food production are overexploited (Gleeson *et al.*, 2012). Over 545 km^3 yr^{-1} of groundwater is used for irrigation worldwide (Siebert *et al.*, 2010). In other words, every year the world uses more groundwater for irrigation than would fill Lake Erie, one of the Laurentian Great Lakes.

Given this amount of water used, it is worth considering groundwater-fed irrigation's potential impacts on agricultural C cycling. Aquifers found in formations containing carbonate minerals such as limestone and dolomite, whether as bedrock or in glacial deposits, are often high in calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-) ions. We can calculate the amount of dissolved inorganic C applied to soils via groundwater irrigation by multiplying the concentrations of these ions by the volume of irrigation water applied,. For example, in stream water and groundwater alkalinity in the Kalamazoo River watershed is typically about 5000 ueq L^{-1} (Hamilton, 2017a, Hamilton, 2017b) and irrigated corn receives 0.18 m (7 in) of irrigation water in an "average" growing season (Michigan Dept. of Ag. & Rural Development, 2015 Pers. Comm.). This equates to about 10.7 g C m^{-2} yr^{-1}. If 100% of this C becomes CO_2 it would mean the groundwater irrigation's GWI from inorganic C dissolution (hereafter IC GWI) is 39 g CO_2 m^{-2} yr^{-1}, which is equivalent to the GWI from N_2O emission in the annual cropping systems at KBS. For comparison, N_2O emissions from agriculture make up 78% of US N_2O emissions, and total N_2O emissions are 4% of total US CO_2e emissions (USEPA, 2017a).

The reason CO_2 emissions from inorganic C dissolution are uncertain is that inorganic C in soil is susceptible to two alternative chemical reactions linked to soil pH. The predominant source of soil acidity in fertilized row crops is microbial nitrification of the N fertilizer; harvest also acidifies soil by removing base cations embedded in the grain (Binkley & Richter, 1987, Robertson & Groffman, 2015). Nitrification is the oxidation of ammonia, from either excess N fertilizer or mineralized organic material, which produces nitric acid (HNO_3) (Robertson, 1982). Lime is applied to soils periodically (usually every 2-5 years) to neutralize this acidity. Carbonate mineral dissolution consumes H^+ ions and converts them to either water or HCO_3^-, depending on the reaction, thereby raising soil pH. The first of two alternative reactions for $CaCO_3$ dissolution involves a strong acid such as HNO_3, which produces CO_2, i.e. "strong acid dissolution":

$$CaCO_3 + 2HNO_3 \rightarrow Ca^{2+} + 2NO_3^- + H_2O + CO_2 \qquad \text{Eqn. 1}$$

HCO_3^- alkalinity can consume acidity similar to Eqn. 1:

$$HCO_3^- + HNO_3 \rightarrow Ca^{2+} + NO_3^- + H_2O + CO_2 \qquad \text{Eqn. 2}$$

In contrast, carbonic acid (H_2CO_3), a weak acid, is formed in soil solutions as CO_2, produced by microbial and root respiration, accumulates in soil pore spaces and diffuses into water:

$$CO_2 + H_2O \leftrightarrow\ H_2CO_3 \qquad \text{Eqn. 3}$$

When H_2CO_3 reacts with calcite, CO_2 (in the form of carbonic acid) is converted to HCO_3^-, producing a net C sink:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad \text{Eqn. 4}$$

Eqn. 4 produces 2 moles of HCO_3^-. The HCO_3^- from lime does not count as a C sink as it is not a net transfer of atmospheric C to the soil. However the HCO_3^- from CO_2 (in the form of H_2CO_3) counts as a C sink, because it is a net removal of actively cycling C. This HCO_3^- in excess of H^+ is conserved along its flowpath from the soil to the ocean, which can take decades to centuries (Lal, 2008, Oh & Raymond, 2006).

The stoichiometry of these reactions has been used to calculate the net balance of inorganic C dissolution from waters draining agricultural soils in humid regions, defined here as where annual precipitation is greater than evapotranspiration. This calculation assumes natural dissolution of carbonate materials is a relatively minor contributor to ionic concentrations of soil solutions collected beneath the root zones of limed cropping systems, where native carbonate minerals are not present in the soils. If all carbonate were lost by reaction with HNO_3, we would expect no HCO_3^- to be produced (Eqn 1). On the other hand, if all carbonate were to react with H_2CO_3, we would expect 2 milliequivalents (meq) of HCO_3^- to be produced for every meq of Ca^{2+} + Mg^{2+} (Eqn 4). The Ca^{2+} and Mg^{2+} concentrations are summed because sometimes dolomite ($CaMg(CO_3)_2$) is used as lime. In other words, comparing HCO_3^- to the lime-derived cation concentrations shows how much HCO_3^- is "missing" or "extra." The stoichiometry gives the following equation for calculating a percentage of inorganic C sequestered based on water chemistry measurements, first proposed in Hamilton *et al.* (2007):

$$CO_2 - C\ sink\ strength\ (\%) = \frac{HCO_3^- - 0.5(Ca^{2+} + Mg^{2+})}{0.5(Ca^{2+} + Mg^{2+})} * 100 \qquad \text{Eqn 5}$$

where concentrations are in meq L^{-1}. This equation's numerator can be re-arranged to compute CO_2 that is produced by lime dissolution and, by incorporating drainage volume, expressed as GWI:

$$Leachate\ IC\ GWI = [0.5(Ca^{2+} + Mg^{2+}) - HCO_3^-] * \frac{drainage\ L}{m^2\ yr} * \frac{1\ eq}{1000\ meq} *$$

$$\frac{61\ g\ HCO_3^-}{eq\ HCO_3^-} * \frac{1\ mol\ HCO_3^-}{61\ g\ HCO_3^-} * \frac{1\ mol\ C}{1\ mol\ HCO_3^-} * \frac{12\ g\ C}{mol\ C} * \frac{44\ g\ CO_2}{12\ g\ C} = \frac{g\ CO_2}{m^2\ yr} \qquad \text{Eqn 6}$$

Negative IC GWI values represent CO_2 sequestration as HCO_3^-.

METHODS

Study site

KBS is located in southwest Michigan (42° 24′ N, 85° 24′ W, elevation 288 m) in the northeast part of the US corn belt, it drains to the Kalamazoo River and Lake Michigan. From 1981-2010 the mean annual precipitation at KBS was 1,007 mm, about half of which fell as snow; mean summer and winter temperatures were 22^{o}C and -2.6^{o}C, respectively (NOAA, 2017). From October to April precipitation exceeds evapotranspiration and annual recharge on the glacial outwash plains that are commonly farmed is ~280 mm (Hamilton *et al.*, 2007).

The KBS LTER Main Cropping System and Resource Gradient Experiments (MCSE and RGE) are located on a nearly level glacial outwash plain formed by the retreat of the Wisconsin ice sheet approximately 12,500 to 18,000 years ago (Crum & Collins, 1995). Since deglaciation, native carbonates have been leached out of the upper ~1.5 m of the soil profile by carbonic acid dissolution (Kurzman, 2006). Below this carbonate-leached zone, native calcite and dolomite are equally abundant in KBS soils (Hamilton *et al.*, 2007). The surface soils are moderately fertile, well-drained loams (Typic Hapludalfs) developed on glacial outwash with intermixed loess (Crum & Collins, 1995, Luehmann *et al.*, 2016). Crop yields at KBS and in the surrounding county are similar to national averages (Robertson *et al.*, 2015).

This work was conducted at the RGE, which was initiated in 2005. Prior to 2005, alfalfa, which has high lime requirements, was grown in the RGE field from 1989-1993 and from 1995-2002. Corn was grown in 1994 and this was the last time the soil was plowed, after which the RGE field has been managed as no-till. In 2003 the RGE field grew soybeans followed by winter wheat. The RGE was initiated with corn in 2005 and since then it has followed the same corn-soybean-wheat rotation as the adjacent MCSE (Robertson & Hamilton, 2015). The RGE is managed in the same way as the MCSE no-till treatment (T2). Across the gradient of N fertilization rates (described below), the RGE treatment level F6 is the same N fertilization level as the MCSE T2.

The goal of the RGE design is to investigate how crop yield and ecological processes differ when N and water resources do not limit growth. As such, it includes nine N fertilizer treatments (F1-F9), which for corn range from 0 to 291 kg N ha^{-1}, and in wheat range from 0 to 157 kg N ha^{-1}. For corn and wheat years between 2005-2013 liquid urea ammonium nitrate (UAN, 28-0-0) was broadcast with a sprayer. From 2014 to 2017 UAN was knifed 13-15 cm (5-6 inches) below the soil surface. Soybeans are normally not fertilized, but in 2012 they were fertilized at half the rate of corn with granular ammonium nitrate. The nine fertilizer treatments are replicated as 5 x 28 m plots in eight blocks. Four of these blocks are irrigated with groundwater.

Irrigation scheduling

Growing season precipitation, irrigation amount, and crop rotation per year are shown in Figure 1.1. Note that the growing season in 2012 suffered a severe drought, and that 2017 was almost as dry. From 2005 – 2011 irrigation was applied using solid set irrigation and was scheduled at the LTER farm manager’s discretion taking into consideration soil moisture, crop development, and previous rainfall. Since 2011 irrigation has been applied using a linear move irrigation system (Valley Model 8000, 360^{o} drops every 3 m, total length 70 m). Since then

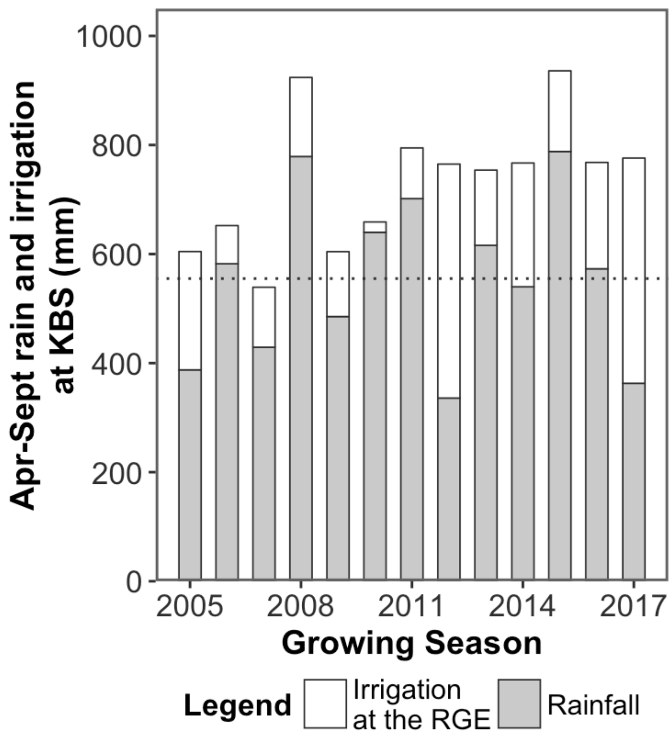

Figure 1.1. Growing season (Apr-Sep) rainfall and irrigation amounts at the Kellogg Biological Station's Long Term Ecological Research Resource Gradient Experiment. The dotted line is mean growing season rainfall over the period shown (555 mm). Labeled years are corn years, followed by soybeans and wheat. The 2012 growing season had a severe drought and 2017 was almost as dry.

irrigation has been scheduled using a soil water budget. Daily maximum evapotranspiration (ET_{max}) data for the budget were simulated by the Systems Approach to Land Use Sustainability (SALUS) model (model details below) using KBS weather data from 1984-2010 and crop-specific growth and development data from the MCSE annual crops. Daily ET_{max} is the date- and crop-specific average of a 100-year SALUS simulation. The sum of ET_{max}, daily precipitation, and irrigation is positive when soil water is available and negative when there is a deficit—similar to irrigation schedulers or checkbooks promoted by Michigan State University Extension (Kelley & Miller, 2016). Irrigation is scheduled following two consecutive days of a soil water deficit and the amount applied replaces the previous days' deficit. Total irrigation per season at KBS is similar to the average amount of irrigation for corn farms in southwest MI, 0.18 m (7 in) as reported by the Michigan Department of Agriculture and Rural Development (Michigan Dept. of Ag. & Rural Development, 2015 Pers. Comm.) and southwest Michigan farmers (Chapter 3, this volume).

Soil pH

Beginning in 2011 I collected soil cores from each RGE plot for soil pH and other analyses. This dataset is available through the KBS LTER database (https://lter.kbs.msu.edu/datatables/357). Each fall (typically in Oct) four cores (1.9 cm diameter by 25 cm deep) were collected with a push corer from each plot—two cores within rows and two between rows, all at least 1 m from plot edges. These were composited and sieved with a 4 mm screen. Field moist soil was refrigerated usually for 2 days (5 days max) prior to pH analysis on two duplicate 15 g subsamples. A slurry of 15 g field moist soil and 30 g deionized water was shaken by hand for a few seconds, then allowed to settle for 30 min before measuring pH using a calibrated, glass pH electrode and pH meter. The slurry was gently swirled until the pH reading was stable.

Liming

Lime was applied to the RGE field in 1996 at 2.2 Mg ha^{-1} (1 US ton ac^{-1}) and in 2000 at 2.5 Mg ha^{-1} (1.1 ton ac^{-1}). In May 2012 lime was applied following the plot-specific liming recommendations from the 2011 soil samples and pH measurements. Application rates ranged from 0 to 4.5 Mg ha^{-1} (2 ton ac^{-1}). Most of the plots that received lime were rainfed (non-irrigated) with high N fertilizer treatments (Table A.1.1).

Soil water chemistry

To collect soil water samples for chemistry analysis, I installed soil water samplers in April 2014. The samplers are silica carbide tension pore-water samplers that are 6 cm long and 2 cm in diameter (Model SIC20, UMS, Munich, Germany). The silica carbide construction is chemically inert. The manufacturer recommended pulling a vacuum on the samplers using deionized water before installation to leach any residual chemicals from the sampler and to verify that all the tubing was intact. I did this with the samplers leaving them in a bucket of deionized water under a vacuum for at least 24 hours before installation. The vacuum was released immediately prior to installation. Chemistry from the first 500 mL of sample was not included in data analysis.

RGE plots are 4.6 x 27.4 m each, neighboring plots run along the long edge of each plot. Each lysimeter is 1.2 m deep, 2.3 m from adjacent plots, and 3.8 m from the nearest short edge. I installed the samplers at a 51^{o} angle from the soil surface so as not to disturb the soil directly above the sampler. The first 1.2 m of the lysimeter hole was drilled using a 2.2 cm diameter probe on a hydraulic soil corer, and the last 30 cm of probing was hammered by hand using a 2 cm diameter aluminum rod to minimize widening the hole. The rod was was withdrawn, and the sampler was inserted by hand another 10 cm beyond the hole made by the rod to ensure the sampler had direct contact with the soil. The lysimeters' 1.2 m depth puts them below the rooting zone of the annual crops but still within the carbonate-leached upper soil profile. Additional samplers were installed at 2.5 and 3.3 m depths, but data are not shown here. In 2014, samplers were installed in N fertilization treatments F1-F8 in one rainfed and one irrigated block. In Dec. 2015, additional samplers were installed in the remaining 6 blocks in N treatments F1, F5, and F8, bringing the total number of samplers at 1.2 m depth to 34.

Soil water samples were collected using a hand-operated vacuum floor pump (Model VPS-2, UMS, Munich Germany) to achieve -0.6 atm in the sampler, similar to the MCSE protocol (https://lter.kbs.msu.edu/protocols/41). The samplers required about 5-7 days of holding the vacuum to collect enough soil water volume for multiple lab analyses (≥50 mL). Not all samplers produced water at every sampling date. Sampling was conducted at approximately two-week intervals year round except when soils were frozen. Sampling outside of the growing season is important as 90% percent of nitrate leaching in corn years occurs outside the growing season at the KBS MCSE (Syswerda *et al.*, 2012). Soil water samples were immediately transported to the aquatic biogeochemistry lab at KBS where they were filtered using a Supor 0.45 μm membrane filter (Pall Corporation; Ann Arbor, Michigan, USA). Sample conductivity and alkalinity were measured on the same day. For these waters, total alkalinity is considered as HCO_3^- because the ion concentrations and pH range suggest that total alkalinity is almost entirely carbonate alkalinity in the form of HCO_3^- (Hamilton et al 2007). Alkalinity was measured on filtered samples using Gran titration with 0.02N HCl and an auto-titrator (Metrohm 877 Titrino plus with 862 Compact Titrosampler, Metrohm; Riverview, Florida). Samples were refrigerated until analysis by membrane-suppression ion chromatography within one week (Dionex ICS-1100, ThermoFisher Scientific; Waltham, Massachusetts). This provided concentrations for the major anions (nitrate, sulfate, chloride, fluoride, and bromide) and cations (calcium, magnesium, potassium, sodium, and, if present in sufficiently high concentrations, ammonium). Ammonium concentrations were always undetectable (<0.1 mg L^{-1}). Dissolved organic C (DOC) was measured within one week on a high-temperature Pt-catalyzed TOC analyzer (TOC-VWS and

ASI-V autosampler, Shimadzu; Columbia, Maryland). Samples were also analyzed for soil solution pH, total N, total dissolved phosphorus, and silicate, but data are not shown here.

Soil water drainage simulations

Soil water drainage was modeled using SALUS, which was developed and validated at KBS (Basso & Ritchie, 2005, Basso & Ritchie, 2015, Syswerda *et al.*, 2012). Briefly, SALUS is designed to simulate crop growth while also estimating management and weather effects on soil, water, and nutrient processes (Basso & Ritchie, 2015). Simulations are on a daily time step over multiple years. The crop growth module incorporates crop genetics and planting details to inform simulation of crop growth and development using a leaf area index curve and thermal time calculation. Crop rotation, irrigation and fertilizer applications, tillage, harvest, residue management and daily weather conditions are also incorporated into the model. The SALUS water balance submodel estimates root water uptake from the crop growth module, which along with precipitation, temperature and irrigation, computes daily evapotranspiration, surface runoff (negligible at KBS), infiltration and drainage on a daily time step. Soil water chemistry was combined with SALUS drainage volume to get mass flux rates per unit area. For annual total mass flux, ion concentrations were linearly interpolated between soil water observations (typically 10-14 day intervals, up to six weeks when soils were frozen).

Statistical analyses

Linear regression analyses were conducted to predict actual daily observations as well as overall annual fluxes, including interpolations, to determine whether results differed between the two time periods. Further, daily observations and annual fluxes were each tested against leachate nitrate flux and N fertilization treatment separately, for a total of four models. The two N variables were tested separately because nitrate leachate flux might explain IC GWI variability in more detail, but it is not measured at most farms. So nitrate flux will not likely be available for future estimates of IC GWI from all cropland. N fertilization rate is more available, if the farm operator is willing to provide it, for calculating IC GWI per farm or at a national scale. I compared IC GWI model predictions based on nitrate leachate flux vs. N fertilization rate (hereafter, with chemistry vs. without chemistry models) to test whether N fertilization rate can be used in lieu of nitrate leachate flux. Hereafter, annual or year refers to the "crop year" (1 June – May 31). The following other independent variables were also tested in each model and the four most parsimonious and best fitting models are presented: 2012 liming treatment, irrigation treatment and amount, crop year (1 June – 31 May), date, day of the year, leachate dissolved organic C (DOC) flux, and % yield difference between irrigated and rainfed plots. For the daily models, linear mixed effects modeling accounts for the random effect of block, but block was not important in the soil pH or annual IC GWI models.

All models presented meet standard model assumptions for homogeneity of variances, normally distributed and independent errors, and non-collinearity among predictors. Transformations were necessary to meet these assumptions in a few cases. N fertilizer (kg ha^{-1}) as a predictor of pH was divided by ten to bring its numeric range (0, 291) closer to the pH numeric range (5.20, 7.62), then squared, and multiplied by -1 to better fit the pH at the zero N plots. pH is the -log transformation of the soil H^+ concentration. Soil pH data were more normally distributed than soil H^+ concentration. Statistical analyses were conducted in R version 3.4.2 (R Core Team, 2017) using packages "lme4" for mixed effects modeling (Bates *et al.*, 2015) and “ggplot2” for plotting (Wickham, 2009).

RESULTS

Soil pH

In 2011 before liming, soil pH in rainfed plots ranged from 5.5 in the high N treatments to 6.5 in the low N treatments (Figure 1.2). In 2011, soil pH in irrigated plots was higher, ranging from 6.0 (high N) to 6.7 (low N). In the spring of 2012, lime was added to plots based on their

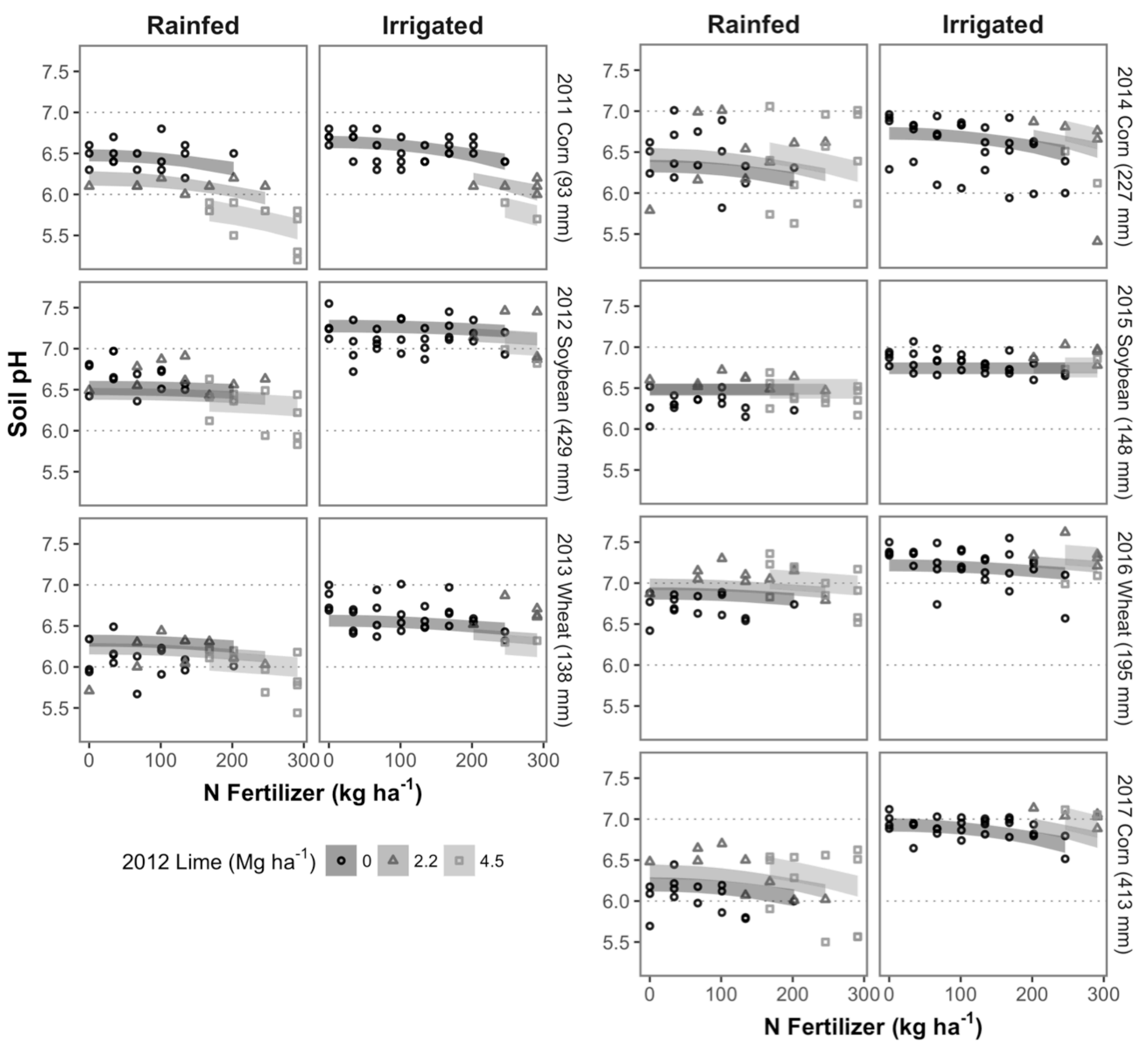

Figure 1.2. Mean soil pH (points) and 95% confidence interval for Model 1 (ribbons) at the KBS LTER Resource Gradient experiment. Showing all years at corn fertilizer rates for comparison.

previous pH measurements. Rainfed plots whose pH was acceptable were not limed, their fall 2012 pH ranged from 6.4 (high N) to 6.7 (low N). Rainfed plots that were limed had soil pH measurements ranging from 6.1 (high N) to 6.9 (medium N) (Figure 1.2). Many irrigated plots did not receive lime in the spring. Then the 2012 growing season was a drought, so irrigated plots received a larger than usual dose of groundwater alkalinity. Soil pH in the fall of 2012 in irrigated and unlimed plots ranged from 7.0 (high and low N) to 7.3 (low N), and in irrigated-limed plots soil pH ranged from 7.0 (high N) to 7.2 (high N). In general, soil pH has declined since 2012, except for an unusual increase in 2016 (Figure 1.2). Soil pH interannual variability (standard error) ranged from 0.05 to 0.31 (Table A.1.2). In most cases, the 2016 pH data are significantly higher than other years. Without a lime application or other change in management in 2016, this pH increase suggests the measurements may be specious, but without a clear reason to disregard the 2016 data they are included in the analysis below.

Interannual variability in a plot's fall soil pH was predicted by the amounts of irrigation, N fertilizer and lime that plots received:

$$pH \sim -\left(\frac{Nfert\ (kg\ ha^{-1})}{10}\right)^2 + irrigation\ (mm) + \ lime\ (ton\ ac^{-1}) * year(factor)$$

Model 1

The overall model is significant (p<0.0001) and accounts for 70% of the variance in pH (adjusted R^2) (Table 1.1, Figure 1.2). Block, yield, crop, and other co-variates were excluded from Model 1 (Table A.1.3). Annual irrigation amount (mm) significantly increased the predicted mean pH by 0.002 pH units per mm. Irrigation accounts for 35% of the total variance explained in the model. At the highest irrigation amount (429 mm in 2012), the model predicts irrigated soil pH to be 0.7 units greater than rainfed soil pH (Figure 1.2, second panel).

Table 1.1. **Best predictors of soil pH by linear regression at the Resource Gradient Experiment from 2011 to 2017.** Soil cores (0-25 cm) were collected in the fall of each year. N kg/ha varies by N treatment and crop year. Lime was applied in May 2012. This model has 474 degrees of freedom. Also see Figure 1.2 and Table A.1.3.

	Estimate	SE	t-value	Pr(>|t|)	% of $R^{2,a}$	Adj. R^2
Model 1: pH ~ $(-N/10)^2$ + IRR + crop year * lime				**<0.001**		**0.70**
Reference levels: 0 N, 0 IRR, 2011, no lime						
(Intercept)	6.48	0.04	172.6	<0.001		
(N kg/ha /10)^2	-0.0004	0.00008	5.3	<0.001	5	
IRR (mm)	0.0018	0.00009	19.0	<0.001	35	
Crop year 2012	0.01	0.06	0.3	0.80	42	
Crop year 2013	-0.17	0.05	-3.3	<0.01		
Crop year 2014	-0.15	0.05	-2.9	<0.01		
Crop year 2015	-0.02	0.05	-0.3	0.77		
Crop year 2016	0.38	0.05	7.2	<0.001		
Crop year 2017	-0.30	0.05	-5.4	<0.001		
Lime 2.2 Mg/ha	-0.27	0.08	-3.4	<0.001	8	
Lime 4.5 Mg/ha	-0.56	0.08	-6.6	<0.001		
2012 : Lime 2.2 Mg/ha	0.38	0.11	3.5	<0.001	10	
2013 : Lime 2.2 Mg/ha	0.27	0.11	2.5	<0.05		
2014 : Lime 2.2 Mg/ha	0.44	0.11	4.2	<0.001		
2015 : Lime 2.2 Mg/ha	0.42	0.11	3.8	<0.001		
2016 : Lime 2.2 Mg/ha	0.52	0.11	4.9	<0.001		
2017 : Lime 2.2 Mg/ha	0.58	0.11	5.4	<0.001		
2012 : Lime 4.5 Mg/ha	0.37	0.11	3.3	<0.01		
2013 : Lime 4.5 Mg/ha	0.34	0.11	3.1	<0.01		
2014 : Lime 4.5 Mg/ha	0.83	0.11	7.7	<0.001		
2015 : Lime 4.5 Mg/ha	0.52	0.11	4.6	<0.001		
2016 : Lime 4.5 Mg/ha	0.74	0.11	6.8	<0.001		
2017 : Lime 4.5 Mg/ha	0.84	0.11	7.7	<0.001		

[a]The relative importance of each predictor as the % of its contribution to the model R^2.

N fertilizer represents 5% of the variance explained in the model. With each kg ha^{-1} increase in N fertilizer, pH decreased significantly by ~ .0004. At the highest N fertilizer treatment (F9, 291 kg ha^{-1} in corn years), N fertilizer decreased soil pH by 0.1 unit, seven times lower than the positive effect of the highest irrigation amount. In 2011 (reference year, pre-liming) lime was significantly and negatively related to pH, because prior to liming, the plots that later received lime had the lowest pH, which also tended to be plots with higher N treatments (Table A.1.1).

Crop year by irrigation was a significant interaction in Model 1, altogether accounting for 60% of the variance explained in the model (Table 1.1). More of the high N rainfed plots were limed than high N irrigated plots (Figure 1.2, Table A.1.1). For unlimed rainfed plots in most years the interaction of crop year and lime was slightly negative to not significant except in 2016 (a significant positive effect). Here negative or positive is with respect to the y-intercept of the reference level (no N, rainfed, year 2011, and no lime). The interaction had a positive effect on soil pH in unlimed irrigated plots every year. For plots limed at 2.2 Mg ha^{-1} (both irrigated and rainfed) the interaction increased soil pH every year (except rainfed plots in 2013) by 0.1 to nearly 1 pH unit. For rainfed plots limed at 4.5 Mg ha^{-1} (mainly high N plots) the interaction was negative in years 2012 and 2013, but became positive in 2014 and 2016. For irrigated plots limed at 4.5 Mg ha^{-1} (mainly high N plots) the interaction was slightly negative in 2013, but positive in all other years.

Global warming impact of inorganic carbon fluxes

The IC GWI (Eqn. 5) was modeled in four ways: for both daily and annual flux estimates as well as with and without chemistry predictors.

Daily with chemistry model. Irrigation amount, nitrate flux, and DOC flux can predict daily IC GWI:

$$daily\ IC\ GWI \sim irrigation + DOC * NO_3^- + block(random) \quad \text{Model 2}$$

Fluxes are in mg m^{-2} d^{-1}. The asterisk indicates that both the main effects and interaction term were included. Model 2 explains 70% of the variability in 974 daily IC GWI estimates, and each term significantly improves upon simpler models (Table 1.2). Model 2 includes fewer

Table 1.2 Best predictors for linear regressions for transformed (Eqn. 7) daily inorganic C global warming impact (IC GWI). Measured from soil leachate chemistry at the Resource Gradient Experiment in crop years 2014-2017 (corn, soybean, wheat, and corn, respectively).

	Estimate	SE	t-value	Pr(>|t|)	%t[a]	Adj. R^2
Model 2[b]: Daily IC GWI ~ irr(mm) + DOC flux * nitrate flux + (1|block)						**0.70**
(Intercept)	3.83	9.06	0.42	NS		
Irrigation (mm)	-0.09	0.02	-3.79	<0.001	9	
DOC flux	-6.57	0.54	-12.27	<0.0001	30	
Nitrate flux	1.91	0.13	15.11	<0.0001	37	
Nitrate:DOC	0.11	0.01	9.90	<0.0001	24	
Model 3[c]: Daily IC GWI ~ N fertilization : IRR + month + (1|block)						**0.23**
Reference levels: 0 N, Rainfed,						
(Intercept)	-6.87	13.26	-0.52	NS		
Aug	21.40	8.80	2.43	<0.05		
Dec	9.81	15.91	0.62	NS		
Feb	-13.15	17.26	-0.76	NS		
Jan	3.03	24.35	0.12	NS		
Jul	26.05	8.38	3.11	<0.01		
Jun	43.61	7.70	5.66	<0.0001	36	
Mar	6.93	8.54	0.81	NS		
May	-0.63	9.04	-0.07	NS		
Nov	-1.18	11.21	-0.11	NS		
Oct	4.93	10.66	0.46	NS		
Sep	0.45	10.10	0.05	NS		
246 N: Irrigated	-7.71	17.46	-0.44	NS		
202 N: Irrigated	-14.40	18.89	-0.76	NS		
168 N: Irrigated	25.70	18.82	1.37	NS		
134 N: Irrigated	14.28	17.42	0.82	NS		
101 N: Irrigated	21.40	20.40	1.05	NS		
67 N: Irrigated	31.58	20.72	1.52	NS		
34 N: Irrigated	23.81	19.22	1.24	NS		
0 N: Irrigated	-54.74	18.69	-2.93	<0.05	64	
246 N: Rainfed	-8.97	9.97	-0.90	NS		
202 N: Rainfed	83.54	17.31	4.83	<0.0001		
168 N: Rainfed	124.25	19.88	6.25	<0.0001		
134 N: Rainfed	6.98	9.28	0.75	NS		
101 N: Rainfed	25.30	18.01	1.40	NS		
67 N: Rainfed	-12.46	12.71	-0.98	NS		

[a]Relative importance of predictor as % of non-intercept t-values.
[b]Model 2 includes chemistry predictors and has 970 degrees of freedom (Figure 1.3a and 1.3b).
[c]Model 3 does not include chemistry predictors, has 1030 degrees of freedom, and does not include rainfed 34 kg N / ha (n=1) because that sampler did not yield water (Figure 1.3c).
N fertilization rates (kg N ha^{-1}) refer to corn year rates.
NS = not significant (p>0.05).
SE = standard error

observations than Model 3 below, because fewer DOC measurements were made due to limited sample volumes. According to Model 2, for every 1 mg increase in NO_3^- flux (mg N m^{-2} d^{-1}), daily IC GWI significantly increased by 1.9 mg CO_2 m^{-2} d^{-1} (Table 1.2, Figure 1.3a and 1.3b).

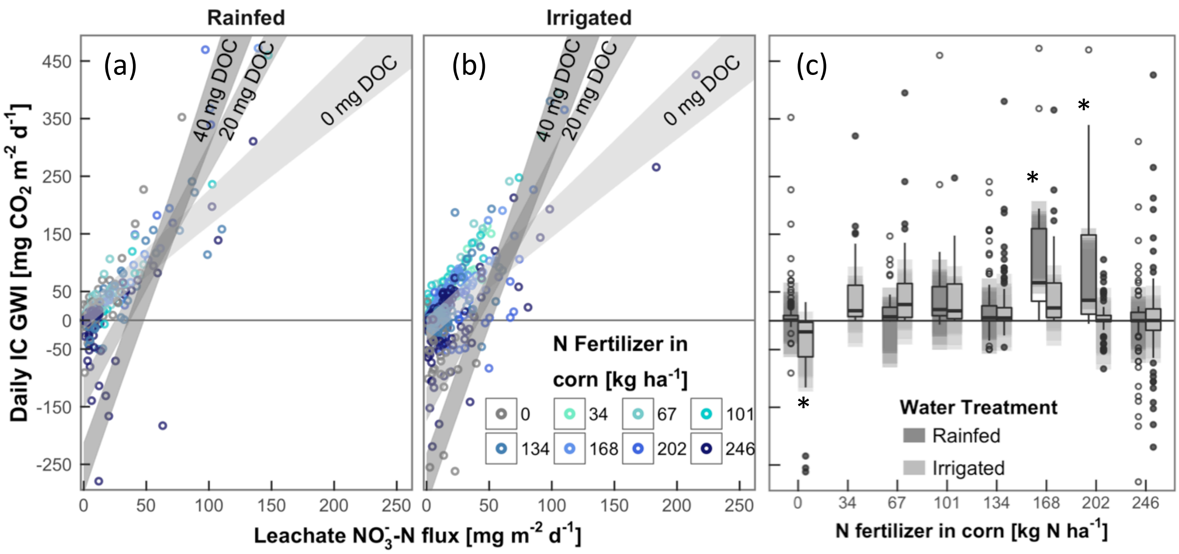

Figure 1.3. Daily inorganic C global warming impact (IC GWI) observations (no interpolated data) at the Resource Gradient Experiment from 2014-2017 and confidence intervals for with (a, b) and without (c) leachate chemistry. (a, b) gray ribbons are the 95% confidence interval from Model 2 (Table 1.2) for the predicted mean IC GWI at three dissolved organic C concentrations (mg DOC m^{-2} d^{-1}). (c) Observations (box and whisker plots with outliers) and each shaded bars (no outline) are made of 12 overlapping bars representing each month's 95% confidence intervals for the predicted mean from Model 3 (Table 1.2). Daily IC GWI in irrigated 0 kg N ha^{-1} plots was significantly ($p<0.05$) less than rainfed 0 N. Daily IC GWI in rainfed 168 and 202 kg N ha^{-1} plots were significantly ($p<0.0001$) > irrigated plots at those N levels. The y-axis is scaled to show the middle 99% of the data.

But for every mg increase in DOC flux (mg m^{-2} d^{-1}), IC GWI significantly dropped by 6.6 mg CO_2 m^{-2} d^{-1}. NO_3^- accounted for 37% of the total t-value, more than DOC flux or NO_3^-*DOC. Every 100 mm of irrigation significantly decreased daily IC GWI by 9 mg CO_2 m^{-2} d^{-1} (Figure 1.3a vs. 1.3b). The significant interaction between NO_3^--N and DOC reduced the negative effect of DOC on IC GWI from -6.6 mg CO_2 m^{-2} d^{-1} (at 0 NO_3^- flux) to -6.5 mg CO_2 m^{-2} d^{-1} in the presence of NO_3^-N (Table 1.2, Figure 1.3a and 1.3b).

Daily without chemistry model. Using the 1,058 daily IC GWI measurements and excluding leachate chemistry data, N fertilization treatment can predict daily IC GWI as follows:

$$daily\ IC\ GWI \sim N\ treatment\!:\!irrigation + month + block(random)$$

Model 3

The colon indicates that the model includes only the interaction term, not the main effects. Model 3 explains 23% of the variability in daily IC GWI and each term significantly improves upon simpler models (Table 1.2, Figure 1.3c). IC GWI across the N treatments did not differ significantly except in three instances. IC GWI at the irrigated unfertilized (F1) N treatments was significantly ($p<0.05$) lower than at their rainfed counterparts by 55 mg CO_2 m^{-2} d^{-1}. The IC GWI estimates for the rainfed F6 and F7 plots were significantly ($p<0.0001$) greater than the other treatments by 124 and 84 mg CO_2 m^{-2} d^{-1}, respectively. The interaction of N treatment and irrigation accounted for 64% of the variability explained by the model (Table 1.2). Additionally, the months of June, July, and August had significantly ($p<0.05$) higher IC GWI than other months by 44, 26, and 21 mg CO_2 m^{-2} d^{-1}, respectively.

Annual with chemistry model. For prediction of annual (crop year) IC GWI, fluxes of NO_3^--N and DOC fluxes explained 65% of the interannual variability:

$$annual\ IC\ GWI \sim NO_3^-\text{-}N + DOC \qquad \text{Model 4}$$

This model was significant ($p<0.001$) (Table 1.3) and resembles Model 2. Sample size is low, *n*=45, because individual measurements are summed together by year and treatment. Fluxes are in g m^{-2} yr^{-1}. NO_3^- flux accounts for 74% of the variability explained by the model (Figure 1.4a). For every increase in g DOC m^{-2} yr^{-1}, IC GWI dropped significantly ($p<0.0001$)by 12.7 g CO_2 m^{-2} yr^{-1} (Figure 1.4b). In contrast, for every gain in g NO_3^--N m^{-2} yr^{-1}, IC GWI increased significantly ($p<0.0001$) by 3.1 g CO_2 m^{-2} yr^{-1}. Irrigation was not significant and excluded from

Table 1.3. Linear regression for annual inorganic C global warming impact (IC GWI) at the Resource Gradient Experiment from crop years 2014, 2015, and 2016 (corn, soybean, and wheat respectively).

	Estimate	SE	t-value	Pr(>|t|)	%t[a]	Adj. R^2
Model 4[b]: Annual IC GWI ~ nitrate flux + DOC flux				**<0.001**		**0.65**
(Intercept)	1.81	0.95	1.90	NS		
Nitrate flux	3.06	0.28	10.90	<0.0001	74	
DOC flux	-12.73	1.63	-7.79	<0.0001	26	
Model 5[c]: Annual IC GWI ~ N fertilization + IRR				**<0.01**		**0.31**
Reference levels: 0 N, rainfed						
(Intercept)	2.20	1.82	1.21	NS		
34 kg N / ha	14.03	4.06	3.45	<0.01		
67 kg N / ha	8.09	3.04	2.66	<0.05		
101 kg N / ha	10.72	3.96	2.70	<0.01		
134 kg N / ha	6.80	2.28	2.99	<0.01	82	
168 kg N / ha	14.94	3.30	4.52	<0.0001		
202 kg N / ha	6.75	3.30	2.04	<0.05		
246 kg N / ha	5.06	2.44	2.07	<0.05		
Irrigated	-4.82	1.63	-2.95	<0.01	18	

[a]Relative importance of predictor as % of non-intercept t-values.
[b]Model 4 includes chemistry predictors and has 42 degrees of freedom (Figure 1.4a and 1.4b).
[c]Model 5 does not include chemistry predictors, has 36 degrees of freedom (Figure 1.4c).
N fertilization rates refer to corn year rates.
NS = not significant ($p>0.05$).
SE = standard error

Model 4, however DOC fluxes from irrigated plots were significantly ($p<0.05$) greater than in rainfed plots by 0.24 g DOC m^{-2} yr^{-1} (data not shown).

Annual without chemistry model. Excluding leachate chemistry, annual IC GWI was best predicted using N fertilization and irrigation treatments as follows:

$$annual\ IC\ GWI \sim N\ treatment + irrigation\ treatment \qquad \text{Model 5}$$

This model accounts for 31% of the variability in annual IC GWI, with N treatment explaining 82% of the total variability explained (Figure 1.4c and Table 1.3). The IC GWI of the F1 (unfertilized) rainfed plots was predicted at 2.2 g CO_2 m^{-2} yr^{-1} with the IC GWI at all other N treatments being significantly greater than at F1 by a mean of 9.5 g CO_2 m^{-2} yr^{-1}. Irrigated plots' IC GWI, at all N levels, were 4.8 g CO_2 m^{-2} yr^{-1} lower than their rainfed counterparts (Figure

1.4c).

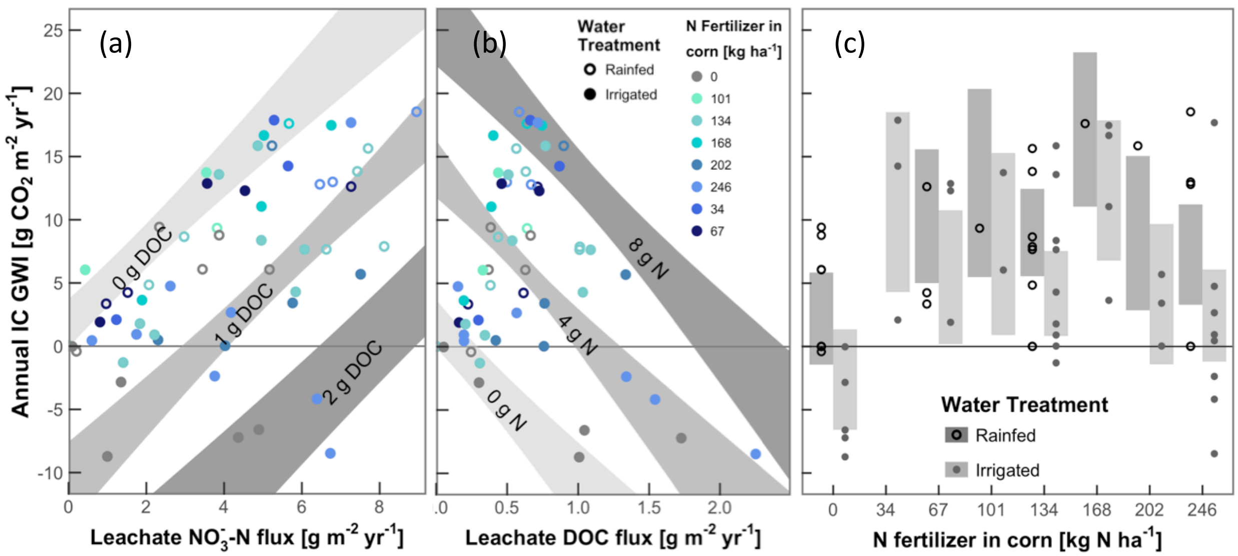

Figure 1.4. Annual inorganic C global warming impact (IC GWI) (sum of observations and interpolated data) at the Resource Gradient Experiment from 2014-2017 and confidence intervals for with (a, b) and without (c) leachate chemistry. (a, b) Gray ribbons are the 95% confidence interval from Model 4 (Table 1.3) for the predicted mean annual IC GWI (a) by NO_3^--N flux at three dissolved organic C fluxes (mg DOC m^{-2} d^{-1}) and (b) by DOC flux at three NO_3^--N fluxes (mg N m^{-2} d^{-1}). (c) Bars are the 95% confidence interval for the mean annual IC GWI at each N fertilizer level (treated as categorical) and points are observations. All rainfed N levels are significantly ($p<0.05$) > rainfed 0 N. All irrigated N levels are significantly ($p<0.01$) < their rainfed counterpart (Table 1.3).

DISCUSSION

In this study I investigated the net effect of N fertilization amount, alkaline groundwater-fed irrigation amount, and liming on soil pH and IC GWI in a Midwest US no-till corn-soybean-wheat cropping system. N fertilizer reduced soil pH, while irrigation and lime increased soil pH—though the main effect of liming was a weak predictor of interannual variability in soil pH (only 8% of R^2, Model 1). In general, IC GWI was positive (contributing to global warming), but the IC GWI in irrigated plots was significantly less positive than rainfed plots (Figure 1.4c). Surprisingly, liming was not significant in either the daily or annual IC GWI models (Table 1.2 and Table 1.3), though this could be a false negative (type II error) given the unbalanced lime application across treatment combinations, discussed below. DOC flux was surprisingly important in predicting IC GWI on both daily and annual time periods (Figs. 3 and 5).

Interannual variability in soil pH

Soil pH controls many chemical and biological processes, and managing pH is essential for maximizing crop productivity. The negative effect of N fertilizer on soil pH was expected given that nitrification produces two moles of hydrogen ions per mole of NO_3^- (Driscoll & Likens, 1982). The positive effect of liming on soil pH was also expected given that lime dissolution consumes 1 mole of H^+ per mole $CaCO_3$ dissolved (Binkley & Richter, 1987). However, few studies have looked at the relative importance of N fertilizer, liming, and alkaline irrigation for soil pH. Model 1 predicted that soil pH in plots that received 2.2 Mg ha^{-1} (1 ton ac^{-1}) lime was 0.1 units above unlimed plots within one year; the soil pH in plots treated with 4.5 Mg ha^{-1} (2 t ac^{-1}) lime was 0.27 units greater than unlimed plots within three years. The pH changes described here apply to pH values near 6.5 and are not applicable in other pH ranges due to the log scale of pH. The model predicted that soil pH in plots at the highest level of N fertilizer (291 kg N ha^{-1} in corn years) dropped by 0.12 between 2011-2017—about half the magnitude of liming's positive effect. This helps explain why lime is not applied every year: one dose of lime can neutralize two or more years of N fertilizer-derived soil acidity. Model 1 also predicted that the highest amount of irrigation observed in the study period (429 mm in 2012) increased soil pH by 0.68 unit—nearly seven times greater than the acidification ascribed to the N fertilization effect.

The average N application rate for corn in Michigan in 2016 was 136 kg N ha^{-1} yr^{-1} (USDA NASS, 2017). At this rate in the KBS system, the model predicts pH would drop by 0.05 units per year. The average irrigation rate for field corn in southwest Michigan is 180 mm (Michigan Dept. of Ag. & Rural Development, 2015 Pers. Comm.). At this rate of irrigation pH would increase by 0.28 unit per year—outpacing the decrease in pH from N fertilizer by a factor of five per year. This could explain why some irrigators in southwest Michigan have reported not liming irrigated corn fields for up to 20 years (Chapter 3, this volume). Therefore at average N application rates, irrigation and liming together effectively neutralized acidity resulting from nitrification of excess N in the soils, and irrigation with alkaline groundwater reduced the need for liming.

Controls on the IC GWI

Several reasons may explain why the effect of liming was evident in soil pH but more difficult to determine for IC GWI. First, the soil pH dataset covers 2011-2016 with a single annual soil pH measurement at each of the 72 plots, whereas the IC GWI dataset only covers 2014-2017 for daily measurements and 2014-2016 for annual crop year totals. Also it includes fewer replicates of the treatments (see Methods), reducing the statistical power to detect an effect. Additionally, the lime was applied as a soil management practice rather than as an experimental treatment, and thus it was added on an as-needed basis rather than consistently across N fertilization treatments, which tended to confound the effects of high N fertilization in rainfed and irrigated plots that were limed. Therefore, I was unable to distinguish whether liming is truly insignificant in determining IC GWI, or if liming is significant but I was unable to detect its effect.

Measured IC GWI is the sum of several potential sources of soil inorganic C dissolution including 2012 liming, previous liming, irrigation water alkalinity, and possibly the presence of small amounts of native carbonates in the soil profile overlying the samplers. The total alkalinity input from irrigation over the lifetime of the RGE (2005-present) is about twice the alkalinity input from liming over the same period (applied once in 2012): irrigation added 1.73 Mg alkalinity-C ha^{-1} (2.44 m irrigation at 5.9 meq alkalinity L^{-1}) vs. 0.27-0.67 Mg alkalinity-C ha^{-1} from liming. Measurements of carbonate minerals in cores taken from the upper 1.2 m of KBS soils have repeatedly been shown concentrations to be minute (Hamilton, 2017 Pers. Comm.). Therefore, the predominant sources of inorganic C in the irrigated plots are the groundwater and liming (where applied), whereas in rainfed plots the main source of inorganic C is liming.

Irrigation amount, N fertilization amount, and DOC leaching fluxes were significant predictors of IC GWI. It was surprising that DOC flux was a significant negative predictor of IC GWI. Others have found that increasing soil pH intensifies physical, chemical, and biological processes leading to greater DOC flux in leachate (Karlik, 1995) and drives patterns in water DOC flux over time (De Wit *et al.*, 2007, Evans *et al.*, 2012). We know that N fertilization decreases soil pH and I showed here that irrigation increases soil pH. Also, irrigated plots tended to have significantly lower NO_3^--N and higher DOC fluxes per unit N fertilization than their rainfed counterparts (data not shown). Perhaps DOC flux is determined by soil organic C (SOC) accumulation, because at the RGE the SOC pool is also greater in irrigated plots compared to rainfed plots (Chapter 2, this volume). Liming also increased SOC. So it seems that the pH balance has a strong effect on the processes determining the fate of SOC (e.g., Fornara *et al.*

(2011) and Chapter 2 (this volume)) *and* inorganic C (present study). Thus, DOC flux as a proxy for SOC sequestration is a predictor of IC GWI. Also, if irrigation shunts SOC to another pool like groundwater DOC then soils could potentially continue to accumulate SOC once they've reached their limit. Whether this is a net increase in C sequestration depends on the fate of the leached DOC.

Prediction of IC GWI without leachate chemistry

The without chemistry models were developed to test how well IC GWI can be predicted given only farm management information such as irrigation and N fertilization amounts. The daily and annual without chemistry models explained less than half as much of the variability in IC GWI (adjusted R^2 was 23% and 31%, respectively) than the daily and annual with chemistry models (70% and 65%, respectively). This makes sense as the without chemistry models have fewer predictors and lower temporal resolution in the underlying data. The much larger sample size of daily measurements vs. the small number of annual totals (n=~1,000 vs. 45) enabled the daily model to incorporate more variables and interactions than the annual model. The without chemistry models found a negative effect of irrigation and positive effect of N treatment on IC GWI, in agreement with the daily with chemistry Model 2 and the NO_3^- effect demonstrated in Hamilton et al. (2007). Thus the with chemistry models better explained the IC GWI variability and provided information about possible mechanisms for the patterns (e.g., DOC and NO_3^- fluxes in relation to time, precipitation and drainage—see below). But the without chemistry models also captured the opposing effects of nitrification (acidification) and irrigation (acid neutralization), in agreement with the pH model.

Model predictions of daily vs. annual IC GWI

Both the daily and annual with chemistry models showed the importance of irrigation, NO_3^-, and DOC (recall DOC "represents" irrigation in Model 4). Hereafter I focus on the without chemistry models (3 and 5) because they are potentially more widely applicable for predicting IC GWI on farms. The daily and annual "without chemistry" models have similarities, i.e. for rainfed crops, N fertilization treatments F5-6 in the daily model and F2-8 in the annual model had significantly higher IC GWI than the unfertilized plots (Table 1.2 and Table 1.3). When irrigated, the daily IC GWI of unfertilized plots was lower than the rainfed unfertilized ones, but the remaining N fertilization levels when irrigated were not significantly different from rainfed unfertilized.

Daily estimates of IC GWI during Jun-Aug were significantly higher than other months. This is not completely surprising. In 11 years of nitrate leaching data from the MCSE no-till treatment (corollary to RGE), 95% and 56% of total crop year NO_3^- leaching flux in soybean and wheat years, respectively, occurred in season, i.e. during the growing season (Syswerda *et al.*, 2012). In corn years, only 10% was found to occur in the growing season. The daily IC GWI dataset covers Apr 2014 – Sep 2017 (corn, soybean, wheat, and corn years) with the majority of observations in 2015-2016. Precipitation and drainage during June and July 2015 were higher than usual (data not shown) and 2015 was a soybean year (high in-season NO_3^- leaching), resulting in high NO_3^- leaching, as was observed in my leachate samples. Models 2 and 4 show a positive relationship between NO_3^- flux and IC GWI. So, Model 3's predicted high IC GWIs for Jun-Aug are likely driven by the confluence of weather and crop in Jun-Aug 2015.

But why is daily IC GWI in the highest N fertilization treatment (F8) in rainfed plots not significantly greater than the IC GWI in rainfed plots with low N fertilizer (Figure 1.4c)? I would expect that as N fertilization increases, so does nitrification, especially where yield plateaus at the higher N fertilization rates. More strong acid dissolution would reduce the amount of HCO_3^- in soil water relative to Ca^{2+} and Mg^{2+}, meaning higher IC GWI. However, rainfed high N plots also tended to receive lime and more of it in 2012 than low N plots (Table A.1.2). In these plots, the 2012 liming would have neutralized much of the acidity by 2014, the start of my measurements. In fact, by 2014 soil pH in limed plots was greater than soil pH in unlimed plots (Table 1.1). Therefore, I would expect to see what I observed: soil leachate chemistry of rainfed high N (and high lime) plots had extra C (in the form of HCO_3^-) as a product of Eqn. 3 (lime dissolution by carbonic acid).

The irrigated unfertilized treatment (F1) had a significantly lower daily IC GWI (less CO_2 emissions) than the rainfed F1. This was the only irrigated treatment that was significantly different from rainfed F1 in the daily model (Model 3). The high-N, irrigated plots did not need as much lime as their rainfed high N counterparts in 2012 because of the irrigation water alkalinity inputs. Irrigation had a stronger positive effect on soil pH than N fertilizer's negative effect (Model 1, Table 1.1). Therefore, I would expect to see less buildup of strong acid in the irrigated plots and a continued input of HCO_3^- in excess of HNO_3. Irrigation keeps the soils moist, encouraging microbial respiration and production of CO_2 and H_2CO_3. The irrigation water itself is high in HCO_3^- alkalinity (mean HCO_3^- alkalinity was 5.9 meq L^{-1} and mean Ca^{2+} + Mg^{2+} was 7.3 meq L^{-1}), which is about five times the alkalinity of irrigated soil leachate. So the measured leachate HCO_3^- alkalinity in excess of Ca^{2+} and Mg^{2+} could result from diluted groundwater alkalinity or H_2CO_3 weathering (Eqn. 4).

Model 5 predicts annual (crop year) IC GWI at F5 for rainfed and irrigated plots to be 9.0 and 4.2 g CO_2 m^{-2} yr^{-1}, respectively (Table 1.3). The annual climate benefit of irrigation on IC dissolution was apparent across all N treatments compared to rainfed plots (Figure 1.4c). In the unfertilized plots annual (and daily) IC GWI in irrigated plots was significantly lower than in the rainfed F1 treatment and was negative (-2.6 g CO_2 m^{-2} yr^{-1}). In the unfertilized F1, the HNO_3 would come from nitrification of organic matter, a small pool of HNO_3 relative to fertilized plots. In irrigated F1 plots, very little of the groundwater alkalinity underwent strong acid weathering. The rest either consumed H^+ from carbonic acid—not a net C sink like $CaCO_3$ dissolution by carbonic acid (Eqn. 3)—or were merely diluted along their flowpath to the soil water samplers.

These results suggest that groundwater-fed irrigation can reduce IC GWI of cropping systems, but it is unclear to what extent the groundwater alkalinity plays a role in the measured soil leachate alkalinity. Soil water may move quickly through the sandy soil and macro-pores resulting from no-till—too quickly to react with soil chemistry. In this case, the alkalinity in excess of Ca^{2+} and Mg^{2+} may simply be diluted irrigation water and not a C sink. But we know this is not the case, because the alkalinity affects soil pH. Irrigation water may increase microbial and root respiration, which could increase CO_2 emissions and/or H_2CO_3 in the soil, promoting weak acid dissolution of any remaining lime or native carbonates. Alternatively, pockets of native carbonates remaining in the upper soil profile could make leachate chemistry appear to be a C sink; but this is unlikely given the similar responses observed among replicates that are tens of meters apart.

Our results suggest that liming, in contrast to irrigation, has a net positive GWI. The majority of IC in the rainfed plots would be from the 2012 liming application. My measurements show that by 2014, HCO_3^- flux in rainfed soil leachate was disproportionately low compared to Ca^{2+} and Mg^{2+} flux, suggesting the loss of HCO_3^- alkalinity as CO_2. This finding that consumption of HCO_3^- alkalinity can be a significant source of CO_2 is in agreement with soil CO_2 emission measurements using stable isotopes that showed that CO_2 derived from inorganic C made up 26-35% of the total soil emissions among calcareous, loess, acidic, and acidic limed agricultural soils (Bertrand *et al.*, 2007). Gelfand et al. (2015) assumed that lime dissolution had a net neutral GWI, but the fuel used to apply lime in the KBS no-till system between 1989-2009 had a GWI of 4 g CO_2 m^{-2} yr^{-1}. If I update that figure for 2017 and include the 2012 liming at the MCSE, the GWI of fuel emissions embedded in lime application is 3.5 g CO_2 m^{-2} yr^{-1}. But irrigation can reduce the need for liming and the GWI of IC dissolution by 4.8 g CO_2 m^{-2} yr^{-1} (Model 5). This is not the net GWI of irrigation as it does not take into consideration how irrigation affects other processes contributing to its net GWI (cf. Chapter 2, this volume).

In samples of water from agricultural tile drains and streams, Hamilton et al. (2007) often observed HCO_3^- alkalinity in excess of that expected based on the dissolved Ca^{2+} and Mg^{2+} ions and the elemental stoichiometry of carbonate minerals, attributing the excess HCO_3^- to capture of CO_2 via the carbonic acid weathering reaction involving liming materials. However my study suggests that total inorganic C dissolution in row crop systems has a net positive GWI. We know that agriculture has increased land drainage over the last several decades and HCO_3^- fluxes are increasing in agricultural (and non-agricultural) watersheds probably due in large part to anthropogenic alteration of landscape hydrology increasing the weathering of native carbonate materials (Raymond & Hamilton, 2018). If Eqn. 6 is applied to these waters, then we would conclude that liming is a net C sink, but the excess HCO_3^- from native carbonate dissolution likely swamps out any detectable signal from lime dissolution. At KBS, the mass of lime applied to soil is miniscule compared to the volume of native carbonate material that infiltrating water is exposed to along its flowpath. Since 1989, lime has been applied at the KBS MCSE every ~10 yr at ~2.2-4.5 Mg ha^{-1} where each application looks like a dusting of powder. In comparison, the driller's log for the groundwater well at the MCSE indicates the depth to the static water table was 14 m and to bedrock was 60 m in 1983. If we assume the upper 1.5 m of the soil profile is carbonate-free and the glacial outwash above the bedrock is 3% $CaCO_3$ by volume and 1.65 g cm^{-3} (USDA Natural Resources Conservation Service, 2017a, USDA Natural Resources Conservation Service, 2017b), then the unsaturated and saturated zones conservatively contain 6,000 and 22,000 Mg $CaCO_3$ ha^{-1}, respectively. It therefore is highly unlikely to be able to detect a lime dissolution signal in soil solutions that have reacted with the abundant native carbonates in the subsoil. This potentially explains why Hamilton et al. (2007) found that soil leachate measurements suggested lime was a C source while stream waters often showed that carbonate mineral dissolution along the subsurface flow paths acted as a net inorganic C sink.

If watershed chemistry studies, which have shown lime is a sink for CO_2 (Hamilton *et al.*, 2007, Oh & Raymond, 2006, Raymond *et al.*, 2008), overestimate the impact of liming on carbonic acid weathering products measured in streams, then studies of field plots (Biasi *et al.*, 2008 and this study) and laboratory soil incubations (Bertrand *et al.*, 2007) should be weighted more heavily when developing an emission factor for lime. The latter three studies found that lime is a source of CO_2, in disagreement with the current USDA emission factor of -0.04 Mg CO_2-

C emissions per Mg lime-C (Ogle *et al.*, 2014). On the other hand, the IPCC GHG Tier 1 inventory method's emission factor of 0.12 Mg CO_2-C emissions per Mg lime-C (or 100%) is likely an overestimate given that liming has potential to sequester some C. Therefore the U.S. EPA emission factor of 0.059 Mg CO_2-C emissions per Mg lime-C (or 50%) (USEPA, 2017b), may be closer to reality, but more plot and field-based studies are needed to verify the 0.059 value.

Liming will continue in step with N fertilizer use in the future to meet rising food demand. As climate change progresses, bringing greater rainfall variability worldwide and drier growing seasons in the US Midwest, the spatial extent and intensity of irrigation are expected to expand. Both liming and irrigation have important implications for agricultural soil chemistry and C balance. Irrigation has the potential to improve IC sequestration in agricultural soils, but more work is needed to understand the mechanisms of these effects and how farm management practices can encourage IC sequestration. Continued long term monitoring of soil leachate at the RGE, including a randomized and replicated lime addition treatment across the RGE N treatments, and new measurements at existing nitrogen and irrigation experiments will provide crucial insights to improve our estimates of the net C balance of liming and irrigation practices.

APPENDIX

Table A.1.1 Water, fertilizer and lime treatments at the Resource Gradient Experiment. Table continued on next page.

Block	Plot	Water treat-ment	N treat-ment	Corn N rate (kg ha^{-1})	Soy N rate (kg ha^{-1})	2012 Soy N rate (kg ha^{-1})	Wheat N rate (kg ha^{-1})	2012 Lime (ton ac^{-1})	2012 Lime (Mg ha^{-1})
1	101	Rainfed	F1	0	0	0	0	0	0.0
1	102	Rainfed	F2	34	0	17	22	0	0.0
1	103	Rainfed	F3	67	0	34	45	1	2.2
1	104	Rainfed	F4	101	0	51	67	0	0.0
1	105	Rainfed	F5	134	0	67	90	0	0.0
1	106	Rainfed	F6	168	0	84	112	1	2.2
1	107	Rainfed	F7	202	0	101	134	0	0.0
1	108	Rainfed	F8	246	0	123	157	2.5	5.6
1	109	Rainfed	F9	291	0	146	179	2	4.5
2	201	Rainfed	F7	202	0	101	134	2	4.5
2	202	Rainfed	F2	34	0	17	22	0	0.0
2	203	Rainfed	F1	0	0	0	0	0	0.0
2	204	Rainfed	F5	134	0	67	90	0	0.0
2	205	Rainfed	F3	67	0	34	45	1	2.2
2	206	Rainfed	F9	291	0	146	179	2	4.5
2	207	Rainfed	F8	246	0	123	157	2	4.5
2	208	Rainfed	F4	101	0	51	67	1	2.2
2	209	Rainfed	F6	168	0	84	112	2	4.5
3	301	Rainfed	F9	291	0	146	179	2	4.5
3	302	Rainfed	F3	67	0	34	45	0	0.0
3	303	Rainfed	F8	246	0	123	157	1	2.2
3	304	Rainfed	F2	34	0	17	22	0	0.0
3	305	Rainfed	F4	101	0	51	67	0	0.0
3	306	Rainfed	F5	134	0	67	90	1	2.2
3	307	Rainfed	F7	202	0	101	134	1	2.2
3	308	Rainfed	F6	168	0	84	112	2	4.5
3	309	Rainfed	F1	0	0	0	0	1	2.2
4	401	Rainfed	F5	134	0	67	90	1	2.2
4	402	Rainfed	F6	168	0	84	112	2	4.5
4	403	Rainfed	F4	101	0	51	67	0	0.0
4	404	Rainfed	F1	0	0	0	0	0	0.0
4	405	Rainfed	F8	246	0	123	157	2	4.5
4	406	Rainfed	F2	34	0	17	22	0	0.0
4	407	Rainfed	F3	67	0	34	45	0	0.0
4	408	Rainfed	F7	202	0	101	134	2	4.5
4	409	Rainfed	F9	291	0	146	179	2	4.5

Table A.1.1 (cont'd)

Block	Plot	Water treat-ment	N treat-ment	Corn N rate (kg ha^{-1})	Soy N rate (kg ha^{-1})	2012 Soy N rate (kg ha^{-1})	Wheat N rate (kg ha^{-1})	2012 Lime (ton ac^{-1})	2012 Lime (Mg ha^{-1})
5	501	Irrigated	F1	0	0	0	0	0	0.0
5	502	Irrigated	F2	34	0	17	22	0	0.0
5	503	Irrigated	F3	67	0	34	45	0	0.0
5	504	Irrigated	F4	101	0	51	67	0	0.0
5	505	Irrigated	F5	134	0	67	90	0	0.0
5	506	Irrigated	F6	168	0	84	112	0	0.0
5	507	Irrigated	F7	202	0	101	134	0	0.0
5	508	Irrigated	F8	246	0	123	157	0	0.0
5	509	Irrigated	F9	291	0	146	179	1	2.2
6	601	Irrigated	F7	202	0	101	134	0	0.0
6	602	Irrigated	F2	34	0	17	22	0	0.0
6	603	Irrigated	F1	0	0	0	0	0	0.0
6	604	Irrigated	F5	134	0	67	90	0	0.0
6	605	Irrigated	F3	67	0	34	45	0	0.0
6	606	Irrigated	F9	291	0	146	179	1	2.2
6	607	Irrigated	F8	246	0	123	157	1	2.2
6	608	Irrigated	F4	101	0	51	67	0	0.0
6	609	Irrigated	F6	168	0	84	112	0	0.0
7	701	Irrigated	F9	291	0	146	179	2	4.5
7	702	Irrigated	F3	67	0	34	45	0	0.0
7	703	Irrigated	F8	246	0	123	157	2	4.5
7	704	Irrigated	F2	34	0	17	22	0	0.0
7	705	Irrigated	F4	101	0	51	67	0	0.0
7	706	Irrigated	F5	134	0	67	90	0	0.0
7	707	Irrigated	F7	202	0	101	134	1	2.2
7	708	Irrigated	F6	168	0	84	112	0	0.0
7	709	Irrigated	F1	0	0	0	0	0	0.0
8	801	Irrigated	F5	134	0	67	90	0	0.0
8	802	Irrigated	F6	168	0	84	112	0	0.0
8	803	Irrigated	F4	101	0	51	67	0	0.0
8	804	Irrigated	F1	0	0	0	0	0	0.0
8	805	Irrigated	F8	246	0	123	157	0	0.0
8	806	Irrigated	F2	34	0	17	22	0	0.0
8	807	Irrigated	F3	67	0	34	45	0	0.0
8	808	Irrigated	F7	202	0	101	134	0	0.0
8	809	Irrigated	F9	291	0	146	179	1	2.2

Table A.1.2. Mean soil pH and standard error (SE) at the Resource Gradient Experiment. NA values in the pH column mean there was no plot at that treatment combination and in the SE column mean there was only one plot at that treatment combination. (Table continues on next page.)

	N	Rainfed				Irrigated			
	treat-	Not limed		Limed		Not limed		Limed	
Year	**ment**	**pH**	**SE**	**pH**	**SE**	**pH**	**SE**	**pH**	**SE**
	F1	6.4	0.09	6.1	NA	6.70	0.04	NA	NA
	F2	6.5	0.07	NA	NA	6.65	0.09	NA	NA
	F3	6.4	0.10	6.1	0.0	6.53	0.11	NA	NA
	F4	6.5	0.15	6.2	NA	6.47	0.09	NA	NA
2011	F5	6.4	0.12	6.0	NA	6.45	0.05	NA	NA
	F6	NA	NA	5.9	0.0	6.58	0.05	NA	NA
	F7	6.5	NA	5.8	0.2	6.60	0.06	6.1	NA
	F8	NA	NA	5.7	0.1	6.40	0.00	6.0	0.10
	F9	NA	NA	5.5	0.1	NA	NA	6.0	0.11
	F1	6.6	0.13	6.4	NA	7.29	0.09	NA	NA
	F2	6.8	0.10	NA	NA	7.02	0.13	NA	NA
	F3	6.5	0.17	6.6	0.1	7.10	0.05	NA	NA
	F4	6.6	0.07	6.8	NA	7.20	0.10	NA	NA
2012	F5	6.5	0.04	6.7	0.1	7.06	0.08	NA	NA
	F6	NA	NA	6.4	0.1	7.25	0.08	NA	NA
	F7	6.3	NA	6.4	0.0	7.21	0.08	7.1	NA
	F8	NA	NA	6.3	0.1	7.06	0.14	7.2	0.23
	F9	NA	NA	6.1	0.1	NA	NA	7.0	0.15
	F1	6.0	0.13	5.7	NA	6.83	0.07	NA	NA
	F2	6.2	0.10	NA	NA	6.55	0.08	NA	NA
	F3	5.9	0.23	6.1	0.1	6.63	0.12	NA	NA
	F4	6.1	0.10	6.4	NA	6.66	0.12	NA	NA
2013	F5	6.0	0.06	6.1	0.1	6.57	0.06	NA	NA
	F6	NA	NA	6.2	0.0	6.70	0.10	NA	NA
	F7	6.0	NA	6.1	0.0	6.57	0.01	6.5	NA
	F8	NA	NA	5.9	0.0	6.38	0.05	6.5	0.29
	F9	NA	NA	5.8	0.1	NA	NA	6.5	0.09
	F1	6.4	0.11	5.7	NA	6.76	0.16	NA	NA
	F2	6.5	0.18	NA	NA	6.70	0.11	NA	NA
	F3	6.5	0.21	6.5	0.4	6.62	0.18	NA	NA
	F4	6.4	0.31	7.0	NA	6.64	0.20	NA	NA
2014	F5	6.2	0.10	6.3	0.1	6.55	0.11	NA	NA
	F6	NA	NA	6.3	0.2	6.50	0.20	NA	NA
	F7	6.3	NA	6.1	0.2	6.41	0.21	6.8	NA
	F8	NA	NA	6.5	0.2	6.20	0.19	6.6	0.15
	F9	NA	NA	6.5	0.2	NA	NA	6.2	0.31

Table A.1.2 (cont'd)

Year	N treat-ment	Rainfed				Irrigated			
		Not limed		Limed		Not limed		Limed	
		pH	SE	pH	SE	pH	SE	pH	SE
2015	F1	6.2	0.14	6.6	NA	6.87	0.04	NA	NA
	F2	6.3	0.03	NA	NA	6.86	0.08	NA	NA
	F3	6.3	0.00	6.5	0.0	6.83	0.07	NA	NA
	F4	6.4	0.06	6.7	NA	6.83	0.04	NA	NA
	F5	6.2	0.05	6.6	0.0	6.75	0.03	NA	NA
	F6	NA	NA	6.5	0.0	6.77	0.06	NA	NA
	F7	6.2	NA	6.4	0.0	6.75	0.08	6.8	NA
	F8	NA	NA	6.3	0.0	6.66	0.01	6.8	0.15
	F9	NA	NA	6.3	0.0	NA	NA	6.8	0.04
2016	F1	6.6	0.14	6.8	NA	7.39	0.04	NA	NA
	F2	6.7	0.05	NA	NA	7.33	0.04	NA	NA
	F3	6.7	0.10	7.1	0.0	7.16	0.16	NA	NA
	F4	6.7	0.09	7.3	NA	7.29	0.06	NA	NA
	F5	6.5	0.02	7.0	0.0	7.19	0.06	NA	NA
	F6	NA	NA	7.1	0.1	7.23	0.14	NA	NA
	F7	6.7	NA	7.1	0.0	7.23	0.03	7.3	NA
	F8	NA	NA	6.8	0.0	6.84	0.26	7.3	0.31
	F9	NA	NA	6.8	0.1	NA	NA	7.2	0.06
2017	F1	5.9	0.15	6.4	NA	6.98	0.05	NA	NA
	F2	6.2	0.08	NA	NA	6.87	0.07	NA	NA
	F3	6.0	0.10	6.5	0.0	6.91	0.04	NA	NA
	F4	6.0	0.10	6.7	NA	6.89	0.06	NA	NA
	F5	5.7	0.01	6.2	0.2	6.93	0.04	NA	NA
	F6	NA	NA	6.2	0.1	6.94	0.05	NA	NA
	F7	6.0	NA	6.2	0.1	6.85	0.04	7.1	NA
	F8	NA	NA	6.0	0.2	6.65	0.14	7.0	0.04
	F9	NA	NA	6.0	0.2	NA	NA	7.0	0.04

Table A.1.3. Co-variates excluded from Model 1 due to auto-correlation, lack of parsimony, and/or did not improve the amount of variation explained by the model.

Excluded co-variate	Variable type	Basis for excluding from model
Block	Factor	Aliased correllated with N treatment and Irrigation
Yield	Continuous (standardized and not standardized by annual mean)	Correllated with N and irrigation, does not improve R^2, if substitute N with yield, lower R^2
Irrigation	Factor	Performs nearly as well as irrigation continuous (mm) continuous but R^2 0.02 lower and BIC higher.
Crop	Factor	Autocorrelated with year. Year better predictor than crop (much higher R^2)
Lime	Continuous (2012 only)	Does not separate limed vs. unlimed plots in other years
Lime.YN	Factor all years	Performs nearly as well as lime (continuous, all years), slightly lower R^2, slightly lower BIC
Irr.mm year	Interaction	Irr (mm) differs by year for IRR plots
N*year	Interaction	N differs by year

Chapter 2 Intensification with irrigation: The net carbon cost of groundwater irrigation at an intensively farmed site in the upper US Midwest

ABSTRACT

Groundwater irrigation is expanding worldwide with poorly known implications for climate change, including its net carbon (C) impact. I measured in a randomized complete block experiment the impact of groundwater irrigation on processes that affect greenhouse gas emissions and determined the net global warming impact of irrigating a corn (maize)-soybean-wheat no-till cropping system in the upper US Midwest, which produces the majority of US corn, soybeans, and wheat. Irrigation significantly increased soil organic C as well as inorganic C stores, but not by enough to make up for the CO_2-equivalent (CO_2e) costs of fossil fuel power, soil nitrous oxide (N_2O) emissions, and evasion to the atmosphere of CO2 and N_2O formerly dissolved in groundwater. A rainfed reference system had a net mitigating effect of -13.9 (± 31) g CO_2e m^{-2} yr^{-1}, but with irrigation at an average rate for the region, the irrigated system was a contributor to global warming with net emissions of 22.6 (± 31) g CO_2e m^{-2} yr^{-1}. Irrigation-associated emissions comprised 30% of the system's total emissions, the majority of which were from increased fossil fuel and soil N_2O emissions (42% and 30%, respectively, of irrigation-associated emissions). However the irrigated system's impact when normalized by crop yield was +0.03 (±0.01) kg CO_2e kg^{-1} yield, much closer to that of the rainfed system, -0.03 (±0.002) kg CO_2e kg^{-1} yield. Intensifying crop yield per unit irrigation water, nitrogen fertilizer, and land area could mitigate this positive feedback between irrigation and climate change but could mean depletion of local water resources.

INTRODUCTION

Global food security depends on irrigation to expand arable land area, intensify crop production, and provide a buffer from increasingly hot and dry growing seasons (Turral *et al.*, 2011). The recent expansion of irrigated acreage is expected to continue in coming decades in response to changing climate, growing populations, and increasing food consumption per capita (Konikow, 2011, Wada *et al.*, 2010). Irrigation accounts for 90% of global consumptive water use, at least half of which is groundwater (Siebert *et al.*, 2010), contributing to worldwide groundwater depletion (Famiglietti, 2014, Gleeson *et al.*, 2012) and sea level rise (Konikow, 2011). Irrigation can affect the global warming impact of agriculture (Mosier *et al.*, 2005, Mosier *et al.*, 2006, Sainju, 2016, Sainju *et al.*, 2014, Trost *et al.*, 2013, Trost *et al.*, 2016), which is a major source of greenhouse gas emissions to the atmosphere (IPCC, 2014). However the few existing studies do not account for all potential sources and sinks or represent the US Midwest (discussed below), and the impacts of irrigation are not accounted for in the greenhouse gas (GHG) inventory methods of the Intergovernmental Panel on Climate Change (IPCC) or US Environmental Protection Agency (De Klein *et al.*, 2006, USEPA, 2017b).

Irrigation has the potential to alter greenhouse gas (GHG) emissions and soil organic C storage. Theory predicts and studies have shown that irrigation encourages soil microbial processes like denitrification, which produce nitrous oxide (N_2O) (Hutchinson & Mosier, 1979, Panek *et al.*, 2000, Robertson & Groffman, 2015, Trost *et al.*, 2013)—a GHG with 298 times the global warming potential of carbon dioxide (CO_2) and a major driver of stratospheric ozone depletion (Myhre *et al.*, 2013). Also, crop responses to irrigation increase productivity and organic matter inputs to soil, which can enhance accumulation of soil organic C (SOC) as well as decomposition of SOC (Lal, 2004).

In addition, another three effects on GHG need to be considered for groundwater-fed irrigation. Fossil fuel-derived energy is commonly required to pump groundwater and drive sprinkler irrigation systems (West & Marland, 2002). The partial pressures of GHGs dissolved in groundwater can be far greater than atmospheric equilibrium, resulting in evasion to the atmosphere during irrigation (Aufdenkampe *et al.*, 2011, Turner *et al.*, 2015, Wood & Hyndman, 2017). GHG evasion is not accounted for in previous studies nor are inorganic carbon reactions. In arid systems, where annual precipitation is less than annual evapotranspiration, evapotranspiration of groundwater produces CO_2 when calcium carbonate ($CaCO_3$) precipitates (Schlesinger, 2000). In humid systems, liming and irrigation with alkaline groundwater can potentially increase carbonic acid dissolution of carbonates, a net carbon sink (Hamilton *et al.*, 2007, Chapter 1, this volume).

Few studies have considered the implications of irrigation for GHG balances. Schlesinger (2000) explored the general concept of the global warming impact (GWI) of irrigation in drylands, accounting for CO_2 evasion from groundwater, increased SOC sequestration, fossil fuel emissions, and carbonate precipitate formation. Mosier *et al.* (2005) and Mosier *et al.* (2006) calculated the GWI of irrigation in a Colorado corn-soybean system, accounting for soil GHG emissions, fossil fuels, nitrogen (N) fertilizer production, and SOC. They found that fossil fuels were the major source of emissions, but no-till management with irrigation sequestered more CO_2 as SOC than the sum of CO_2-equivalent (CO_2e) GHG emissions. Neither of these studies, however, provided a rainfed control that would allow a calculation of irrigation impacts. Others (Jin *et al.*, 2017, Sainju, 2016, Sainju *et al.*, 2014, Trost *et al.*, 2016) have assessed the GWIs of irrigated cropping systems and found that irrigation accounted for a major portion of emissions, sometimes offset by increases in SOC accrual, but none have included GHG evasion from groundwater or inorganic carbon sequestration.

To date there have been no studies of the GWI of irrigation in the US Midwest, in contrast to other studied regions (Trost *et al.*, 2013), a major omission considering the US Midwest produces about 60% of the corn and soybeans in the US and 10% of the wheat (USDA NASS, 2014b). Twelve percent of annual US corn and soybean production is irrigated, 25% of which is in the Midwest (USDA NASS, 2014b). Irrigated acreage in the Midwest is expected to increase as summer rainfall declines and the number of dry days increase (Georgakakos *et al.*, 2014, Pryor *et al.*, 2014); irrigated acreage in Michigan alone increased by nearly 20% between 2007 and 2012 (USDA NASS, 2014a).

Here I investigated how groundwater-fed irrigation affects the net GWI of a Midwestern no-till cropping system, directly comparing irrigated and rainfed systems in a randomized complete block design. I included in my assessment GHG evasion from applied groundwater, changes in SOC and soil inorganic C, changes in soil N_2O emissions, and the CO_2 cost of energy used for pumping.

BACKGROUND

Surface water bodies are known to be a source of methane (CH_4), CO_2 and N_2O emissions as they tend to be supersaturated with these greenhouse gases (GHGs). In the case of headwater streams, the majority of these emissions can result from groundwater inputs (Beaulieu *et al.*, 2011, Hotchkiss *et al.*, 2015, Turner *et al.*, 2015, Werner *et al.*, 2012, Wood &

Hyndman, 2017). Groundwater can accumulate CH_4, CO_2, and N_2O along its flowpath as the result of microbial methanogenesis, respiration, and denitrification, respectively (Kaushal *et al.*, 2014, Wood & Petraitis, 1984). These GHGs evade the surface water in order to equilibrate with the atmosphere.

The magnitude of these emissions can be significant. CH_4 emissions from all inland waters was estimated to be equivalent to 25% of the terrestrial GHG sink (Bastviken *et al.*, 2011). From a review of the literature, Aufdenkampe *et al.* (2011) found that the median pCO_2 in temperate streams was ten times that of the atmosphere and median outgassing was 9.64 kg CO_2 m^{-2} yr^{-1}. A square meter of water can have greater CO_2 fluxes than nearby soil GHG emissions; but the small surface area of streams relative to soil means streams' total emissions are relatively small. Similarly, Beaulieu *et al.* (2008) found that N_2O emissions from streams in southwest Michigan were on average 144 g CO_2e m^{-2} yr^{-1}, which is significant but again, minor relative to the surface area of agricultural soils. N_2O emissions from agricultural soils make up ¾ of N_2O emissions in the US (USEPA, 2017a). The IPCC, U.S. EPA, and U.S. Department of Agriculture (USDA) GHG inventory methodologies account for downstream emissions of N_2O from fertilizer N runoff and leaching, including enhanced leaching with irrigation, but not emissions due to accelerated groundwater outgassing with irrigation (De Klein *et al.*, 2006, Ogle *et al.*, 2014, USEPA, 2017b). In a recent proof of concept paper, Wood and Hyndman (2017) argue that groundwater depletion and the CO_2 it releases could be 1.7 million metric tons CO_2 per year (MMT yr^{-1}) in the US. CH_4 and N_2O releases from groundwater-fed irrigation could also be significant, but have not been estimated or measured. Groundwater-fed irrigation short-circuits its natural flow path, bypassing processes in headwater streams that may consume

GHGs, and enhancing the rate of groundwater exposure to the atmosphere and total GHG evasion in a watershed.

Certain agricultural management practices can encourage, or discourage, soil organic C (SOC) accrual. Plowing agricultural soils and its enhancement of SOC decomposition may have contributed 30-35% to the elevated atmospheric CO_2 since 1750 (Follett, 2001, Lal, 2008). Therefore re-sequestering that C in the soil is a potentially substantial C sink. Practices that directly encourage SOC sequestration do so by increasing C inputs, like residues and roots, or by reducing C losses via SOC decomposition (Lal, 2004, Paul *et al.*, 2015, Paustian *et al.*, 2016, Robertson & Grandy, 2006, West & Marland, 2002). For example, no-till management enables aggregation and protection of organic C from microbial respiration (Six *et al.*, 2000). In a long-term experiment in Michigan, no-till management sequestered 122 g CO_2e m^{-2} yr^{-1} (Syswerda *et al.*, 2011).

Efficient irrigation has been considered a potential mechanism for enhancing SOC sequestration in arid systems by increasing crop biomass and residues (Follett, 2001, Paustian *et al.*, 2016, Trost *et al.*, 2013). Lal (2004) estimated that the world's irrigated soils could sequester 0.037-0.11 Gt CO_2e yr^{-1}. But greater soil moisture also encourages microbial decomposition compared to dry soil (Stockmann *et al.*, 2013). In a review of studies measuring SOC in irrigated vs. non-irrigated systems, Trost et al. (2013) found that irrigation on desert soil can increase SOC by more than two-fold; however changes were minimal or even negative in humid regions. Even though irrigation increased crop biomass in humid regions, the microbial community in the wetter soils had a greater capacity to decompose additional C inputs (De Bona *et al.*, 2008, Trost *et al.*, 2014). Irrigation can affect the balance between SOC inputs and outputs, but only a few studies like this are available in humid areas—none in the US (Trost *et al.*, 2013).

Microbial denitrification plays another potentially important role in irrigation's GWI. In low oxygen conditions, such as water filled soil pore spaces and within soil aggregates, many facultative denitrifiers switch from aerobic respiration to denitrification where nitrate rather than oxygen reduces organic C (Robertson & Groffman, 2015). N_2O emissions increase exponentially with N fertilizer addition (Shcherbak *et al.*, 2014), and agriculture contributes 78% of total anthropogenic N_2O emissions in the US (USEPA, 2017a). The net GWI of a rainfed cropping system tends to be determined by the strength of SOC sequestration relative to N_2O emissions (Gelfand & Robertson, 2015, Robertson *et al.*, 2000). In an irrigated cropping system in Colorado, N_2O emissions were about half the amount of emissions associated with energy production for pumping the water, which dominated the system's net GWI (Mosier *et al.*, 2005). The few studies incorporating a direct comparison of N_2O emissions from irrigated and non-irrigated fields generally show that irrigation increases N_2O emissions (Trost et al. 2013; cf. Trost et al. 2016). No studies are available comparing N_2O emissions from irrigated and rainfed cropping systems in the U.S. Midwest.

Fossil fuels are another major contributor to net GWI in rainfed (Gelfand and Robertson 2015), and even more so in irrigated, cropping systems (Mosier *et al.*, 2005, Sainju *et al.*, 2014, Trost *et al.*, 2016). West and Marland (2002) estimated that groundwater pumping using electricity to then apply 0.4 m of water to one ha requires 5.32 GJ of energy or 13.3 GJ ha^{-1} m^{-1} irrigation water.

Finally, inorganic C reactions can also be a source or sink for CO_2. Using soil leachate chemistry, I showed in Chapter 1 that irrigation increased opportunities for carbonic acid (H_2O + CO_2) in the soil to react with the groundwater's bicarbonate (HCO_3^-), sequestering CO_2 as additional HCO_3^-, following this reaction:

$$CaCO_3(s) + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad \text{Eqn. 1}$$

(Hamilton *et al.*, 2007). Soil water HCO_3^- in excess of hydrogen ions (i.e., alkalinity) is conserved along its flowpath to the ocean, which can take decades to centuries, qualifying it as a potential C sink (Hamilton *et al.*, 2007, Lal, 2008, Oh & Raymond, 2006, Wood & Hyndman, 2017). Alternatively, when nitric acid (HNO_3, a product of nitrification) dissolves carbonate minerals CO_2 is produced:

$$CaCO_3 + 2HNO_3 \rightarrow Ca^{2+} + 2NO_3^- + H_2O + CO_2 \qquad \text{Eqn. 2}$$

(Hamilton *et al.*, 2007). Inorganic C can also produce CO_2 when evapotranspiration (ET) concentrates groundwater salts, including calcium (Ca^{2+}) and HCO_3^-, which precipitate, producing CO_2 as Eqn. 1 proceeds right to left (Schlesinger, 2000, Wood & Hyndman, 2017). In arid environments, where 100% of irrigation likely evapotranspires, one mole of CO_2 is produced with each mole of $CaCO_3$. If the Ca^{2+} concentration in groundwater is 0.04 g L^{-1} in an arid system, ET and the above reaction would produce 44 g CO_2e m^{-2} yr^{-1} m^{-1} irrigation water (Schlesinger 2000). ET and Eqn. 1 (right to left) can occur with groundwater-fed irrigation in humid environments, but later in the year precipitation, infiltration, and recharge re-dissolves the $CaCO_3$: Eqn. 1 would proceed left to right, consuming CO_2, and making the reaction C-neutral on an annual time scale.

As noted earlier, the IPCC and EPA GHG inventory methods do not account for GHG emissions associated with irrigation. However, the USDA GHG inventory method accounts for irrigation's effect on SOC change, soil N_2O emissions, and fossil fuel consumption. The method uses a process-based simulation model that accounts for irrigation method, amount, and timing, among other management practices to estimate SOC change and N_2O emissions (Ogle *et al.*, 2014). Soil moisture and other variables control how the model simulates SOC decomposition and N_2O emissions. The USDA inventory also estimates CO_2 emissions from fossil fuel-derived electricity consumption on farms, some of which is energy for pumping groundwater (Duffield, 2016). Annual energy expense data for farms are divided by energy prices to estimate energy use. Because this estimate is not broken down by operation (e.g., irrigation) I am unable to discern patterns in irrigation energy use over time and space. None of the three inventory methods (IPCC, EPA or USDA) account for GHG evasion by irrigation or inorganic C reactions (Eqn. 1).

METHODS

Study site

We conducted this study at the Michigan State University Kellogg Biological Station (KBS), located in southwest Michigan (42° 24′ N, 85° 24′ W, elevation 288 m) and the northern US Corn Belt. Mean annual precipitation from 1987-2010 at KBS was 1007 mm, half of which fell as snow (NOAA, 2017). Mean summer and winter temperatures from 1987-2010 were 22^{o}C and -2.6^{o}C, respectively. Oct through Apr precipitation exceeds evapotranspiration, and annual recharge is 280 mm (Hamilton et al. 2007). The site is located on a nearly level glacial outwash plain resulting from the Wisconsin ice sheet retreat ~18,000 years ago (Robertson & Hamilton, 2015). Soils are moderately fertile, well-drained loams (Typic Hapludalfs) developed on glacial outwash with intermixed loess (Crum & Collins, 1995, Luehmann *et al.*, 2016). KBS's and the surrounding county's crop yields are similar to US Midwest averages (Robertson *et al.*, 2015).

This study was conducted at the KBS LTER Resource Gradient Experiment (RGE) and draws on data from the adjacent KBS LTER Main Cropping System Experiment (MCSE) (Robertson & Hamilton, 2015). The RGE is managed as a no-till corn (*Zea mays L.*)-soybean (*Glycine max L.*)-wheat (*Triticum aestibum L.*) rotation and includes irrigated and rainfed treatments while the MCSE is managed identically but rainfed; a previous life cycle analysis at the MCSE provides a GWI for the rainfed no-till cropping system (Gelfand & Robertson, 2015). The RGE was established in 2005 and includes nine N fertilization treatments (F1-F9) replicated across eight blocks, half of which are irrigated with groundwater (irrigation details below).

The RGE rainfed N treatment F6 matches the management of the no-till treatment at the MCSE. For the present study, I focus mainly on RGE treatment F6 to best compare to the MCSE. N fertilizer in F6 is added to corn (168 kg N ha-1 yr-1) and wheat (112 kg N ha-1 yr-1). When F6 data were unavailable, I used F5 where fertilization treatments in corn, soybean, and wheat years are 134, 0, and 90 kg N ha^{-1}, respectively. For corn and wheat years between 2005-2013 liquid urea ammonium nitrate (UAN, 28-0-0) was broadcast with a sprayer. In 2012 the F6 soybeans were fertilized with UAN at 84 kg N ha^{-1}. From 2014 to 2017 UAN was knifed 13-15 cm below the soil surface. The F6 rates are similar to the state averages: in 2016 the average application rate for corn gown in Michigan was 136 kg N ha^{-1} (USDA NASS, 2017). Lime was applied in 2012 as a management practice rather than experimentally, where each plot received 0, 2.2, or 4.5 Mg dolomitic lime ($CaMg(CO_3)_2$) ha^{-1} (0, 1, or 2 ton ac^{-1}) based on soil pH. Rainfed plots and plots with higher N fertilization tended to receive more lime than the others.

Growing season (Apr – Sep) precipitation and irrigation totals since 2005 show a severe drought (336 mm) during the 2012 growing season, and 2017 was almost as dry (363 mm) (Figure 2.1). From 2005 – 2011 irrigation was applied using solid set irrigation and was

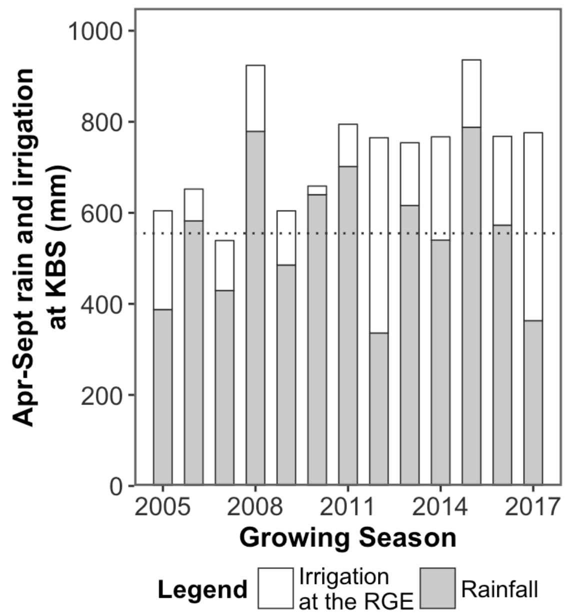

Figure 2.1. Growing season (Apr-Sep) rainfall and irrigation amounts at the Kellogg Biological Station's Long Term Ecological Research Resource Gradient Experiment. The dotted line is mean growing season rainfall over the period shown (555 mm). Labeled years are corn years, followed by soybeans and wheat. The 2012 growing season had a severe drought and 2017 was almost as dry.

scheduled using the rainfall deficit, which calculates the amount of irrigation needed using the difference between average rainfall and received rainfall. Since 2011 irrigation has been applied using a linear move irrigation system (Model 8000, 360^{o} drops every 3 m, total length 70 m, Valley Irrigation, Valley, NE, US) and scheduled using a soil water budget. The Systems Approach to Land Use Sustainability (SALUS) model was used to estimate evapotranspiration for the budget (Basso & Ritchie, 2015). SALUS models crop growth as well as environmental processes accounting for soils, management practices, and weather. It was developed and has been validated at KBS (Basso & Ritchie, 2015). For the soil water budget, SALUS simulated daily maximum evapotranspiration (ET_{max}) data using KBS weather data from 1984-2010 and crop-specific growth and development data from the MCSE annual crops. Daily ET_{max} is the date- and crop-specific average of a 100-year SALUS simulation. The sum of ET_{max}, daily precipitation, and irrigation is positive when soil water is available and negative when there is a deficit—similar to irrigation schedulers or checkbooks promoted by Michigan State University Extension (Kelley & Miller, 2016). Irrigation is scheduled following two consecutive days of a soil water deficit and the amount applied replaces the previous days' deficit. Total irrigation per season at KBS is similar to the average amount of irrigation applied to commercial corn fields in southwest Michigan, 0.18 m (7 in) as reported by Michigan Dept. of Ag. & Rural Development (2015 Pers. Comm.) and southwest Michigan farmers (Chapter 3, this volume).

GHG evasion from groundwater

Two KBS groundwater wells were sampled for dissolved CO_2 and N_2O: one that provides irrigation water for the RGE and another used for irrigation at the KBS pasture dairy. These wells were sampled four times over the 2016 growing season, and the RGE well was sampled ten times over the 2017 growing season. In the summer of 2016, additional wells were sampled from the surrounding southwest Michigan region: five within a 10 km radius of KBS (Kalamazoo River watershed) and 17 in the St. Joseph River watershed. In St. Joseph County, within the St. Joseph watershed, 73% of corn cropland is irrigated (USDA NASS, 2014a). Water samples were collected at each gas sampling event.

The gas sample collection method followed that of Hamilton and Ostrom (2007). At each well, samples were collected after the pump had been running for at least 15 min. Well pumps typically had a sample valve or hose that allowed us to draw 30 mL of water into a 60 mL gas tight syringe. To ensure the sampled water was not exposed to the atmosphere, the water was drawn through a narrow piece of polypropylene tubing attached to the syringe and inserted directly inside the pump valve or inserted below the surface of an overflowing bucket filled by a hose. Then I drew 30 mL of ambient air into the same syringe and gently shook the syringe for five minutes to achieve equilibration. I then injected 10 mL of the headspace gas into a 5.9 mL glass vial (now over-pressurized) capped with a rubber septum (Exetainer, Labco Ltd, High Wycombe, UK). Gas samples were collected in triplicate at each site along with a fourth sample of ambient air. I recorded the temperature of the water in the syringe and the air.

Gas samples were stored at room temperature and analyzed at KBS within 30 days on a gas chromatograph (Agilent 7890, Agilent Technologies, Santa Clara, CA, US). CO_2 was detected with a Licor 820 Infrared Gas Analyzer coupled to the GC and N_2O with a 63Ni electron capture detector at 350oC. The GC was coupled to a Gerstel MPS2XL automated headspace sampler (Gerstel, Mülheim an der Ruhr, Germany). The system had a two-column back-flush configuration using Restek PP-Q 1/8"OD, 2.0mm ID, 80/100 mesh, 3 m packed columns (Restek, Bellefonte, PA, US). The oven was set to 90oC. CH4 concentrations were negligible and are not included here.

The dissolved CO_2 and N_2O concentration calculations followed those of Hamilton and Ostrom (2007). The Bunsen solubility coefficient, Henry’s Law, and the Ideal Gas Law were used to calculate the gas concentration in the original water sample, accounting for the contribution from the original headspace (ambient air) gas concentrations (Weiss, 1974, Weiss & Price, 1980). Then, I estimated the amount of gas dissolved in the water when it infiltrated the soil assuming it was in equilibrium with the atmosphere and subtracted this from the original water sample's gas concentration to estimate the amount of additional gas the water accumulated as it flowed through the unsaturated and saturated zones. Finally, the reported amount of gas that evades the groundwater upon equilibration with the atmosphere at irrigation is the difference between the atmospheric equilibrium concentration and the original water sample's concentration, converted to g CO_2e m^{-2} yr^{-1} using the annual amount of irrigation. N_2O was converted to CO_2 equivalents (CO_2e) by multiplying by a factor of 298—the global warming potential of N_2O relative to CO_2 over a 100-year period used by the IPCC in national GHG inventories (Myhre *et al.*, 2013).

SOC

The difference between SOC in the irrigated and rainfed treatments was used to estimate change in SOC due to irrigation (sensu Syswerda et al. 2011). In Nov 2016, soils were collected using a double cylinder, 5.08 cm diameter hammer corer (AMS Soil Corer Model 404.05, American Falls, Idaho). For each core the 0-10 cm and 10-25 cm depths were collected separately. The 25 cm depth represents the no-till A horizon (Syswerda *et al.*, 2011). Deeper soils were not sampled as previous studies have shown that significant decadal SOC change at this site has occurred only in the upper soil profile (Kravchenko & Robertson, 2011, Syswerda *et al.*, 2011). Three cores were collected per plot and analyzed separately. I sampled the two depths in F1 (unfertilized), F5 (~average N fertilization), and F8 (high N fertilization) plots from four blocks, two of which were rainfed and two irrigated (n=72). Soil bulk density (g cm^{-3}) was calculated using oven-dry soil weight and core volume (Elliott *et al.*, 1999). Soils were sieved through a 4 mm mesh to remove roots and debris, then pulverized using a shatterbox (SPEX SamplePrep 8530 Enclosed Shatterbox, Metuchen, New Jersey), and analyzed with a CHN analyzer (Costech Elemental Combustion System CHNS-O ECS 4010, Valencia, California). The CV for all replicate CHN samples was <10% (<5% in most cases). Soil C concentration was converted to kg C m^{-2} using bulk density. Rainfed SOC was subtracted from its irrigated N treatment counterpart, then divided by the 12 years of the experiment (2005-2016), and by the total m irrigation over that period to provide kg SOC m^{-2} area yr^{-1} m^{-1} irrigation water. I conducted regression analysis to determine the effect of irrigation on SOC.

Soil N_2O emissions

From 8 May to 6 Sept 2013, soil N_2O emissions were measured simultaneously in one rainfed and one irrigated block for N treatments F1, F3-F6, and F8 (*n*=10 chambers). N fertilizer was applied on 13 May 2013 and wheat was harvested on 19 Jul 2013. Between those dates, 138 mm of irrigation water was applied. N_2O emissions were measured with an automated chamber system similar to Rowlings *et al.* (2012). Briefly, chambers were connected to an automated sampling system and a trailer-mounted gas chromatograph. Each 0.5 × 0.5 m stainless steel chamber base was inserted 10 cm into the soil so that the base was flush with the soil surface. The chamber (0.5 × 0.5 × 0.15 m), fitted with an automated, pneumatic lid, was attached to the base. Headspace gas was pumped to the GC (SRI Instruments, SRI 8610C, Torrance, CA, US) fitted with a ^{63}Ni electron capture detector for N_2O analysis (stainless steel column with Hayesep N: 2 m, 1/8 inch, 60/80 mesh, Alltech, US) in an oven at 60°C delivering gas at 30 mL min^{-1} to a detector at 330°C, with N_2 5.0 UHP carrier gas (Linde, US). Each chamber was closed for 48 min. per incubation with four gas measurements per incubation and four incubations per chamber over each 24 hours. Two chambers were closed for incubations simultaneously, so one full closure cycle for the ten chambers involved five closure periods. The GC analyzed three N_2O standards at the beginning and end of each full cycle and a N_2O check standard between each individual closure period. Incubations were automatically aborted and chambers opened during rain and irrigation events to avoid the effect of water exclusion. Because flux was calculated on average four times per day, the data include over 400 flux measurements per chamber during the May – Sep 2013 period.

Hourly flux rates of N_2O (μg N_2O–N m^{-2} h^{-1}) were calculated from the linear part of the relationship between N_2O peak area (concentration) and chamber closure time (minutes), and corrected for air temperature, pressure and the ratio of chamber headspace volume to soil surface area using the equation:

$$\mu g\ N_2O - N\ m^{-2}h^{-1} = \frac{\alpha V W_A * 60}{A M V_{corr}} \qquad \text{Eqn. 3}$$

Where α is the change in headspace concentration during chamber closure period (ppmv min^{-1}), V is the headspace volume of the chamber (in L), W_A is the atomic mass of nitrogen in N_2O (28.0), 60 is the conversion from minutes to hours, A is the soil surface area covered by the chamber (m^2), and MV_{corr} is the temperature- and pressure-corrected mol volume (in L). I conducted regression analysis to determine the effect of irrigation on soil N_2O flux. The regression includes daily precipitation and mean temperature from the LTER weather station archive (https://lter.kbs.msu.edu/datatables/7). Daily irrigation amounts were recorded in the narrative agronomic log for the RGE (https://lter.kbs.msu.edu/datatables/299).

Fossil fuel emissions from pumping

The EPA Power Profiler (USEPA, 2017c) provides the % of energy that comes from oil, natural gas, coal, and other energy sources by postal code (KBS is in 49060). The US Energy Information Administration (2017) reports source-specific CO_2 emissions per GJ energy. West and Marland (2002) provide an estimate of the energy required to pump groundwater (13.3 GJ ha^{-1} m^{-1} irrigation water), used also in Mosier et al. (2005) and Sainju et al. (2014). I used the % energy from fossil fuels, CO_2 emissions per GJ of fossil fuel energy (specific to each type of fossil fuel), and energy required to pump from the well to the sprinkler at the site to calculate total fossil fuel CO_2 emissions per m of pumped groundwater for irrigation.

Inorganic C fluxes

Considering the stoichiometry of Eqns. 2 and 3, the comparison of HCO_3^- relative to Ca^{2+} and Mg^{2+} indicates net CO_2 production or sequestration in HCO_3^- resulting from carbonate dissolution when carbonate minerals are the main source of Ca^{2+} and Mg^{2+}, as is the case at my study site (Hamilton et al. 2007). In addition to concentrations, I used the volume of water percolating downward from the root zone (drainage volume) to estimate inorganic C export. To estimate percolation, the SALUS water balance submodel simulated root water uptake from the crop growth module, which along with precipitation, temperature, and irrigation, provided daily rates of evapotranspiration, surface runoff (negligible at KBS), infiltration, and drainage. For more details on SALUS see Basso and Ritchie (2015). Annual inorganic C GWI was calculated using the daily drainage rates from SALUS and interpolated daily HCO_3^- Ca^{2+}, and Mg^{2+} concentrations, assuming half of the HCO_3^- came from CO_2 as in Eqn. 2. I assumed $CaCO_3$

precipitate formation was net C neutral in Michigan's humid climate.

Net irrigation impacts

We calculated net irrigation GWI for two different irrigation scenarios at KBS: 0.18 m, which is the average annual irrigation amount for southwest Michigan (R. Pigg, Michigan Department of Agriculture and Rural Development, 2015 Pers. Comm.), and 0.43 m, which was the amount applied at KBS during the 2012 drought and the maximum applied to date. These irrigation scenarios are hereafter referred to as average and dry. I assume a linear relationship between irrigation amount and process rates. I estimated the impact of irrigation on the total GWI of the KBS LTER no-till cropping system by adding the irrigation GWIs measured here to the known GWI for the KBS LTER rainfed no-till system (Gelfand & Robertson, 2015). Finally, I calculated the cropping systems' GHG intensity (GHGI, kg CO_2e kg^{-1} yield): I divided the total system emissions and sinks (kg CO_2e ha^{-1} yr^{-1}), separately, calculated from each year's irrigation amount (if irrigated) by each year's annual crop yield (kg ha^{-1} yr^{-1}) for 2005-2016 at the F6 plots (*n*=4 rainfed, *n*=4 irrigated). GHGIs were averaging by crop with five years of corn and four years of both soybean and wheat data.

Multiple linear regression analyses were conducted in R version 3.4.2 (R Core Team, 2017) using package ggplot2 for plotting (Wickham, 2009).

RESULTS

Mean dissolved CO_2 concentrations among the irrigation wells sampled in the KBS, Kalamazoo, and St. Joseph areas were 27.9 (±1.9) mg L^{-1}, 20.8 (±3.2) mg L^{-1}, and 14.2 (±1.2) mg L^{-1}, respectively (Table A.2.1), ranging from 2.6 – 73.0 mg L^{-1} (1,800-40,600 ppmv). Mean dissolved N_2O-CO_2e concentrations in the KBS, Kalamazoo, and St. Joseph wells were 14.2 (±1.0) mg L^{-1}, 3.7 (±0.9) mg L^{-1}, and 1.5 (±0.4) mg L^{-1}, respectively (Table A.2.1), ranging from 0 – 47.7 mg L^{-1} (0-26,000 ppmv). The GWI of evasion of CO_2 and N_2O dissolved in groundwater at KBS in the average and dry irrigation scenarios was 7.0 and 16.8 g CO_2e m^{-2} yr^{-1}, respectively (Figure 2.2). KBS groundwater had somewhat higher mean concentrations of N_2O and nitrate (9.8±0.2 mg NO_3^--N L^{-1}) than the other wells I sampled (3.7±1.4 mg NO_3^--N L^{-1}) (Figure A.2.1).

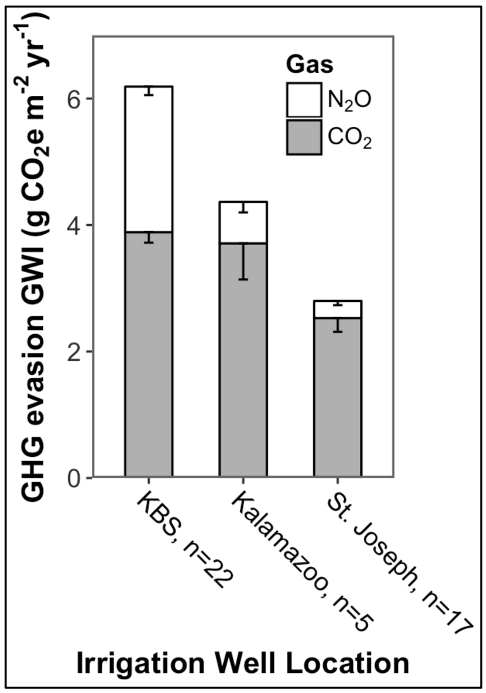

Figure 2.2. Greenhouse gas evasion from groundwater global warming impact for an average irrigation year (0.18 m applied). The KBS bar represents 22 measurements (not including sample replicates) from two irrigation wells at KBS. The Kalamazoo and St. Joseph bars represent the 5 and 17, respectively irrigation wells sampled in the Kalamazoo River and St. Joseph River watersheds, respectively. Error bars represent the standard error of the mean of all replicates per region per gas (only showing lower SE bar to avoid overlapping bars).

SOC pools in the irrigated plots were significantly greater than in the rainfed plots (Table A.2.2). The following model accounted for 79% of the variability in SOC and is significant (p<0.001):

$$kg\ SOC\ m^{-2} \sim irrigation * lime + irrigation * depth + N\ fertilizer$$

Eqn. 4

(Figure 2.3, Table 2.1). According to the model, the upper 25 cm of irrigated soils had 2.45

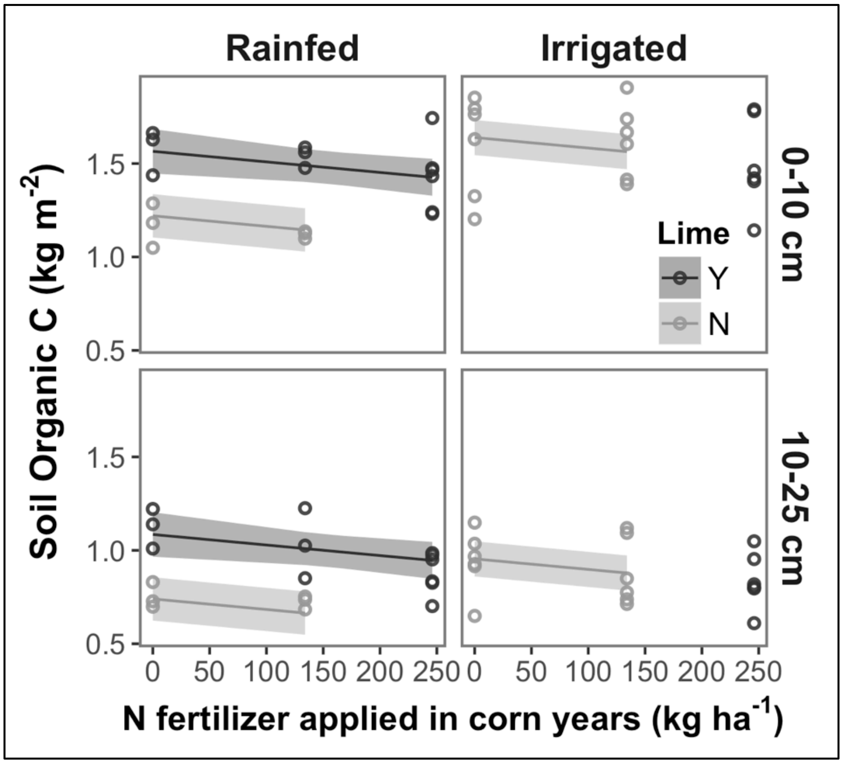

Figure 2.3. Soil Organic C (SOC) at the Resource Gradient Experiment in N fertilization treatments F1, F5, and F8. Points are individual cores (jittered on the x-axis to improve visibility). Lines and shaded areas represent the model mean predictions and 95% confidence interval, respectively (Table 1.1).

(95% CI: [2.23, 2.67]) kg SOC m^{-2} while rainfed soils had 2.15 [1.95, 2.35] kg SOC m^{-2}. Meaning irrigated soils had accumulated on average 0.30 kg SOC m^{-2} over 12 years or 25 g SOC m^{-2} yr^{-1} more than the rainfed soils. Depth (0-10 cm vs. 10-25 cm), irrigation, and lime (yes/no) were significant categorical variables, while N fertilization rate in corn was a significant continuous variable. The variables lime, irrigation, and N fertilization rate were also significant predictors of soil pH (Chapter 1, this volume). Hence, SOC can be modeled almost as well using simply depth and pH: SOC was positively correlated with pH, negatively correlated with depth (model R^2=0.69 and model p<0.0001). Predictions of the SOC model included: (1) SOC pools in the

Table 2.1. Regression analysis predictors of soil organic C pools (SOC, kg C m^{-2}) and soil N_2O emissions (g N_2O-N ha^{-1} d^{-1}) at the Resource Gradient Experiment (RGE).

	Estimate	SE	t-value	Pr(>|t|)	% of $R^{2,a}$	Adj. R^2
SOC Model: kg C m^{-2} ~IRR*lime+ IRR*depth + N fert.				**<0.001**		**0.79**
Ref. levels: Rainfed, No lime, Depth 0-10 cm, 0 N fert.						
(Intercept)	1.22	0.06	21.1	<0.001	--	
Irrigated	0.42	0.07	6.0	<0.001	3	
Yes lime	0.34	0.06	5.5	<0.001	3	
Depth 10-25 cm	-0.48	0.06	-8.7	<0.001	83	
N fert.(kg/ha) corn years	-0.0006	0.0003	-2.2	<0.05	2	
Irrigated : Yes limed	-0.33	0.09	-3.9	<0.001	6	
Irrigated : Depth 10-25 cm	-0.20	0.08	-2.6	<0.05	3	
Soil N_2O Model: (N_2O flux)$^{1/3}$~Wet/dry day + Temp. + IRR + N fert.*Harvest date + N Fert. date				**<0.001**		**0.32**
Ref. levels: Dry day, Rainfed, 0 N fert., Before harvest, > 10 days after N fert.						
(Intercept)	0.18	0.01	13.9	<0.001	--	
Wet day	0.06	0.01	11.9	<0.001	26	
Mean daily temp. (^{o}C)	-0.0014	0.0006	-2.4	<0.05	1	
Irrigated	0.05	0.00	10.8	<0.001	21	
N fert. (kg/ha) wheat	0.0005	0.0001	7.1	<0.001	26	
After harvest	0.02	0.01	2.3	<0.05	9	
≤10 days after N fert.	0.09	0.01	9.4	<0.001	14	
N fert.: After harvest	0.0004	0.0001	3.5	<0.001	2	

[a]Relative importance as a percent of adjusted R^2.

upper rainfed and irrigated soils (0-10 cm) were 0.48 and 0.68 kg m^{-2} greater than in the 10-25 cm soils, respectively (i.e., rainfed and irrigated soils accumulated 40 g SOC m^{-2} yr^{-1} and 57 g SOC m^{-2} yr^{-1} faster, respectively, than 10-25 cm soils); (2) liming increased SOC by 29 g m^{-2} yr^{-1} in rainfed plots and by 0.8 g m^{-2} yr^{-1} in irrigated plots; and (3) N fertilization in rainfed and irrigated plots reduced SOC by 5 g m^{-2} yr^{-1} per 100 kg fertilizer-N ha^{-1}. The difference between estimated SOC in irrigated F5 plots and rainfed F5 plots for the total sample depth (0-25 cm) reached 0.30 kg SOC m^{-2} (average of limed and unlimed effects) over 12 years (or 25 g SOC m^{-2} yr^{-1}) and 1.91 m irrigation water. Therefore, the irrigation SOC GWI in an average irrigation year at KBS (0.178

m of water applied) was -8.5 g CO_2e m^{-2} yr^{-1}.

Soil N_2O flux was significantly higher in the irrigated plots. The following model explained 27% of the variability and is significant (p<0.001):

$$\left(N_2O\text{-}N\ g\ ha^{-1}d^{-1}\right)^{\frac{1}{3}} \sim (wet\ or\ dry\ day) + daily\ mean\ temp + (rainfed\ or\ irr.) + N\ fert.rate * harvest + (limed\ or\ not\ limed) + N\ fert.date \qquad \text{Eqn. 5}$$

(Figure 2.4, Table 2.1). N_2O flux was cube-root transformed to improve its right-skewed distribution. Units are as follows: measurements were categorized into dry and wet days depending on whether that plot received 0 or >0 mm rainfall and/or irrigation, respectively; daily mean temperature is ^oC; N fertilization rate is kg N ha^{-1}; harvest is a factor for before or after 19 Jul 2017; lime is yes or no; fertilization date is a factor grouping the date N fertilizer was applied and the 10 days following it versus all other dates. N_2O flux increased on wet days and with N fertilization rate. The positive relationship with N fertilization rate was steeper after harvest. N_2O emissions decreased at higher mean daily temperatures and were greater in limed plots and during the period of N fertilization. N_2O emissions in irrigated plots were significantly greater than in rainfed plots by 0.05 g N_2O-N ha^{-1} d^{-1} (Table 1).

Instead of using these N_2O measurements from one season as the absolute amount by which irrigation increases N_2O, I used them to calculate a % increase in N_2O emissions due to irrigation and applied this to 20 years of N_2O flux measurements at the rainfed corn-soybean-wheat no-till plots at the KBS LTER MCSE, reported in Gelfand *et al.* (2016). In my model, the N_2O emissions in the F6 irrigated plots were on average 55% (0.02 g N_2O-N ha^{-1} d^{-1}) higher than

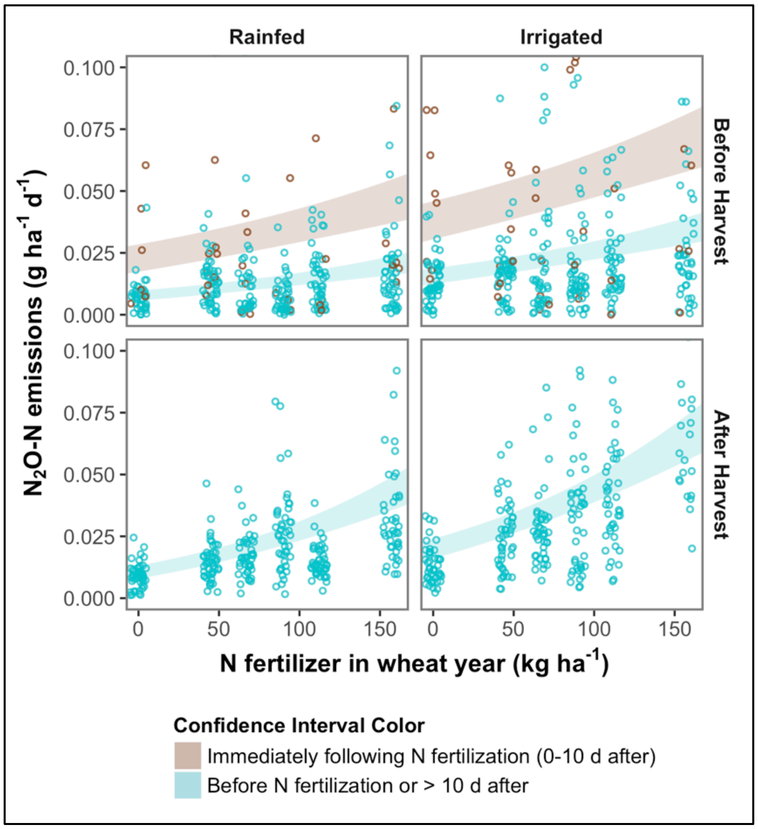

Figure 2.4 Soil N_2O-N emissions at the Resource Gradient Experiment across six N fertilization levels in 2013, a wheat year in the corn-soybean-wheat rotation. Color indicates when the measurement was taken with respect to the N fertilizer application date. The y-axis is scaled to include the lower 95% of data. The ribbons indicate the model's 95% confidence interval for the mean (Table 2.1).

F6 rainfed plots. Dividing this % change by the 0.138 m of irrigation water applied in the 2013 growing season means a 4-fold increase in N_2O emission per m irrigation water. If we apply this to the average annual N_2O emission rate (in g CO_2e m^{-2} yr^{-1}) for the three rainfed rotational crops as reported in Gelfand *et al.* (2016), then irrigation with 0.18 m water increased annual N_2O emissions by 28.1 g CO_2e m^{-2} yr^{-1}.

Fossil fuel CO_2 emissions were calculated using the following % energy from fossil fuels for the KBS area: 1.2% from oil, 15% from natural gas, and 60% from coal (assumed bituminous) (US Energy Information Administration, 2011). The remaining 24% was from nuclear (16%) and non-hydro renewables (6.7%). The fossil fuel percentages were multiplied by the energy required for each irrigation scenario, and CO_2 emissions per source were calculated and summed for total fossil-fuel CO_2 emissions. The fossil fuel CO_2 emissions for the energy required for irrigation are 81.0 g CO_2 m^{-2} m^{-1} of water in agreement with Schlesinger (2000). For an average irrigation season at KBS irrigation fossil fuel emissions were 14.4 g CO_2 m^{-2} yr^{-1}.

Inorganic C fluxes in irrigated plots indicated significantly more carbonic acid weathering of carbonate minerals than in the rainfed plots, resulting in greater C sequestration as dissolved HCO_3^- rather than CO_2 production that would result from strong acid dissolution of carbonate minerals (Hamilton et al., 2007 and Chapter 1). At fertilizer treatment F6 the GWI of inorganic C was -25.4 g CO_2e m^{-2} yr^{-1} per m of irrigation water. In the average irrigation scenario, the GWI of the F6 treatment was -4.5 g CO_2e m^{-2} yr^{-1}.

The net GWIs of irrigation in the average and dry scenarios at KBS were 36.5 and 87.9 g CO_2 m^{-2} yr^{-1}, respectively (Figure 2.5, Table 2.2).

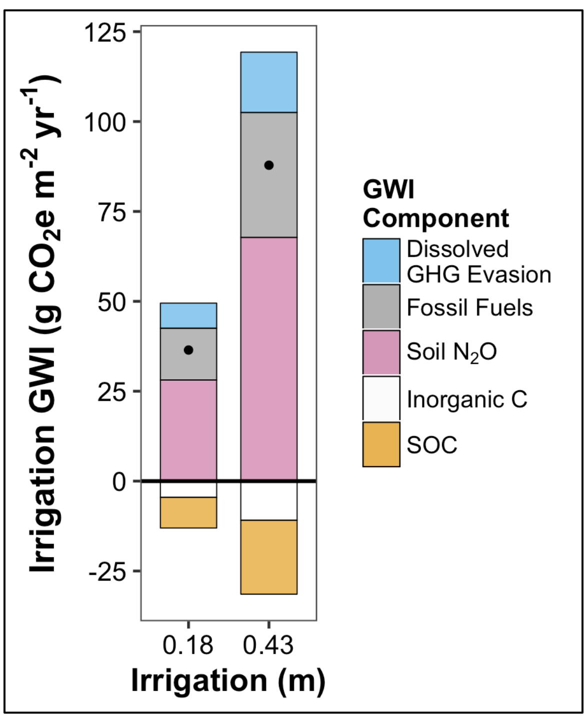

Figure 2.5. Irrigation global warming impact (GWI) for normal and dry scenarios. Points indicate the net GWI of irrigation.

Table 2.2. The global warming impact (GWI) for irrigation at KBS in the average and dry year scenarios.

Irri-gation (m)	*Global Warming Impact (GWI, g CO_2e m^{-2} yr^{-1})*					
	GHG evasion	Fossil fuels	Inorganic C seq.	SOC	Soil N_2O	Irrigation net GWI
0.18	7.0 (±0.2)	14.4	-4.5 (±1.5)	-8.5 (±2.6)	28.1 (±0.1)	36.5 (±2.6)
0.43	16.8 (±0.6)	34.7	-10.9 (±3.7)	-20.5 (±6.2)	67.8 (±0.3)	87.9 (±6.2)

The net GWI for the KBS no-till cropping system without irrigation was -13.9 g CO_2 m^{-2} yr^{-1} (Figure 2.6, Table 2.3,) (Gelfand & Robertson, 2015); whereas the to net GWI for the irrigated no-till treatment in the average and dry year scenarios was +22.6 and 74.0 g CO_2 m^{-2} yr^{-1}, respectively.

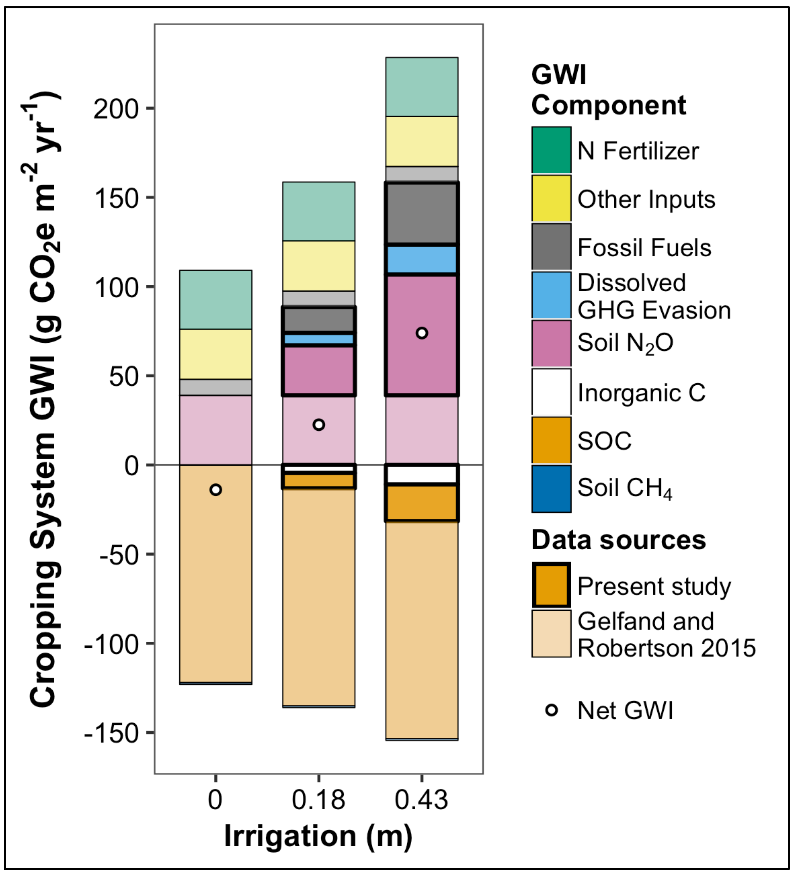

Figure 2.6. Complete GWI for KBS no-till cropping systems with three irrigation scenarios: rainfed, average (0.18 m), and dry (0.43 m) growing seasons. "Other inputs" includes P and K fertilizers, lime, seeds, and pesticides (Table 2.3). These and N fertilizer amounts were the same in rainfed and irrigated plots at the RGE. Soil CH_4 consumption was -1 g CO_2e m^{-2} yr^{-1}.

Table 2.3. Global warming impact (GWI, g CO_2e m^{-2} yr^{-1}) of no-till management at the Kellogg Biological Station (KBS) with and without irrigation.

	Global Warming Impact (GWI, g CO_2e m^{-2} yr^{-1})												
	Components affected by irrigation					*Other inputs*							
Irrigation scenario	**GHG evasion**	**Fossil fuels**	**N_2O**	**SOC**	**SIC**	**N fert.**	**Lime**	**P**	**K**	**Seed**	**Pest**	**CH_4**	**Net**
Rainfed	0.0	9.0	39 (±3)	-122 (±31)	0.0	33	4	0.3	1.3	7	15.5	-1 (±0)	-13.9 (±31)
Average (0.18 m)	7.0 (±0.2)	23.4	67.1 (±3)	-130.5 (±31)	-4.5 (±1.5)	33	4	0.3	1.3	7	15.5	-1 (±0)	22.6 (±31)
Dry (0.43 m)	16.8 (±0.6)	43.7	106.8 (±6.2)	-142.5 (±31)	-10.9 (±3.7)	33	4	0.3	1.3	7	15.5	-1 (±0)	74.0 (±31)

The net GHG intensity (GHGI, GWI Mg^{-1} yield) of the rainfed and irrigated systems was -0.03 (±0.002) and +0.03 (±0.01) kg CO_2e kg^{-1} yield yr^{-1}, respectively, as a rotational mean from 2005-2017 (Figure 2.7, Table 2.4).

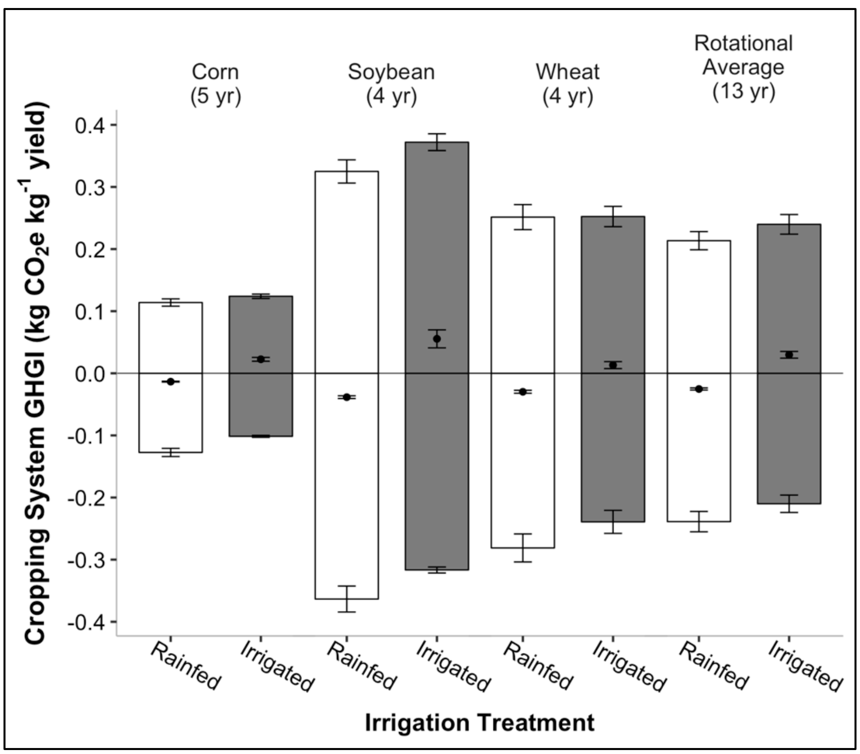

Figure 2.7. Greenhouse gas intensity (GHGI) for the irrigated and rainfed cropping systems at the RGE from 2005-2017. Each year's GHGI incorporates that year's irrigation amount and yield from 4 replicate plots at F6 fertilizer level.

Table 2.4. Mean greenhouse gas intensity (GHGI) at the KBS Resource Gradient Experiment from 2005-2017 (five corn years, four years of both soybean and wheat) using each year's irrigation amount (if irrigated) and mean yield of four replicate F6 plots.

Crop	Irrigation Treatment	Mean GHG Intensity (kg CO_2e kg^{-1} yield) (±SE)		
		Emissions	Sinks	Net
Corn	Rainfed	0.11 (±0.01)	-0.13 (±0.01)	-0.01 (±0.001)
	Irrigated	0.12 (±0.003)	-0.10 (±0.002)	0.02 (±0.003)
Soybean	Rainfed	0.32 (±0.02)	-0.36 (±0.02)	-0.04 (±0.002)
	Irrigated	0.37 (±0.01)	-0.32 (±0.005)	0.06 (±0.01)
Wheat	Rainfed	0.25 (±0.02)	-0.28 (±0.02)	-0.03 (±0.002)
	Irrigated	0.25 (±0.02)	-0.24 (±0.02)	0.01 (±0.01)
Rotational Average	Rainfed	0.21 (±0.01)	-0.24 (±0.02)	-0.03 (±0.002)
	Irrigated	0.24 (±0.02)	-0.21 (±0.01)	0.03 (±0.01)

DISCUSSION

Groundwater-fed irrigation in a Michigan no-till cropping system was a net source of GHG emissions, despite CO_2e sequestration as SOC and HCO_3^-. In an average irrigation year, the irrigated system sequestered 11% more CO_2e than the rainfed system but emitted 43% more CO_2e (Figure 2.6). The increase in soil N_2O, fossil fuel, and GHG evasion emissions due to irrigation alone contributed 17%, 9%, and 4%, respectively, to the system's total emissions in an average irrigation year. SOC dominated sequestration, with irrigation-driven SOC accumulation adding 5% to the system's total sinks. Irrigated systems were a net source of GHGs under both scenarios investigated: an average year of irrigation (0.18 m applied) and a drought year (0.43 m applied). But when I measure the impacts using the yield-normalized GHGI both the rainfed and irrigated systems are nearly neutral.

GHG evasion from groundwater

Evasion of dissolved GHGs from irrigation water contributed 14% of the irrigation-associated GHG emissions at KBS (Figure 2.5). CO_2 emissions from groundwater samples were in a range similar to the CO_2 concentration of 10,000 ppmv in the Southern High Plains aquifer reported by Wood and Petraitis (1984). Mean CO_2 concentrations varied by a factor of two, and mean N_2O concentrations varied by a factor of eight in the same samples (Table A.2.1). KBS wells tended to have higher N_2O and nitrate concentrations than the other samples (Figure A.2.1), but the nitrate concentration (9.8±0.2 mg NO_3^--N L^{-1}) is not unusual for groundwater in US agricultural watersheds (Dubrovsky & Hamilton, 2010). Variability in concentrations of groundwater nitrate (a precursor to N_2O) in aquifers is affected by land use history, groundwater flow patterns, and electron donor availability for biogeochemical reactions (Bohlke *et al.*, 2002). The GHG evasion measurements in the present study may be conservative estimates for two reasons: 1) irrigation increases soil water content, and N_2O is highly soluble in water, so irrigation increasing soil water content slows N_2O diffusion from the soil (Shcherbak & Robertson, 2014) my dissolved GHG concentrations are well below those measured in headwater streams worldwide—where the majority of dissolved GHGs often result from groundwater inputs (Aufdenkampe *et al.*, 2011, Beaulieu *et al.*, 2008, Werner *et al.*, 2012).

SOC sequestration

Over 12 years, irrigation increased SOC in the upper 25 cm of the soil profile at the KBS RGE by 25 g m^{-2} yr^{-1}. This is an SOC pool increase of 1% per year (for a rainfed soil starting with 2.2 kg C m^{-2}), the same rate observed in the A horizon due to no-till at the KBS MCSE (Syswerda *et al.*, 2011). In the Trost et al. (2013) review, the average SOC increase in irrigated arable land compared to non-irrigated in humid climates (one study in each: Germany, Austria, Brazil, and

Ethiopia) was 2.4% over periods ranging from 8 to 60 years. When standardized by study period the average was about a 0.05% (range: -0.22% - 0.38%) increase in SOC per year. Compared to these other studies, the increase and rate of increase in SOC over time reported here seems consistent.

This increase in SOC makes up 62% of the CO_2 sequestered by irrigation at KBS, with inorganic C reactions accounting for the balance (Figure 2.5). My results demonstrate a potential link between SOC and soil inorganic C processes—liming increased SOC at KBS. Indeed, periodic liming since 1876 at the Rothamsted (UK) Park Grass Experiment increased SOC by 2-20 times compared to unlimed plots (Fornara *et al.*, 2011). Here I showed that SOC and pH are positively correlated. At KBS, irrigation seems to have increased SOC sequestration, perhaps by increasing crop productivity more than it increased decomposition. The increased SOC is also partly explained by the chemical effect of groundwater alkalinity, which increases soil pH (Chapter 1, this volume) on soil biology: Fornara et al. (2011) concluded that liming increased soil biological activity and respiration but also increased organic C incorporation into more recalcitrant forms, resulting in a net positive C sink. An additional irrigation treatment with low-alkalinity water could serve to discern the effect of alkalinity vs. higher soil water content on SOC storage in the groundwater-fed irrigation plots.

All of my irrigated plots were under no-till management; so I am unable to compare the effect of irrigation on conventionally tilled vs. no-till plots. However, in dryland agriculture irrigation can stimulate SOC loss in tilled soils, with corresponding GWI costs (Mosier *et al.*, 2006, Sainju *et al.*, 2014, Trost *et al.*, 2013).

Irrigation and no-till seem to have similar rates of change in SOC pools. The F5 irrigated soil had 15% more SOC than rainfed soils after 12 years. At the MCSE, no-till and succession increased the SOC pools by 13% and 41%, respectively, also over 12 years (Syswerda *et al.*, 2011). The eventual steady-state SOC concentrations under irrigation are not known; several of the semi-arid and arid studies included in the review by Trost et al. (2013) demonstrated that SOC concentrations and pools in irrigated cropland were larger than those under native vegetation.

Greater soil N_2O emissions

Denitrification in soil, responsible for the majority of N_2O emissions at the KBS LTER (Gelfand *et al.*, 2016, Ostrom *et al.*, 2010), apparently increased under wetter conditions as irrigation increased soil water filled pore space making the soil environment anaerobic for a greater percentage of time (Robertson and Groffman 2015). Irrigation increased soil N_2O flux by a factor of four per m irrigation compared to rainfed, accounting for 42% of the irrigation-associated GHG emissions at KBS (Figure 2.5). Soil N_2O emissions contributed the most (28.1 g CO_2e m^{-2} in an average year, Table 2.2) to switching the no-till system from a net negative GWI when rainfed to a net positive GWI in irrigated plots (Figure 2.6). In an average irrigation year, irrigation-associated N_2O emissions displaced the irrigation SOC credit for a net balance between the two of 19.6 g CO_2e m^{-2} yr^{-1}. My soil N_2O emissions model (Figure 2.4), predicted that N_2O emissions in irrigated plots at the F6 N fertilization rate were 55% greater than those in the F6 rainfed soils. Of three studies providing a rainfed-irrigated comparison of N_2O emissions with N fertilizer N_2O emissions increased by 55 to 141%, according to a review by Trost *et al.* (2013). Trost et al. (2016) found no significant change in soil N_2O emissions with irrigation in a northeast Germany small grains-potato-oilseed rape rotation, but N_2O emissions at this site are low in general due to sandy soils. A fertilized, irrigated, no-till corn-soybean system in Colorado had soil N_2O emissions of 73 g CO_2e m^{-2} yr^{-1} with 0.48 m of irrigation (but no rainfed control) (Mosier et al. 2005). With a similar amount of irrigation (0.43 m, dry scenario), my model estimates soil N_2O emissions of 96 g CO_2e m^{-2} yr^{-1} in the irrigated system.

Increased fossil fuel emissions

The CO_2 emissions from fossil fuel combustion for energy to pump the groundwater was the second largest source of GWIs after increased N_2O emissions, making up 30% of the irrigation-associated emissions. These fuel emissions more than double the total fossil fuel emissions from no-till management at KBS (Gelfand & Robertson, 2015), increasing total fossil fuel emissions from 9 to 23 g CO_2e m^{-2} in an average irrigation year. If all of the fossil fuel energy used at the KBS well came from burning natural gas, the fuel-related emissions from irrigation would drop from 14.4 to 8.9 g CO_2e m^{-2} yr^{-1} in an average irrigation year and the no-till system's net GWI would down from 19.8 to 14.3 g CO_2e m^{-2} yr^{-1}, an improvement but not enough to switch the GWI from a net source to a net sink. Of course, if the energy source were de-carbonized, the fossil fuel emissions would be closer to zero (West and Marland 2002), and the system's net GWI in an average irrigation year would be 5.4 g CO_2e m^{-2} yr^{-1}. In the KBS irrigated system, total fossil fuel emissions are equivalent to a third of the total soil N_2O emissions.

Inorganic C reactions

Inorganic C reactions were a sink for CO_2. Irrigation enhanced inorganic C dissolution by reaction with carbonic acid (Eqn. 2), sequestering the carbonic acid as bicarbonate dissolved in soil water (Chapter 1, this volume). Soil water that does not evapotranspire (or run off over land, which is minimal at KBS) percolates to the water table and continues along a decades- to centuries-long groundwater flow path before discharging to surface water bodies (Hamilton et al. 2007). Along this flowpath bicarbonate is largely conserved (Hamilton *et al.*, 2007, Lal, 2004, Raymond & Hamilton, 2018, Wood & Hyndman, 2017). At KBS irrigation in the average scenario results in net inorganic C storage of 4.8 g CO_2e m^{-2} yr^{-1} (Table 2.2), which is 38% of irrigation's CO_2 sequestration (the balance is SOC accrual). In drier climates Eqn. 2 is unlikely to provide net C storage because ET exceeds precipitation, preventing recharge, and $CaCO_3$ precipitates (Eqn. 1 in reverse). I assumed that carbonic acid dissolution of $CaCO_3$ was net neutral for C balance in humid regions like Michigan, but in a drier climate where all applied water evaporates, $CaCO_3$ formation could emit about three times as much CO_2 as evasion from groundwater (Schlesinger 2000).

Net GWI of irrigation

In the average irrigation scenario (0.18 m), irrigation was a net source at 31.6 g CO_2e m^{-2} yr^{-1} (Table 2.2), because irrigation-associated fossil fuel use, soil N_2O emissions, and groundwater de-gassing outweighed increased SOC and inorganic C sequestration. The GWI of irrigation would be expected to be higher in a hotter, drier climate with greater irrigation demand. In years like my dry scenario, for example, which may become more frequent with climate change (Georgakakos *et al.*, 2014, Pryor *et al.*, 2014), I calculated an over two-fold increase in the irrigation-associated GWI (Table 2.2). This assumes a linear rate of change in

SOC pool with time and N_2O emissions with irrigation amount. We know from other studies that SOC is a finite pool with a sequestration rate that asymptotically approaches a steady-state balance over time (West & Six, 2007). Although I cannot assess the shape of the curve for SOC accumulation at the RGE, I can estimate a potential steady-state value based on nearby unmanaged soils.

The F5 irrigated plots had 18.7 g C kg^{-1} soil, which is 10.8 g C kg^{-1} soil (or 9.9 kg CO_2e m^{-2} in the upper 0-25 cm) less than the never tilled mid-successional community at KBS on the same soil type (Syswerda et al. 2011). I showed that average annual irrigation increases SOC pools by 7.9 g CO_2e m^{-2} yr^{-1}, and Syswerda et al. (2011) demonstrated that no-till management increases SOC by 122 g CO_2e m^{-2} yr^{-1}, for a total increase of 130 g CO_2e m^{-2} yr^{-1} in the irrigated F5 no-till plots. Both of these rates apply to the first 12 years of the RGE and MCSE, respectively. If these initial rates continue it would take irrigated F5 soils at the RGE another 76 years to reach the SOC concentration of the KBS never tilled mid-successional community. Because the rate of SOC increase is likely not linear, it will slow over time, likely taking longer than 76 years.

Additionally, denitrification likely increases exponentially, not linearly, with increasing soil water filled pore space (WFPS). Bateman and Baggs (2005) found that once WFPS in an agricultural soil exceeded 70%, N_2O emissions increased dramatically. In a meta-analysis of agricultural fields across Great Britain, Dobbie and Smith (2003) showed that N_2O emissions increased exponentially with WFPS due to rainfall. Soil type, N fertilization rate, and timing of rainfall and N fertilization interacted with the rate at which N_2O emissions responded to WFPS. Thus my estimates using all available data may overestimate SOC accumulation and underestimate N_2O emissions as irrigation rate increases, making my estimates of net GWI conservative.

Net effects of the irrigated cropping system

Without irrigation, the cropping system was a net C sink (-13.9 g CO_2e m^{-2} yr^{-1}), mainly due to SOC gains under no-till management (Gelfand & Robertson, 2015). That C benefit is undone with irrigation: the same system with irrigation was a net positive GWI (19.8 g CO_2e m^{-2} yr^{-1}, Table 2.3) in an average irrigation year. As Midwest summers become hotter and drier (Georgakakos *et al.*, 2014, Pryor *et al.*, 2014), years like my dry scenario could become more common, in which case the irrigated system's net GWI increases over three-fold (Table 2.3). Irrigation-associated emissions made up 30% of the system's total emissions and irrigation-associated sequestration made up 10% of the system's total sequestration. Improving irrigation efficiency could both reduce GHG emissions and minimize groundwater extractions, although improving efficiency does not necessarily reduce extraction volumes (Pfeiffer & Lin, 2014).

Irrigation intensifies the crop yield per m^2, reducing the need for crop production (and GHG emissions) elsewhere (Burney *et al.*, 2010, Foley *et al.*, 2005, Mueller *et al.*, 2012, Tilman *et al.*, 2011, Turral *et al.*, 2011). The rotational average of net GHG intensity of the irrigated system was +0.03 (±0.01) kg CO_2e kg^{-1} yield, which is not far from that of the rainfed system (-0.03 (±0.002) kg CO_2e kg^{-1} yield) (Table 2.4). Comparing GHGI to GWI, intensification via irrigation brought the system to near neutral GHGI, and inefficient yield production in the rainfed system reduced the magnitude of its sink strength. Crop yield intensification with appropriate and efficient use of inputs such as irrigation and N fertilizer can achieve economic viability and some environmental conservation (Clark & Tilman, 2017, Millar *et al.*, 2010, Mosier *et al.*, 2006, Trost *et al.*, 2016). Intensification is not a panacea: many of the large aquifers supporting agriculture are already overexploited (Famiglietti, 2014, Gleeson *et al.*, 2012).

Including Irrigation Impacts in GHG Inventory Methods

In contrast to IPCC GHG reporting methodologies (De Klein *et al.*, 2006), USDA GHG inventory methods (Ogle *et al.*, 2014) account for irrigation's effect on SOC as well as emissions of soil N_2O and fossil-fuel CO_2. These three components of irrigation's GWI had the largest absolute values in the present study, suggesting they are the appropriate components to prioritize for inclusion in GHG inventories. We do not yet have a generalizable understanding of inorganic C fluxes associated with irrigation to make predictions at regional or national scales (cf. Chapter 1, this volume). However, we do have the means to include GHG evasion from groundwater. In the present study, GHG evasion made up 14% of irrigation-associated GHG emissions. In order to account for this on a national scale, we need to know the concentration of dissolved GHGs in aquifers used for irrigation and the amount of irrigation water applied. For the former, we need to survey aquifers to measure their dissolved GHG concentrations; I found here that CO_2 varied two-fold and N_2O varied eight-fold across just one region of Michigan.

Conclusions

Irrigation is a means of adapting to climate change but, as we've demonstrated, can also be a net source of GHG emissions. GHG evasion from groundwater and increased soil N_2O and fossil-fuel CO_2 emissions more than counterbalanced the negative GWIs from significantly greater SOC accrual and CO_2 sequestration by inorganic C reactions. As far as I can determine, this is the first study to empirically quantify the GWI for the effect of irrigation on groundwater GHG evasion, soil inorganic C reactions, and soil N_2O emissions relative to a non-irrigated system in the US Midwest. More studies are needed to assess how these impacts vary among locations, cropping systems, and over time; and to understand the social dimensions of irrigation (Chapter 3, this volume). Irrigation should be considered in national and global GHG inventories. Intensification via irrigation can help mitigate GHG emissions from land conversion elsewhere but can have local impacts on water resources—important considerations in a world where precipitation variability and food demand are increasing.

APPENDICES

APPENDIX A: Tables

Table A.2.1. Mean CO_2 and N_2O concentrations dissolved in groundwater exceeding atmospheric concentrations, i.e., the amount of gas that is emitted from the groundwater upon equilibration with the atmosphere.

Well area	Statistic	CO_2 (mg L^{-1})	N_2O (mg L^{-1})	N_2O as CO_2e (mg L^{-1})	Total CO_2e (mg L^{-1})	GWI (g CO_2e m^{-2} yr^{-1}) Average year	Dry year
KBS	Mean (±SE)	27.9 (±1.9)	0.048 (±0.003)	14.2 (±1.0)	42.1 (±2.9)	7.6	18.1
	Range	10.1 - 73.0	0.007 - 0.160	2.2 - 47.7	-	-	-
Kala-mazoo	Mean (±SE)	20.8 (±3.2)	0.012 (±0.003)	3.7 (±0.9)	24.5 (±4.1)	4.4	10.5
	Range	4.9 - 40.3	0 - 0.034	0 - 10.1	-	-	-
St. Joseph	Mean (±SE)	14.2 (±1.2)	0.005 (±0.001)	1.5 (±0.4)	15.7 (±1.6)	2.8	6.8
	Range	2.6 - 32.0	0 - 0.030	0 - 9.1	-	-	-

Table A.2.2. Mean Soil Organic Carbon (SOC) at the Resource Gradient Experiment measured in 2016 after 12 years of treatments.

N Fert. treatment	Depth (cm)	Irrigation treatment	Mean SOC pool (kg C m^{-2}) ± SE	Mean SOC conc. (g C kg^{-1} soil) ± SE
F1	0-10	Rainfed	1.37 (± 0.1)	10.08 (± 0.85)
F1	10-25	Rainfed	0.94 (± 0.09)	7.42 (± 0.73)
F1	0-10	Irrigated	1.57 (± 0.12)	12.05 (± 1.14)
F1	10-25	Irrigated	0.95 (± 0.07)	6.73 (± 0.55)
F5	0-10	Rainfed	1.33 (± 0.1)	10.04 (± 0.77)
F5	10-25	Rainfed	0.88 (± 0.09)	6.7 (± 0.63)
F5	0-10	Irrigated	1.67 (± 0.1)	12.36 (± 0.9)
F5	10-25	Irrigated	0.86 (± 0.09)	6.33 (± 0.74)
F8	0-10	Rainfed	1.43 (± 0.08)	11.12 (± 0.86)
F8	10-25	Rainfed	0.88 (± 0.05)	6.95 (± 0.42)
F8	0-10	Irrigated	1.5 (± 0.1)	11.39 (± 0.79)
F8	10-25	Irrigated	0.84 (± 0.06)	6.58 (± 0.45)

Table A.2.3. Mean N_2O flux at the Resource Gradient Experiment measured in 2013, a wheat year.

N fert. treat-ment	N fert. kg ha^{-1}	Irrigation treatment	Wet day (yes/no)	Before or after harvest	0-10 d or > 10 d after N fert-ilization	Mean N_2O-N flux (g ha^{-1} d^{-1})	Standard error
F1	0	Rainfed	no	before	no	0.0067	0.0009
F3	45	Rainfed	no	before	no	0.0115	0.0013
F4	67	Rainfed	no	before	no	0.0124	0.0049
F5	90	Rainfed	no	before	no	0.0061	0.0011
F6	112	Rainfed	no	before	no	0.0137	0.0018
F8	157	Rainfed	no	before	no	0.0166	0.0033
F1	0	Irrigated	no	before	no	0.0128	0.0016
F3	45	Irrigated	no	before	no	0.0152	0.0012
F4	67	Irrigated	no	before	no	0.0211	0.0065
F5	90	Irrigated	no	before	no	0.0155	0.0031
F6	112	Irrigated	no	before	no	0.0218	0.0051
F8	157	Irrigated	no	before	no	0.0388	0.0085
F1	0	Rainfed	yes	before	no	0.0096	0.0036
F3	45	Rainfed	yes	before	no	0.0175	0.0030
F4	67	Rainfed	yes	before	no	0.0368	0.0182
F5	90	Rainfed	yes	before	no	0.0265	0.0144
F6	112	Rainfed	yes	before	no	0.0351	0.0161
F8	157	Rainfed	yes	before	no	0.0353	0.0157
F1	0	Irrigated	yes	before	no	0.0215	0.0070
F3	45	Irrigated	yes	before	no	0.0227	0.0051
F4	67	Irrigated	yes	before	no	0.0556	0.0224
F5	90	Irrigated	yes	before	no	0.0527	0.0248
F6	112	Irrigated	yes	before	no	0.0536	0.0177
F8	157	Irrigated	yes	before	no	0.0666	0.0243
F1	0	Rainfed	no	after	no	0.0082	0.0008
F3	45	Rainfed	no	after	no	0.0126	0.0009
F4	67	Rainfed	no	after	no	0.0152	0.0011
F5	90	Rainfed	no	after	no	0.0256	0.0031
F6	112	Rainfed	no	after	no	0.0136	0.0008
F8	157	Rainfed	no	after	no	0.0385	0.0066
F1	0	Irrigated	no	after	no	0.0115	0.0011
F3	45	Irrigated	no	after	no	0.0203	0.0018
F4	67	Irrigated	no	after	no	0.0245	0.0020
F5	90	Irrigated	no	after	no	0.0265	0.0030
F6	112	Irrigated	no	after	no	0.0453	0.0069
F8	157	Irrigated	no	after	no	0.0622	0.0074
F1	0	Rainfed	yes	after	no	0.0119	0.0016
F3	45	Rainfed	yes	after	no	0.0207	0.0030
F4	67	Rainfed	yes	after	no	0.0390	0.0109
F5	90	Rainfed	yes	after	no	0.0429	0.0130
F6	112	Rainfed	yes	after	no	0.0184	0.0026

Table A.2.3 (cont'd)

N fert. treat-ment	N fert. kg ha^{-1}	Irrigation treatment	Wet day (yes/no)	Before or after harvest	0-10 d or > 10 d after N fertilization	Mean N_2O-N flux (g ha^{-1} d^{-1})	Standard error
F8	157	Rainfed	yes	after	no	0.0378	0.0068
F1	0	Irrigated	yes	after	no	0.0190	0.0026
F3	45	Irrigated	yes	after	no	0.0371	0.0040
F4	67	Irrigated	yes	after	no	0.0738	0.0321
F5	90	Irrigated	yes	after	no	0.0855	0.0201
F6	112	Irrigated	yes	after	no	0.0759	0.0206
F8	157	Irrigated	yes	after	no	0.0958	0.0144
F1	0	Rainfed	no	before	yes	0.0170	0.0109
F3	45	Rainfed	no	before	yes	0.0378	0.0130
F4	67	Rainfed	no	before	yes	0.0075	0.0038
F5	90	Rainfed	no	before	yes	0.0170	0.0129
F6	112	Rainfed	no	before	yes	0.0086	0.0047
F8	157	Rainfed	no	before	yes	0.0400	0.0179
F1	0	Irrigated	no	before	yes	0.0364	0.0128
F3	45	Irrigated	no	before	yes	0.0316	0.0114
F4	67	Irrigated	no	before	yes	0.0236	0.0098
F5	90	Irrigated	no	before	yes	0.0451	0.0179
F6	112	Irrigated	no	before	yes	0.0504	0.0307
F8	157	Irrigated	no	before	yes	0.1004	0.0651
F1	0	Rainfed	yes	before	yes	0.0345	0.0084
F3	45	Rainfed	yes	before	yes	0.0162	0.0085
F4	67	Rainfed	yes	before	yes	0.0754	0.0383
F5	90	Rainfed	yes	before	yes	0.0061	NA
F6	112	Rainfed	yes	before	yes	0.1083	0.0370
F8	157	Rainfed	yes	before	yes	0.0702	0.0298
F1	0	Irrigated	yes	before	yes	0.0653	0.0097
F3	45	Irrigated	yes	before	yes	0.0223	0.0065
F4	67	Irrigated	yes	before	yes	0.1376	0.0146
F5	90	Irrigated	yes	before	yes	0.1379	0.0246
F6	112	Irrigated	yes	before	yes	0.2154	0.0497
F8	157	Irrigated	yes	before	yes	0.3033	0.0386

APPENDIX B: Figures

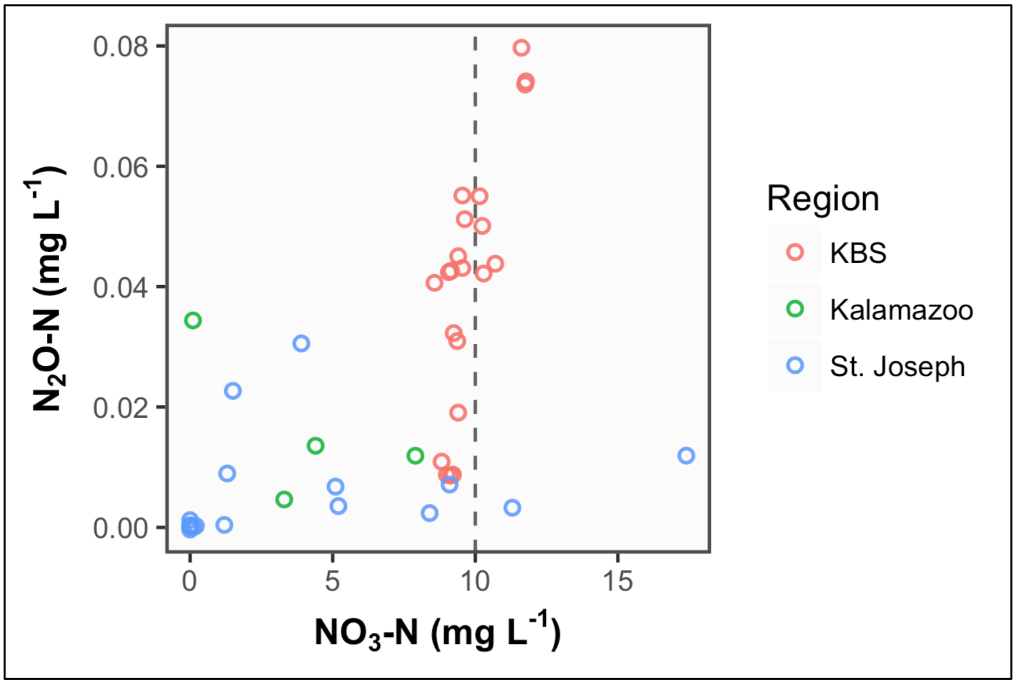

Figure A.2.1. Dissolved N_2O concentrations in groundwater across SW Michigan sampled in 2016. The dashed line indicates the USEPA water quality standard for NO_3^-. The KBS bar represents 22 measurements (not including sample replicates) from two irrigation wells at KBS. The Kalamazoo bar represents the five total measurements (not including sample replicates) from five irrigation wells sampled in the KBS vicinity (Kalamazoo River Watershed). The St. Joseph bar refers to the 17 total measurements (not including sample replicates) from 17 irrigation wells sampled in the St. Joseph River Watershed south of KBS.

Chapter 3 Irrigation and liming decisions in a Midwestern US agricultural coupled human and natural system

ABSTRACT

Agricultural liming and irrigation are important to global food security and potentially important to global carbon cycling. Lime is a carbonate material that is used to neutralize nitrogen fertilizer-associated acidity and can produce carbon dioxide (CO_2) in soil. Groundwater irrigation mitigates crop water stress but can have a positive global warming impact. If future conservation practices need to modify lime and/or groundwater irrigation practices, we need to understand how producers make these decisions. Yet few studies have examined these behaviors or put them in a social theory context. In this study irrigation and lime decision making were explored using focus groups with commercial corn producers and irrigators in southwest Michigan. At follow up farm visits, groundwater samples were collected from several participants' irrigation wells to assess spatial variability in groundwater quality; results were provided to each participant. A modified values-beliefs-norms framework is used within a coupled human and natural systems approach. Participants' perceptions of risks to crop yield was influenced by their awareness of biophysical feedbacks and framed by their stewardship identity. Perceptions of risk and macro-level constraints were directly linked to participants' decision making process. Technology mediated much of the feedbacks from biophysical to human system and vice versa; though its applicability and trustworthiness shifted with context. Producers expressed strong curiosity in biophysical processes they were unaware of. Follow up visits validated their curiosity, provided an opportunity for the researcher to "repay" them with water quality data, and built a sense of two-way learning and trust. This research provides a

first look at lime and irrigation decisions on commercial scale corn farms in the Midwest, and it demonstrates the need for a coupled human and natural systems approach to modern biogeochemistry.

INTRODUCTION

Without liming to adjust soil pH, crop production in the US Midwest would suffer, yet little is known about how agricultural producers in the Midwest make liming decisions. Likewise, irrigation is becoming increasingly important in the Midwest, but no studies exist on how Midwestern irrigators make irrigation decisions. We do know that agricultural intensification drives increasing nitrogen fertilizer use (Tilman *et al.*, 2001), which typically drives liming needs (West & McBride, 2005). Lime neutralizes soil acidity caused by nitrogen fertilizer use in agricultural soils (Brady & Weil, 2008, West & McBride, 2005). Worldwide, irrigation demand will likely increase with the rising demand for food and rainfall variability from climate change (Turral *et al.*, 2011), including the United States (US) (Georgakakos *et al.*, 2014). In the Midwest, summer rainfall is expected to decrease over time and the number of dry days is expected to increase (Pryor *et al.*, 2014). This is likely to exacerbate tensions between irrigation and water management, especially where groundwater extraction exceeds recharge or where extraction lowers stream levels (Famiglietti, 2014). In addition, liming (typically $CaCO_3$ or $CaMg(CO_3)_2$) and groundwater high in bicarbonate alkalinity (HCO_3^-) are sources of carbon to soils, whose carbon flows between soil, groundwater and the atmosphere are poorly studied (Ahmad *et al.*, 2015, Kaushal *et al.*, 2013). Producers' liming and irrigation decisions can have global implications for the carbon and water cycles.

In the Midwest, the aggregate effects of lime and irrigation decisions on carbon cycling are potentially large considering how agriculture, specifically corn production, is the dominant land use. Nearly 60% of land in the Midwest is farmland; about 1/3 of that farmland is used to grow corn for grain (USDA NASS, 2014a). Midwestern corn grain sales total over $40 billion a year, which is 60% of the US corn grain sales (USDA NASS, 2014a). Maintaining these high crop yields depends on nitrogen fertilizer (Robertson & Vitousek, 2009, Vitousek *et al.*, 1997) and its associated lime requirement. In some areas of the Midwest, like southwest Michigan, irrigation is an important water use. In Michigan, irrigation makes up the largest proportion of consumptive water use at 41% of total water use (Great Lakes Commission, 2016). Nationwide, irrigation makes up 81% of consumptive water use (Georgakakos *et al.*, 2014). Groundwater management on large scale farms in a water-rich state like Michigan is important because of localized spatial and temporal water scarcity effects on surface water levels (Mubako *et al.*, 2013). Despite the importance of lime and irrigation for food production, no studies are available on lime decision making (though a few studies have looked at the effect of decision support tools on liming practices, e.g. Walker *et al.* (2009). Studies investigating irrigator behavior in a theoretical context are available, including work by Ostrom (Ostrom, 1992, Ostrom, 1993, Ostrom & Gardner, 1993, Tang & Ostrom, 1993). However, very few studies consider irrigation with groundwater or on commercial farms or in the Midwest.

Several theories previously applied to agricultural decision making could be applicable to liming and irrigation management decisions. Arbuckle *et al.* (2015) employed Stern (2000) values-beliefs-norms (VBN) theory, which uses a linear series of variables to explain variability in environmentally significant behavior. VBN theory explains social behavior through a pathway from information into awareness that informs perceptions of the world, and perceptions of risk ultimately drive behavior (including decision making). In addition, a producers' values and beliefs define their identity, which dictates that their decisions be perceived to be in agreement with their identity (identity theory, (McGuire *et al.*, 2015, Morton *et al.*, 2017). Macro-scale forces like policy and industry standards factor into producers' decision making as well. Stuart and Gillon (2013) and Stuart *et al.* (2014a) found that competitive seed corn contracts incentivized over-application of nitrogen fertilizer, similar to an insurance policy. Additional or early irrigation could also be considered an insurance policy against crop yield losses due to water stress.

In a review of groundwater management, Mitchell *et al.* (2012) found a general lack of studies investigating groundwater user behavior that are evaluated using social theories. Acknowledging that context is critical to agricultural decision making, Mitchell *et al.* (2012) argued that the unique nature of groundwater systems and their use is inherently different from how surface water users make decisions, warranting its own branch of research. Since then, computer modeling of irrigation water demand has shown that irrigators focus their decisions on readily-available information like crop condition and water stress (Andriyas & McKee, 2014) and their decisions are impacted by limitations from well yield (i.e., application rate), supply restrictions, and perception of risk (Foster *et al.*, 2014). An irrigator's perception of water scarcity specifically could also influence their overall perception of risk to crop yield (Kummu *et al.*, 2016). Similar to Arbuckle et al. (2015), groundwater irrigators' perception of risk from anthropogenic climate change was shaped by cultural factors, which in turn determined whether they adopted water-conserving practices (Sanderson & Curtis, 2016).

Adoption of new technology to improve water use efficiency can be limited by knowledge-exchange (Levidow *et al.*, 2014) and enhanced by participation in community organizations (Ramirez, 2013). Despite these valuable insights, neither groundwater irrigation nor lime decision making for commercial scale corn production has not yet been examined using social theory.

This paper explores how corn producers in southwest Michigan make decisions regarding liming and groundwater irrigation. Previous work on nitrogen fertilizer highlights the value of understanding human decision making processes in order to fully study and better predict biogeochemical cycling (Stuart *et al.*, 2015). This approach is intended to improve our ability to manage systems more sustainably and design effective policy (Liu *et al.*, 2007). Therefore, the coupled human and natural systems (CHANS) approach is used here (in addition to theories mentioned above) to identify the iterative feedbacks between the biophysical and human systems in the context of growing corn. I conducted focus groups with large-scale (>100 ac) corn producers in southwest Michigan and used thematic analysis of responses to answer the overarching question: How do Midwestern corn producers make liming and irrigation decisions? Specifically, I address the following questions: (Q1) To what degree are producers aware of how management practices and biophysical processes affect carbon cycling and groundwater level? (Q2) Are producers' perceptions of management practices and biophysical processes shaped by their identities? (Q3) How do biophysical awareness and perceptions (Q1) contribute to lime and irrigation decision making? (Q4) How are lime and irrigation management decisions different?

Study Area

Agriculture is the dominant use of water and land across the Midwest, including in Michigan. Across Michigan's economic sectors, the amount of groundwater used for irrigation is second only to public water use; and as stated above, irrigation water use is the largest consumptive use of water in the state at 41% of total water use (Great Lakes Commission, 2016). The number of applications for a permit to drill a new agricultural irrigation well is dominated by producers in southwest Michigan (Figure 3.1).

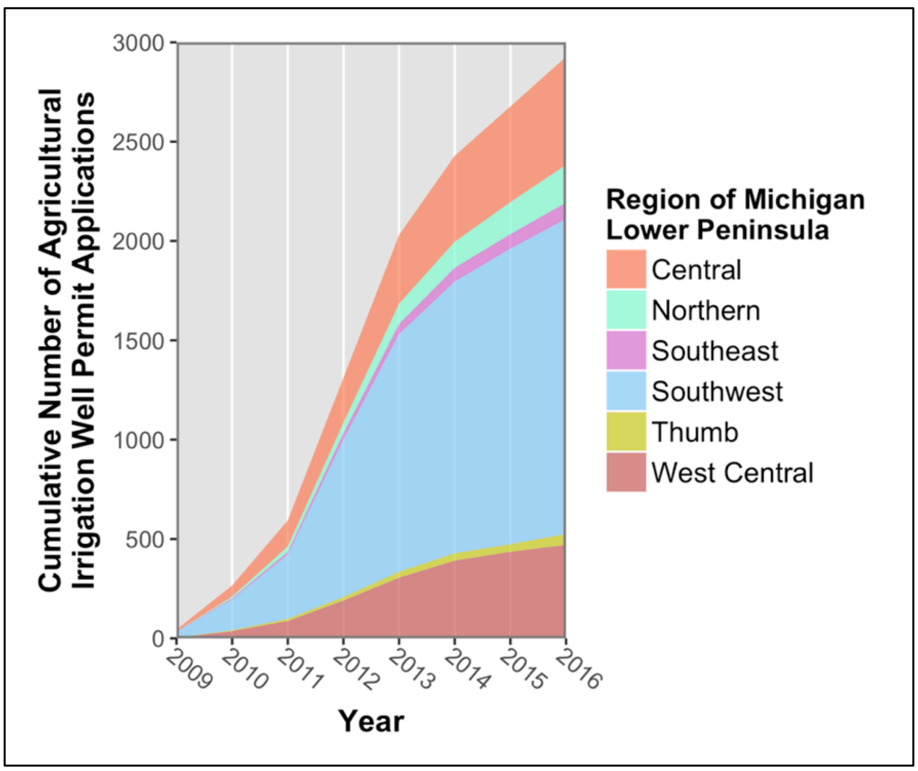

Figure 3.1. Large quantity groundwater withdrawal permit applications for agricultural irrigation by region of Michigan. Data source: Michigan Department of Environmental Quality.

This study focused on the following counties in southwest Michigan: Berrien, Calhoun, Cass, Branch, St. Joseph, and Van Buren. Irrigation is beneficial in this region, because even though rainfed crops can be productive in southwest Michigan, its soils are very coarse and have low water holding capacity (Kehew *et al.*, 1996). Across these counties, the glacial aquifer yield[1] ranges from an estimated 0.8 to over 5.3 m^3 min^{-1}; transmissivity[2] is over 17 m^3 day^{-1}; recharge ranges from 0.2 to 0.6 m yr^{-1}; and the depth to water table in the majority of this area is less than 4.5 m (GWIM, 2006, State of Michigan Public Act 148 Groundwater Inventory and Map, 2006).

These counties range from 43% cropland in Berrien County to 75% cropland in Branch County with an average of 57% (USDA NASS, 2014a). They represent over 440,000 acres of corn, 41% of which are irrigated across 465 farms (USDA NASS, 2014a). In St. Joseph County, 73% of the land area used to grow corn is irrigated (USDA NASS, 2014a). The Census of Agriculture does not differentiate between seed and commercial/grain corn, however the industry estimates there are about 100,000 acres of seed corn in southwest Michigan (Stuart & Schewe, 2016).

In Michigan, the groundwater is accessed privately and, since 2009, regulated by the state through a permitting process for the installation of new wells (Steinman *et al.*, 2011). Water scarcity in other regions of the US has spurred water-wealthy states in the Great Lakes Basin to more closely manage their use of water resources, including groundwater, to prevent out-of-basin diversions or withdrawals (Figure 3.2) (Henry, 2005, Hobbs & Osann, 2011). In this region, stream base flow is predominantly groundwater-fed, and many of these streams are characterized as cold water providing habitat for native trout populations (Steinman *et al.*, 2011, Zorn *et al.*, 2002). The connectivity between the groundwater and surface water means

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[1] Groundwater yield is the amount of water that can be removed from a well. Here it was calculated as the pumping rate at which the depth to water table drops by 50% (Michigan Dept. of Environmental Quality *et al.*, 2005).
[2] Transmissivity is the rate at which water flows horizontally through a unit of an aquifer. It is calculated as the product of hydraulic conductivity and the saturated thickness of the aquifer (Fetter, 2001).

that groundwater withdrawals can affect stream levels in the area (Mubako *et al.*, 2013, Steinman *et al.*, 2011). The potential impact of groundwater withdrawals on streams and fish characterizes a telecoupling between a human system and an indirectly linked biophysical system (Liu *et al.*, 2013). According to the regulations, Michigan landowners must get state approval for new large quantity withdrawal wells (Figure 3.1). Permit approval is determined based on the state's hydrogeological models of groundwater availability in individual subwatersheds (Steinman *et al.*, 2011). A variety of stakeholder groups have engaged in discussions with the state through an advisory council, where sustainable use (i.e. number of new wells) continues to be a contentious matter (Water Use Advisory Council, 2014). In interviews, many irrigated seed corn growers agreed that tensions around water availability and irrigation issues are likely to increase in the near future (Stuart & Schewe, 2016).

Figure 3.2. A 2001 Michigan billboard sponsored by the non-profit Citizens for Michigan's Future advocating against out-of-basin exports and diversions from the Great Lakes (Henry, 2005). State water managers have referenced this image as embodying the motivation for the Great Lakes Compact, including regulation of new large quantity withdrawal groundwater wells. Image source: http://www.waterencyclopedia.com/Ge-Hy/Great-Lakes.html.

METHODS

Due to the exploratory nature of this research, conducting focus groups using open-ended questions was more appropriate than deployment of a quantitative survey (Buckingham & Saunders, 2007). Focus groups are particularly useful for gaining insight into people's perceptions, attitudes and thinking around complicated topics (Krueger & Casey, 2009). Focus groups have been successfully implemented in many studies of agricultural decision making, (Doll *et al.*, 2017, Prokopy *et al.*, 2017, Stuart & Schewe, 2016, Stuart *et al.*, 2014a).

In the late fall of 2015, I conducted three focus groups with three to five participants each, for a total of twelve participants. By the third meeting the participants' responses were largely reiterating what was said in previous meetings, so, even though the sample size is low, increased sampling effort was deemed unnecessary for this exploratory study. I collaborated with Michigan State University Extension to recruit producers operating at least 100 acres who use irrigation and grow corn for seed, grain, or sileage. Because of this method of recruitment, the participants might not represent the full range or proportions of attitudes among the total population of their peers. The participant pool might be biased toward producers who seek out new information, more strongly identify as environmental stewards, value extension, and are open-minded and knowledgeable. Because of this the data can only be analyzed qualitatively and with certain caveats about who the results apply to. However, this method of recruitment was deemed appropriate for the exploratory, not quantitative, aims of this study. Focus group meetings were held at an MSU Extension office, county fair office, and a restaurant.

To begin the focus groups I introduced myself, and I briefly explained how the focus group would work including encouraging participants to interact with each other as well as myself. Then, participants were asked to fill out a short questionnaire detailing the size of their operations, number of acres irrigated, as well as lime, nitrogen, and irrigation types and amounts (Figure A.3.1). The questionnaire and focus group guide (Table 3.1) were first tested with farm managers at the Kellogg Biological Station (KBS). The participants in the focus groups managed over 23,600 acres of corn. The average farm size was 1,900 acres.

Because the basis for the focus groups was inorganic carbon, an unusual topic, the discussion began with a brief introduction using Figure 3.3 to illustrate inorganic carbon cycling in agricultural systems involving lime and groundwater irrigation. This introduction was

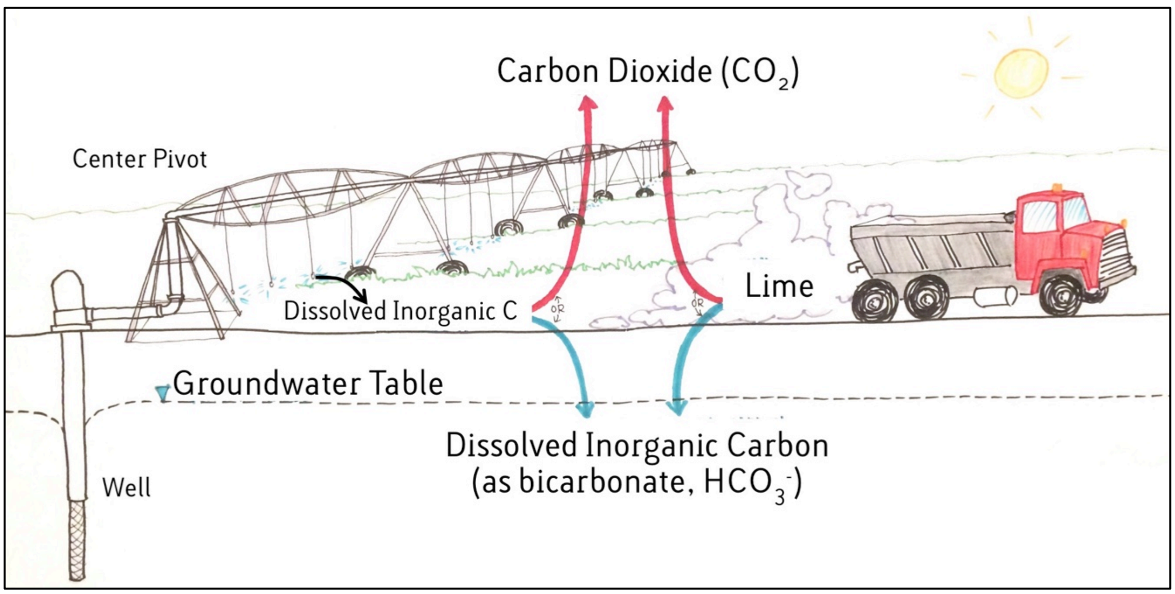

Figure 3.3. Poster board illustration used during focus groups to explain inorganic carbon cycling in row crop systems. The red and blue arrows indicate the potential fates for inorganic carbon from lime and groundwater irrigation: carbon dioxide or dissolved in soil water, respectively. The red arrows indicate a net emission of CO_2 and the blue arrows represent a net storage.

important for justifying my study and the focus group discussion questions. It also demonstrated that the researcher was a source of information, encouraging two-way questioning. In this introduction I mentioned that I calculated the amount of “dissolved lime” and nitrate applied through irrigation at KBS, using concentrations of bicarbonate and nitrate in the groundwater and volume of water applied. Between 2004 and 2015 KBS applied 1.5 m of irrigation groundwater, the equivalent of 8.7 Mg ha^{-1} (3.9 US tons ac^{-1}) and 172 kg NO_3^--N ha-1 (154 lb ac^{-1})—these numbers are relevant to the results below. Next, I asked open-ended questions about lime and irrigation management decisions (Table 3.1).

Table 3.1. Focus group guide.

Lime questions
· How do you decide <u>when your fields need</u> lime?
· How do you decide <u>how much</u> lime to apply?
· Do you notice nitrogen fertilizer affecting soil pH / lime requirements
· Do you notice irrigation affecting soil pH?
· Do you notice if the crop type affects soil pH?
· Are there other factors that also affect soil pH that I haven't mentioned?
· Have liming practices in your area changed over the last 10 to 20 years? If so, how?
Irrigation questions
· Let's compare a growing season with near normal rainfall (such as 2014 or this year) with an extremely dry (drought) growing season (such as 2012). How do you make decisions about when and how much to irrigate?
· Have irrigation practices in your area changed in the last 10-20 years? If so, how have they changed?
· Are there any questions I did not ask that I should have regarding liming or irrigation?

A secondary goal of this study's focus groups was to engage producers in a dialogue with scientists and build trust and capacity for future collaborations regarding issues like lime and controversial issues like groundwater management. Participants were asked at the end of the discussion if they would like for me to visit their farm and collect water samples from their irrigation wells. In the summer of 2016 I visited eight participants' farms and sampled 17 irrigation wells. Samples were stored on ice, filtered, and analyzed at the KBS aquatic biogeochemistry lab using standard methods for conductivity, alkalinity, pH, and major cations and anions. Note alkalinity in these waters is the concentration of bicarbonate (HCO_3^-) in excess of hydrogen ions, which is the equivalent of "dissolved lime."

The questionnaire data were entered into a spreadsheet, and the totals and averages are summarized in Table A.3.1. These numbers are only used here to describe participants' farm size (see above) and their reported irrigation amounts (see below). The focus group discussions were audio recorded and transcribed. I performed qualitative thematic analysis following the approach of Braun and Clarke (2006). Thematic analysis involves re-reading the transcripts and searching across the data for patterns of meaning that provide insight. Themes emerge by identifying relationships between coded data and, eventually, relationships between themes and sub-themes that tell a story representing the data. Finally, qualitative conclusions were drawn from the themes and how they relate to the research questions. Quotes are used below as representative of themes.

RESULTS & DISCUSSION

The present study was conducted to explore how producers make decisions about liming and irrigation management, both of which are important to Midwestern crop production and potentially global carbon cycling. Irrigation is also critical to groundwater resource management. Use of lime and irrigation is expected to increase as agricultural production intensifies (Tilman *et al.*, 2001, West & McBride, 2005) and precipitation becomes more variable (Turral *et al.*, 2011). This study sheds new light on these decision making processes using CHANS and a modified VBN framework (Figure 3.4, next page). Seven themes emerged from the data and are described below (Table 3.2).

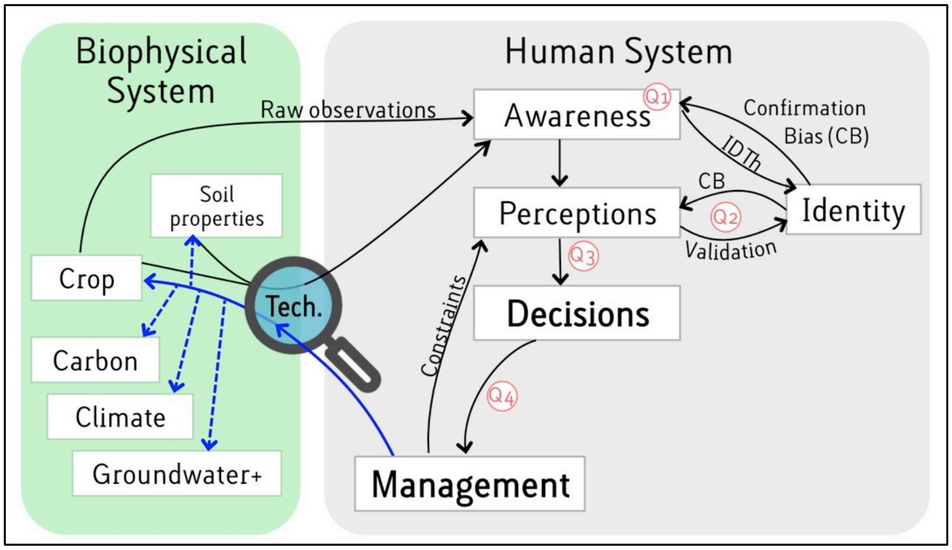

Figure 3.4. Conceptual model for coupled human and natural system in a row crop system incorporating a modified values-beliefs-norms framework, i.e. awareness-perceptions-decisions. Blue arrows indicate human feedbacks to the biophysical system; dashed arrows indicate unintentional consequences. IDTh =Identity Theory. "Constraints" includes macro-level constraints and practical limitations. H=Hypothesis. "Groundwater+" refers to the effect groundwater extraction can have on other biophysical systems, i.e. streams. Magnifier source: http://openclipart.org.

Table 3.2. Themes and definitions.

Theme		Definition
1	**Ecological Explanations**	Descriptions of how biophysical processes work
2	**Curiosity**	Investigating boundaries of awareness
3	**Groundwater identities**	Practices conform with good environmental steward identity
4	**Soil Testing**	Measures of biophysical feedbacks, which are used in decision making
5	**Technology**	Data collection to increase awareness and support decision making
6	**Biophysical Heterogeneity**	Increased awareness of variability in biophysical system (via 4 & 5)
7	**Shades of Applicability**	Technology is not an umbrella solution to all potential scenarios. Applicability changes with context (e.g. climate), ranging from "trusted" to "considered" to "does not apply/ not trusted".

Q1: To what degree are producers aware of how management practices and biophysical processes affect carbon cycling and groundwater level?

Awareness and perceptions are important given how they influence attitudes, choices, and behaviors (Arbuckle *et al.*, 2015, Baumgart-Getz *et al.*, 2012, Prokopy *et al.*, 2008). How producers view the land can define their approach to agriculture (McGuire *et al.*, 2015). Theme 1: Ecological Explanations summarizes producers' expressions of their awareness of the ecology of liming and irrigation.

Most participants were unaware that lime is a carbon input to their soils or that, like all carbon, it has the potential to emit carbon dioxide to the atmosphere. One producer responded to the carbon information with, "You're saying that as we spread this material, some of it escapes in the air?" Despite their lack of awareness, the focus group discussions were designed to enable participatory learning, such that the participants were encouraged to, and did, probe my knowledge of the biogeochemistry and hydrogeology of their systems. As such, Theme 2: Curiosity emerged via participants' questions and eagerness to learn about inorganic carbon cycling in row crop systems. Curiosity is an important ingredient for increasing awareness. Participants asked many thoughtful questions. One producer asked, "Do you find that all soils pretty much perform the same, or is there a lot of variation in what's going on based on what type of soil?" They also asked about how I measure the movement of inorganic carbon from the field to the atmosphere, soils and groundwater. They asked questions about what proportion of total carbon in groundwater-fed rivers, lakes and streams is from lime and irrigation carbon; how lime carbon flows; and what is the effect of rainfall, irrigation, tillage, and time. This curiosity indicated an eagerness to expand their awareness of the role of lime in their systems and an openness to talk with a scientist and the extension educators present as trusted sources of information.

It was not surprising that producers were initially unaware of lime's role in carbon cycling—in my experience many terrestrial earth scientists are unfamiliar with this link. Further, carbon does not directly factor into a producer's intended use of lime, which is for its effect on pH. For now, the global warming impacts of liming are uncertain, however, producers' curiosity leaves the door open for future programs to improve awareness and perhaps effect change in liming practices that will sequester carbon.

Regarding groundwater irrigation's potential to neutralize soil acidity, several producers offered compelling evidence that they saw a groundwater irrigation effect on their soil pH, further examples of Theme 1. One producer had observed that plants in the dry corners (corners of an irrigated field outside the center pivot's circular area) tended to show a magnesium deficiency while the irrigated plants do not. He said,

> *For some reason we seem to get more magnesium deficiency in those dry corners, too. I don't know if its overall from this liming or… We use more hi-cal lime [lime that does not contain magnesium] across the whole field just because we don't want to get too carried away with magnesium, but a lot of the fields you'll find yellow striping on the corn [an indication of magnesium deficiency] in the spring in the dry corners, if it's commercial corn.*

Given this information from a peer, a skeptical producer seemed to warm to the idea that groundwater irrigation delivers a liming effect to soils: "…Back to the magnesium thing, so the water might be applying 20% of your lime needs? So that would have magnesium too in it, at least our water has a lot of calcium and magnesium, that might be enough to…." And another finished, "…explain the dry corner magnesium deficiency." Here the participants are demonstrating one of the benefits of focus groups: the potential for social learning. Overall, awareness of how management practices affect inorganic carbon processes was low among many participants.

In each focus group, at least one producer raised questions about the spatial and temporal variability of alkalinity content in groundwater, again demonstrating Theme 2: Curiosity. These questions may have helped motivate participants to volunteer for the follow up visits to collect irrigation well water samples. Measured alkalinity ranged from about 3000 to over 6000 µeq L^{-1}, meaning the groundwater's liming effect doubles across these wells' range (Figure 3.5). The amount of irrigation reported by participants in a normal year was, on average,

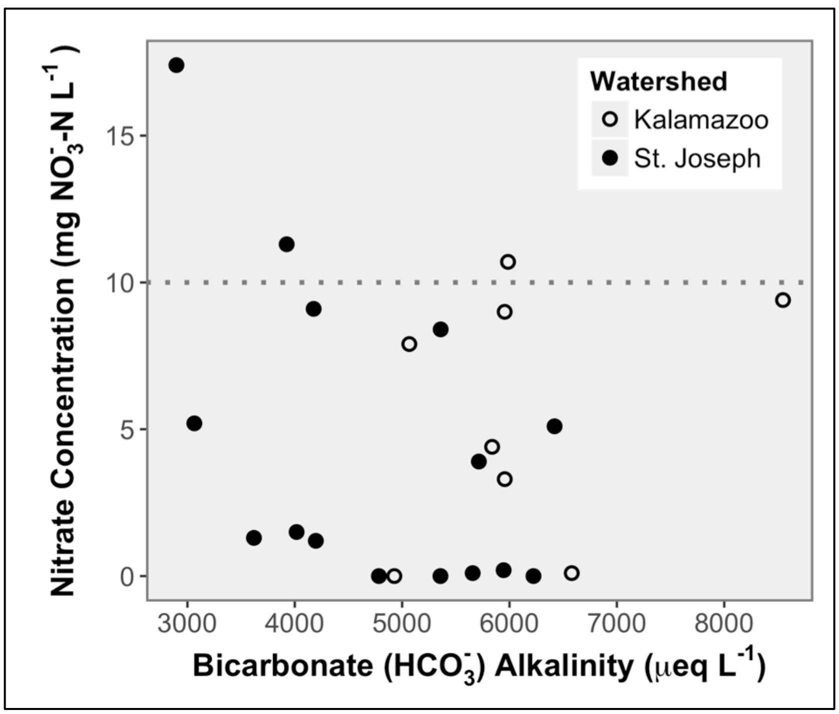

Figure 3.5. Groundwater chemistry of irrigation wells in southwest Michigan sampled in the summer of 2016. Filled circles represent wells in the St. Joseph River Watershed and were used by participants in the focus groups. Samples from irrigation wells in the neighboring Kalamazoo River Watershed are shown for comparison over a larger area.

127 mm (5 in) and 280 mm (11 in) in an extremely dry year[3] (Table A.3.1). According to the Michigan Dept. of Agriculture and Rural Development, the average may be closer to 180 mm (7 in) (personal communication, 27 Mar 2015). At KBS, the average irrigation in the corn years of the crop rotation is 220 mm (8.6 in). During the drought of 2012, a soybean year in the crop rotation, KBS applied 430 mm (17 in). If a producer applies 127 mm of groundwater, the concentration range translates into 0.4 to 0.8 Mg lime ha^{-1} yr^{-1} (0.2 to 0.4 tons ac^{-1} yr^{-1}). As stated above, the KBS groundwater irrigation system applied 8.7 Mg lime ha^{-1} over 11 years.

Several factors could explain why many producers were unaware of the potential liming effect of groundwater irrigation. For example, producers whose wells have lower alkalinity concentrations (Figure 3.5) may not have enough of a liming effect to notice it; they may not irrigate heavily; and/or their nitrogen fertilizer use may be driving the pH down faster than the irrigation is driving pH up. So I was unable to distinguish between a true lack of awareness or lack of opportunity to make such observations. But as shown above, several producers were aware of the impact of irrigation on soil pH and had observed it on their fields. As with lime, participants' curiosity about variability in groundwater quality could be a promising platform for future discussions around how groundwater quality affects soil chemistry.

Q2: Are producers' perceptions of management practices and biophysical processes shaped by their identities?

In southwest Michigan, groundwater use for irrigation is perhaps even more

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[3] According to the Michigan Dept. of Agriculture and Rural Development, the average may be closer to 180 mm (7 in) (pers. comm.). At KBS, the average irrigation in the corn years of the crop rotation is 220 mm (8.6 in). During the drought of 2012, a soybean year in the crop rotation, KBS applied 430 mm (17 in).

controversial than nitrogen pollution. Exploring irrigators' awareness of how management practices and biophysical processes affect groundwater level is important for understanding how they view the system and, in turn, use it (McGuire 2015). These results are nested within Theme 1: Ecological Explanations, under Theme 3: Groundwater Identities, where identities shapes attitudes and actions (sensu McGuire *et al.* (2015)).

In order to drill a new well, irrigators in Michigan must apply for a permit from the state, but many irrigators in southwest Michigan believe their access to water should not involve state regulation or be contingent on ecosystem impacts (Ford, 2012). In my observations at the Water Use Advisory Council meetings from 2013-present, irrigators' frustrations with groundwater management also stem from what they perceive as a sluggish permitting process for new wells and a lack of consensus defining both sustainable use and connectivity between groundwater and surface water. Naturally, the irrigation portion of the focus group discussion triggered some participants to make a variety of remarks in defense of irrigation, even though the focus group questions were not designed to elicit this response.

Many participants tried to demonstrate how little water they use by comparing their water use to irrigators in the western US, which may be connected to the fear of Figure 3.2. As one participant put it, "We have a dry year we gotta put a foot of water on. You look out at California or Arizona they talk about they're just irrigating in feet of water." In another group, one producer said, "I talk with guys who are out in Idaho, and they turn theirs [irrigation pumps] on in the spring and they don't turn them off til they harvest!" By insinuating that western irrigators are worse environmental stewards (Figure 3.2) these statements seem to normalize the participants' water use practices, and thus confirm their identity as good, or at least better, environmental stewards. Similarly, Stuart and Schewe (2016) found that seed corn producers denied their role in climate change by pointing the finger at other groups, e.g. urban and suburban residents and industries.

Participants brought up irrigation recharge—the fraction of irrigation water, escaping evapotranspiration and plant uptake, that infiltrates the soil and returns to the groundwater (Fetter, 2001, Gliessman, 2007). A producer asked, “I wonder what percent, like if you put an inch of water on, how much ends up back down in the ground?” Another replied, “It all depends on when you do it,” implying that the environmental conditions e.g., temperature, dictate how much irrigation water infiltrates the soil and returns to the groundwater. One producer compared southwest Michigan to the “Thumb” region of Michigan, which makes up only a small fraction of irrigation well applications (Figure 3.1). They said, “…there is more recharge in southwest Michigan because the soils are sandier, the water infiltrates faster, so even if they’re using more water in southwest Michigan, more of their water is recharging the aquifer.” One producer surmised, “We must be sitting on one big aquifer because with all the pivots running in our neighborhood nobody’s wells have run dry that I know of.” Another replied, “It regenerates, it’s not like it’s an aquifer like they have out west where it’s just, glacial [fossil] water that they’re just pulling out and it’s depleting.” Although, participants were aware that in the 2012 drought “pumps went dry in some areas.” The glacial outwash aquifers used by irrigators in southwest Michigan are well recharged annually (State of Michigan Public Act 148 Groundwater Inventory and Map, 2006), obscuring any effect of groundwater extraction on the region’s overall water table. Though local, seasonal cones of depression are common (Kelley, 2017 Pers. Comm.) and groundwater depth measurements are scarce. Groundwater extractions in this area are known to potentially reduce stream levels (Mubako *et al.*, 2013).

Changes in water table level were brought up in the groups. Water table levels are dynamic and it is poorly understood how water table levels change over time and space in southwest Michigan. But irrigators can be aware of local water table levels from recent municipality or irrigation well studies, gages on their own wells, and from changes in the well pump's energy efficiency (Kelley, 2017 Pers. Comm.). On this subject, I observed what seemed to be a social pressure not to report observations of water table decline. For example, here is an interesting exchange between participants:

Participant A: Has anyone had any problems geologically [as opposed to politically] getting water?

Participant B: No not geologically. Water table's down overall, but—

Participant A: —this year.

(Group expressed agreement.)

Participant B: Yes, this year, thank you for the clarification.

Participant A: I won't let you say anything that's not true. (laughing)

Participant B: We've all had that conversation, it looks like water table's down, but yeah geologically there's water there.

Participant C: Our water table will vary a couple feet over a 10 to 15 year period, but it goes up and goes down, goes both ways.

Participant D: …It stays pretty stable.

Participant A appeared to be "checking" the way the others talked about the water table depth. This might have happened because they wanted to present a rosy picture, Participant A could be enforcing a confirmation bias that reinforces the belief that the groundwater table is not affected by extraction, and/or Participant A could have a dominant personality type. I have also heard this boilerplate statement about the water table not changing from irrigators and industry groups at WUAC meetings. The lack of available data and studies conclusively explaining the status of groundwater levels over time and across southwest Michigan sharply contrasts with irrigators' expressed beliefs in the stability of the system.

By recharging more water than western irrigators, more water than they withdrew, or believing in a steady water table, participants' beliefs portrayed a confirmation bias in the information they use to shape their understanding of aquifer recharge and the belief that Michigan is water-rich. This is another example of the stewardship identity feeding into awareness and perceptions. Specifically, overusing groundwater would contradict good stewardship identity, so information leading to the conclusion that the groundwater is overused was downplayed or refuted. This identity shaped a perception that current use is not putting the groundwater at risk. Further, the perception of low risk to the aquifer means it is not necessary to use water conservatively. This is similar to the Iowan and Australian producers where those that did not believe climate change was occurring, i.e. low perceived risk, were less likely to participate in climate change mitigation practices (Arbuckle *et al.*, 2015) or water conservation practices, respectively (Sanderson & Curtis, 2016).

Q3: How do biophysical awareness and perceptions contribute to lime and irrigation decision making?

Above I focused on perceptions, awareness, and identities; I now broaden the focus to include inputs such as information sources, how they affect perceptions, awareness, and identities; and outputs, i.e., decisions. These decisions center around where, when, and how much lime or water to apply. Farm management decisions might sound simple to an outsider, but they actually require a delicate balance among complex considerations like cost, time, labor, short and long term goals, effect on yield, and possibly environmental impact. In our discussions participants explained their lime and irrigation decision making processes, the factors they weigh, their sources of information and how much they trust them. Each producer had their own way of making these management decisions, due in part to the spectrum of degrees of awareness and perceptions of their systems. Lime decision making results are discussed first and grouped under Theme 4: Soil Testing. Next, I focus on Theme 5: Technology and Theme 6: Biophysical Heterogeneity, which pertain to both lime and irrigation. Then, I turn to irrigation decision making, whose results are grouped under Theme 7: Shades of Applicability.

Soil testing is an important tool for helping producers decide when and how much to lime. Soil cores and their associated pH measurements can be geo-located to use for variable rate applications of lime. Observing such patterns depends on how frequently in time and intensely in space producers soil sample every field. Soil testing is limited by its cost. Most participants described their soil sampling plan as collecting several cores from one third of their fields every year, so that after three years all their fields have been sampled; the sequence varied between two to five year sampling plans. Participants expressed unquestioned trust in the soil test's pH measurements and lime recommendations, which are straightforward laboratory measurements and calculations. One participant put it simply, "You lime when you need it." This was a universal attitude among participants. When asked if the cost of lime ever factors into the decision to lime, one captured the majority of attitudes with, "If it needs it, it needs it." Another said of lime, "It's so important to everything else that you can't skimp there thinking you're going to save money." Lime's return on investment is $5-10 per $1 spent on lime (Bast *et al.*, 2011), however one participant pointed out that variable rate sampling and liming application costs about twice as much as the lime itself. For lime, the interplay of information, risk perception, and behavior was streamlined and straightforward. The information was unquestioned, its prescribed liming response was accepted, and the belief in the return on investment was well understood. Here beliefs about controversial issues like climate change or aquifer depletion did not interfere. If future lime research shows a change in practices could encourage carbon sequestration, resource managers hoping to change liming behavior should frame their outreach to producers within this "pipeline" from soil testing to pH information to yield risk perception to liming decisions.

In recent years, farming technology, Theme 5, and data collection have grown exponentially. Many described a tradeoff between how their decision-making benefited from technology but how technology also made decision-making more complicated by increasing their awareness of heterogeneity in their biophysical system, Theme 6. In this way, Themes 5 and 6 are closely linked. For example, crop (or grain) yield monitors on combines coupled to global positioning systems have increased producers' awareness of spatial variability within each of their fields. As one producer put it, "Once you start seeing the variance in there…it doesn't answer questions it makes more." More precise technology enables "Precision Agriculture".

Precision agriculture relies on detailed information to enable producers to manage their fields more precisely (Brady & Weil, 2008). In that way, precision agriculture's high-resolution information could deepen a producer's awareness of their biophysical system, increase perceptions of risk and uncertainty, and, thus, change behavior. For example, a participant said, "Just there's so much more [technology] out there for you….I think that lets people go 'Well why am I spending all this money to put it [lime] there, where I'm clearly yielding more in this other management zone?'…That doesn't make us much money." The technology has transformed their perceptions of their fields from single homogeneous units to colorful "heat maps" of variability in properties like soil pH or yield. Rather than seeing information at the field or acre scale, it is now seen per square foot. Technology acts as a lens through which producers perceive their systems with increasing resolution as time goes on, while other technologies provide producers with management practices that incorporate greater detail within a single field.

Variable rate technology allows producers to apply different amounts of inputs like lime and fertilizer throughout a field to address some of their newly-discovered heterogeneity in their fields (Patzold *et al.*, 2008). Indeed, the participants thought the variable rate technology is common among their peers, including as an industry standard for lime application. Many participants have many irrigated fields, often scattered across many miles. Simultaneously monitoring these irrigation systems can be challenging, leading to uncertainty and anxiety about whether the systems are working properly. New irrigation systems have wireless transmitters so users can monitor them using their smart phone or laptop. As one producer put it, "…I mean, it's just so much more relaxing that I can check it at two in the morning if I feel like it, 'yep it's working not having any problems.'" Another participant was excited about new irrigation technology "where you can create…settings where you can slow the pivot down or speed it up because you know that that's just a different soil type…and you know we don't need to drown it or that [other] area will never get too wet." Thus, technology can both contribute to uncertainty, through increased awareness of variability, and alleviate uncertainty depending on the context. The difference in context seems to stem from whether the technology is increasing or decreasing a producers' perception of risk to the biophysical system.

In particular, the applicability of irrigation technology seemed to change with context, defining Theme 7: Shades of Applicability. Context change could alter the way the information or technology shapes beliefs, perceptions, and ultimately behavior. For example, producers can use irrigation scheduling software (or "schedulers") to help make irrigation decisions. Essentially, schedulers calculate the soil water deficit by accounting for crop growth, evapotranspiration, soil moisture, and recent rain and irrigation history (Jones, 2004). Irrigators explained how drought, such as 2012, reduced the applicability of schedulers. As one participant put it, "In a dry season…you don't schedule anything, you just keep going [irrigating]." As drought severity increases, an irrigator's capacity to keep up with a crop's soil water deficit decreases due to limitations in time, aquifer physical characteristics, and equipment failures—not accounted for in schedulers (Figure 3.4 "constraints"). This results in an increased perceived risk of poor crop yield. For example, one participant explained that the aquifer at one of their wells had low productivity:

> *Like if I go back to 2012, we literally turned it on and just let it run because that was what I had to do to just hold a medium line [soil moisture]…If we had a well that put out a thousand pounds a minute instead of what we've got, well we could have let it run for a couple of days then be down a day and repeat that. And I would say that amongst all of us as a group there's a great amount of variation in what the productivity of the particular aquifer that we're working in is.*

When asked about the difference between making decisions in a "normal" vs. "dry" growing seasons (i.e. different contexts), they reported a change in how they framed their choices and how they perceived the utility of scheduling tools. "…Think back to 2012, scheduling was more like 'how do we keep everything running and what crops do we sacrifice?'" It appears that as climate change brings less precipitation and more dry days to the Midwest, (Theme 6: Biophysical Heterogeneity) (Pryor *et al.*, 2014), irrigators' utility for different technologies may change. Context and compatibility have strong influences on whether a producer adopts a new practice or technology (Reimer *et al.*, 2012).

Even in a normal growing season, many participants reported using schedulers and soil moisture sensors as pieces of information but not the ultimate deciding factor. Uncertainty in rainfall predictions at critical crop development periods can drive an irrigator to turn on the pumps, regardless of whether rain is predicted in the forecast. They "don't want to get behind," in terms of crop water needs. One producer explained, " …So I'll start [irrigation] two days ahead of where I think it should be and hopefully be able to shut it off and curse my luck for doing so much work, for starting early when a rain came." Uncertainty in the rainfall predictions contributes to irrigation acting like an insurance policy for crop yield, similar to fertilizer application (Stuart et al. 2012, 2014). The perception of uncertainty and risk to crop yield is driving irrigation decisions.

Furthermore, irrigators are constrained by multiple other considerations, meaning, paradoxically, irrigation decisions are not entirely driven by the crop's water needs or the weather. These constraints can increase the mismatch between technology or information and practice (Theme 7) (Figure 3.4 "constraints"). A participant said, "They [technology] can't tell when the leaves are starting to wilt…or whether the pivot is gonna take four days to get around instead of three." One seed corn grower explained how schedulers do not account for the timing of other management requirements; they said, "[If the workers are coming for] the de-tassling[4]… a lot of times you might take that schedule and throw it out the window because you know they're coming two days from now and you're gonna be out in the field for three or four days [and can't irrigate]." (De-tassling is when female seed corn rows' tassels are removed to prevent them from self-pollinating in order to produce hybrid varieties of corn.) Many participants explained the risk of irrigation equipment failure mid-season, where they may have to wait days for technicians to fix it, putting crop yield at risk. A producer said, "…this [scheduler] is a theory because something is gonna break!" Similar to above, these considerations and fears appeared to incentivize applying more water ahead of time. Again, irrigating more ahead of time is like yield insurance by protecting against crop yield losses due to future possible interruptions in watering or increased water stress.

Along with applicability, trust in technology in a dry year was diminished. One participant said about dry years, "We've used TDR probes, capacitance probes [soil moisture sensors], but the hands and the brain are the final say…All those fancy things do, [is] hopefully give you confidence in what you're already doing." This is an example of confirmation bias, reinforcing prior perceptions of risk and decisions. Further, others have shown how the degree of trust in sources of information is related to how much that source influences perceptions of risk and decisions (Arbuckle *et al.*, 2015, Stuart *et al.*, 2012). But risk and trust are dynamic. When risk was greater, human knowledge and experience seemed to trump technology. As

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[4] In order to produce hybrid varieties of corn, the seed corn is planted in male and female rows, where the female rows' tassels are removed to prevent them from self-pollinating. The female plants will bear the seed corn for harvest.

one participant put it, “These guys that I work with have been doing it for years, it’s just a way of life here. Everybody knows.” They expressed a deeper trust in the knowledge gained from experience and direct interaction with the system, in contrast to weaker trust in new decision support tools. This indicates that if resource managers hope to someday change producers’ irrigation practices, new technology alone will not bring about change. They will also need to build trust in the new information provided by the technology and its utility in different contexts (e.g. drought vs. “normal” year). Developing trust in new technology could be facilitated by field trials and incentives for producer experimentation on their own land.

Ultimately, the adoption of precision technology has ecological implications by improving the efficiency of resources used or changing the amount of inputs used. However, efficiency can paradoxically increase groundwater depletion either through biophysical feedbacks (Ward & Pulido-Velazquez, 2008) or human feedbacks (Pfeiffer & Lin, 2014). A few participants mentioned installing new irrigation sprinkler heads to increase water use efficiency, but as explained above, the tendency among the participants in our groups was to err on the side of using more water rather than less to insure maximum crop yield. A producers’ adoption of these technologies, or practices in general, depends on its applicability across changing biophysical contexts and parallel changes in trust.

Q4: How are lime and irrigation management decisions different?

Differences between lime and irrigation decision making stem from contrasting characteristics of their biophysical-human system feedbacks. First, the over-application of lime is just as detrimental to soils as not applying enough; whereas fear of over applying irrigation water was not a concern voiced by any participants. Over-liming is uncommon on fine-textured and well buffered soils, but for coarse-textured soils low in organic matter over-liming is a hazard (Brady & Weil, 2008).

If soils are over-limed and exceed a pH of seven, certain essential nutrients become unavailable to plants, especially phosphorus, iron, and manganese (Brady & Weil, 2008). In one focus group, a producer talked about a field they were worried about because the pH is mysteriously rising:

> *Participant A: It's an odd thing happening on my farm though. My pH is creeping up on me…Most of my pH's are 7.2 to 7.5's.*
>
> *Researcher: Are those irrigated fields?*
>
> *Participant A: Yes, good crop land.*
>
> *Participant B: Something coming through the water maybe?*
>
> *Participant A: I don't know but its…*
>
> *Participant C: Getting scary?*
>
> *Participant A: Yeah, I don't want it getting to 8!*
>
> *Participant C: That's right, 8's bad.*

This exchange illustrates how producers manage lime carefully so pH is not too low or too high. This sharply contrasts with extra irrigation water acting like crop yield insurance. Producers closely read their soil's pH as a biophysical feedback. They rely on soil testing (Theme 4) and resulting lime recommendations to determine when and how much lime to apply—a rather direct "pipeline" from information to perception to behavior.

Irrigation decisions, in many cases, are made considering a "constellation" of information, perceived risks and other factors that sometimes have nothing to do with plant water stress. Above I discussed how irrigation is planned around other management requirements, equipment failures, and aquifer limitations. Participants also expressed a context dependency for the applicability and trust in irrigation technologies like soil moisture sensors and schedulers. This contrasts with the unquestioned "You lime when you need it" attitude.

The two practices also differ by time scale. Irrigation has immediate impacts on crop growth and yield, but the impact of lime on pH occurs over two to three years after application (Bast *et al.*, 2011). An experienced producer explained, "If you are applying lime because you need it, you probably should have been adding lime before that because you don't get an immediate response…so lime application is a long term thing." The problem that the lime is addressing, soil acidity, accrues over several years, though faster if applying high amounts of nitrogen fertilizer. Whereas the problem irrigation is addressing, plant water stress, can develop over a matter of days such that the consequences of not irrigating are felt immediately. A seed corn grower explained, "It doesn't matter if it's wet or dry. That seed [corn] gets behind, it hurts us. It's competitive." Another added, "If you get behind, you're behind. Very seldom is there ever a catch up." Irrigation illustrates a daily feedback between the biophysical system (weather, crop, soil) and human system (competitive contracts, risk to yield, potential equipment failure, other management needs, time); whereas the lime feedback occurs over years with fewer macro-level factors.

Unlike lime, irrigation tends to be a controversial subject, including in southwest Michigan. Groundwater pumping can put aquifers and streams at risk, and the latter is the basis for Michigan's groundwater regulations. Participants expressed defensive posturing and a confirmation bias when discussing issues around groundwater quantity, but expressed no defensiveness when discussing lime. Other research has found that confirmation bias tends to be more apparent in the context of more controversial issues. In an experiment designed to test for confirmation bias, researchers intentionally chose highly controversial topics like gun control and affirmative action (Taber & Lodge, 2006). They surmised that more controversial topics would elicit a larger effect size than prior studies that used mild topics; indeed they found strong confirmation bias effects on attitude polarization. Because overusing groundwater contradicts the stewardship identity, perceptions of groundwater might be more strongly influenced by identity and confirmation bias; whereas lime was not affected by identity.

Lime and irrigation's different pathways (pipeline vs. constellation) through the awareness-perceptions-decisions framework, highlights how theories can apply broadly to many agricultural decisions but each practice deserves detailed investigation to understand nuances. Irrigation management was similar to nitrogen management described in other studies (Schewe & Stuart, 2017). Lime provides a useful contrast to irrigation and nitrogen management, demonstrating how differences in the nature of biophysical feedbacks produce different management approaches. Lime is linked to nitrogen fertilizer use, both of which will continue to play a key role in global food production. Groundwater irrigation is expanding across agricultural regions world wide as producers adapt to more droughts and variability in precipitation regimes (Turral *et al.*, 2011). Both lime and irrigation have the potential to be the focus of carbon dioxide mitigation practices as biogeochemical research further uncovers their importance in the global carbon cycle (Chapters 1 and 2, this volume). In order to help producers adapt to climate change using irrigation and/or mitigate carbon dioxide from liming and irrigation, resource managers need an understanding of how producers make those management decisions. This study is an early attempt to fill the large gap in this area of knowledge.

SUMMARY

This study demonstrates that lime and irrigation decision making can be analyzed using existing social frameworks. The coupled human and natural systems approach pushes an analysis focusing on the feedbacks between human and biophysical systems (Figure 3.4). This approach has been offered as a useful way of understanding these feedbacks between producers and biogeochemical cycles (Stuart *et al.*, 2015). Biophysical feedbacks were often mediated by technology and ranged from relatively objective to confirmation-biased (Figure 3.4 arrows leading to awareness box). This web of iterative feedbacks shaped perceptions of risk and decisions (Figure 3.4 bubbles for Q1-3). Furthermore, the VBN framework allowed me to find the different cognitive and social elements such as awareness and identity that fit together by way of mechanisms like confirmation bias and macro-level forces to ultimately influence decision making. Awareness, perceptions, and identities informed lime and irrigation decision making, similar to their roles in adoption of practices like climate change adaptation or mitigation, water conservation, and soil and water conservation (Arbuckle *et al.*, 2015, Baumgart-Getz *et al.*, 2012, McGuire *et al.*, 2015, Prokopy *et al.*, 2008, Sanderson & Curtis, 2016) (Figure 3.4 Q3). By fitting within the VBN and CHANS frameworks, future research could quantify these behaviors across different farm types, crops, regions, and time.

These findings support previous work that demonstrated that producers' decisions are driven by their identity, which is shaped by their awareness and perceptions of the land (McGuire *et al.*, 2015, Stuart *et al.*, 2012). In this study I showed how that pathway works in reverse as well: producers' awareness and perceptions of the biophysical system are shaped by their stewardship identities, sometimes by way of a confirmation bias.

Conservation implications

The themes that emerged in this study have important implications for conservation, though the ability to generalize the findings is limited by the nonrandom sampling design and small sample size. The participatory learning involved in our two-way discussions demonstrated the potential for this approach to expand producers' awareness of how their practices affect biophysical systems. Confirmation bias is real, so presenting information on topics that threaten their stewardship identity will be met with doubt, but building trust in the information source can help. The irrigation discussion in my focus groups benefited by following the positive discussion of carbon cycling and lime, which may have built trust in the group and the researcher allowing for a more open irrigation discussion. Following up the focus groups with voluntary farm visits further developed a sense of two-way learning and trust between the producer and researcher. It also validated participants' curiosity in certain questions and provided an opportunity for me to "repay" them with water quality data from their wells.

Soil testing has been recognized as a gateway for changing or influencing producer practices (Weber & McCann, 2015). Indeed soil testing was highly trusted and important in lime decision making. Technology brought both greater awareness of biophysical heterogeneity as well as tools for addressing the heterogeneity. Precision agriculture, mapping, and variable rate technology enable producers to see their system with greater spatial resolution. These could enable greater efficiency in resource use or, by increasing awareness of a resource need, could increase resource use—warranting further study of how precision agriculture and irrigation schedulers affect resource use. Context, especially drought, can reduce the applicability and trust in different technologies. Indeed, the perception of uncertainty and risk to crop yield was driving irrigation decisions. The design and testing of decision support tools should account for changing contexts and address trust; otherwise these tools will not change practices, especially at times like drought when conservation is most important to groundwater-fed streams.

As climate change and population growth strain water resources and food security, lime and irrigation have and will continue to enable agricultural intensification and extensification. This study shines light on how producers make liming and irrigation decisions, enabling biogeochemists and hydrogeologists to better predict resource use and understand what factors are driving these ecosystems. As the carbon and climate change implications of liming and groundwater irrigation become clearer, resource managers may need to affect change in these practices. This study provides a rough blueprint for understanding how producers make those decisions, increasing the likelihood of success for conservation practice design, outreach, and ultimately adoption.

APPENDICES

APPENDIX A: Tables

Table A.3.1. Focus group questionnaire results for southwest Michigan corn growers and irrigators (*n*=12).

		Question	Average	Std. Dev.	%
Size	**Size of operation (acres)**	Acres own	864.1	713.0	67.1
		Acres rent	693.6	1139.0	32.9
		Total acres	1969.6	2010.0	
Tillage	**% Participants practicing tillage type (sum >100%)**	Conventional			33.3
		Reduced tillage			66.7
		No-till			25.0
Lime	**Form of Lime**	Dolomite ($CaMg(CO_3)_2$)			75.0
		Calcite ($CaCO_3$)			41.7
		Marl			16.7
	pH	Average pH target	6.6	0.2	
	Lime application frequency (years)	Irrigated corn	4.8	3.9	
		Non-irrigated corn	5.7	4.5	
	Lime rate (ton/acre)	Irrigated corn	1.4	0.4	
		Non-irrigated corn	1.4	0.5	
Nitro-gen	**N form**	Use ammonium based N fertilizer(s)			100.0
	N rate (lb N /acre)	Pre-plant	23.4	38.7	
		Starter	30.3	10.4	
		Sidedress	100.8	41.7	
		Fertigation	26.0	36.9	
		N total	180.5	52.8	
Irri-gation	**Irrigation source**	Groundwater			83.3
	Irrigated acres	Irrigated acres	1520.8	1617.3	71.7
	Average annual irrigation amount (inches)	Normal year	5.2	2.1	
		Extreme dry year (i.e., 2012)	11.1	2.6	
Con-cerns	**0= not at all concerned, 1= it has crossed my mind, 2= sometimes I think about it, 3= I think about it daily**	Price of corn	2.4	0.8	
		Cost of irrigation energy	2.0	0.7	
		Cost of inputs	2.8	0.4	
		Short-term rainfall predictions	2.7	0.7	
		Long-term climate variability	1.6	0.5	
		Water use regulations	2.5	0.5	

APPENDIX B: Figures

Date__________ Participant no. ________

Lime & irrigation survey

This survey is confidential—your name will never be used in connection with your responses. Please answer the questions with your <u>most "typical" irrigated field corn management area in mind</u> (exclude your exceptional cases).

PART 1: ABOUT YOUR OPERATION

1. The size of your operation: I **own** _________ acres and **rent** _________ acres.

2. Which tillage system best describes your usual practice? (Please check one box.)

□ Conventional tillage (such as chisel or moldboard plow, field cultivator)
□ Reduced tillage (such as disking, finishing, or vertical / strip tillage)
□ No-till

PART 2: LIMING PRACTICES

3. What form of lime do you most typically use for neutralization? (Check one.)

□ Dolomitic lime (calcium magnesium carbonate)
□ Calcitic lime (calcium carbonate)
□ Other ___________________

4. What is your target field pH for corn? from pH ____ to pH _____

5. Liming frequency. (Fill in the blanks)

a) In general, I lime my *irrigated corn* fields every _________ years.

b) In general, I lime my <u>*non*</u>*-irrigated corn* fields every _________ years.

6. What is a typical rate of lime application for your *irrigated corn* fields?

__________ tons / acre
Exceptions: ____

7. What is a typical rate of lime application for your <u>*non*</u>*-irrigated corn* fields?

__________ tons / acre
Exceptions: ____

8. Nitrogen fertilizer is one of the primary sources of acidity in cultivated soils. Because of its link to soil pH and liming, I would like to know what form of nitrogen fertilizer do you <u>*typically*</u> apply to your <u>*irrigated*</u> corn. Is it ammonium-based (such as UAN, anhydrous ammonia, ammonium nitrate, or aqua ammonia)? (Check one.)

□ Yes □ No, I use _________________________ nitrogen fertilizer.

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Figure A.3.1. Focus group written questionnaire. Continued on next page.

Figure A.3.1 (cont'd)

Date__________ Participant no. ________

9. How much nitrogen fertilizer do you *typically* apply to your *irrigated* corn?

Time	Rate
Pre-plant	___________ lbs N / acre
Starter	___________ lbs N / acre
Sidedress	___________ lbs N / acre
Fertigation	___________ lbs N / acre
Other:_____________________	___________ lbs N / acre

10. Are these rates different in your non-irrigated corn fields? How? ___________________________

____

PART 3: IRRIGATION—The next few questions are about irrigation practices. **I am interested in irrigation for its contribution to the movement of carbon**.

10. On your farm, the irrigation water comes *primarily* from: (Check one.)

□ Groundwater □ Surface water

11. Of the acres you farm how many have irrigation (on average)? _______ acres

12. How does your use of irrigation differ between a growing season with near normal rainfall and an extremely dry growing season (such as 2012)?

a) In a *normal year* my corn fields receive _____ **inches** of irrigation water.

b) In an *extremely dry year* my corn fields receive _____ **inches** of irrigation water.

13. I'd like to get an idea of your level of concern about water-related topics. When you think about irrigation, how concerned are you about the following topics, if at all? (Please circle a number for each issue listed.)

	Not at all concerned	*It has crossed my mind*	*Sometimes I think about it*	*I think about it daily*
Price of corn	0	1	2	3
Cost of irrigation energy	0	1	2	3
Cost of inputs	0	1	2	3
Short-term rainfall predictions	0	1	2	3
Long-term climate variability	0	1	2	3
Water use regulations	0	1	2	3

THANK YOU for completing this survey!

Please use the area below to write any comments about the survey or anything else:

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Chapter 4 Complex interactions among climate change, sanitation, and groundwater quality: A case study from Ramotswa, Botswana

ABSTRACT

With population growth, rapid urbanization, and climate change, groundwater is becoming an increasingly important source of drinking water around the world, including in southern Africa. The present study is an investigation into the coupled human and natural system linking climate change, droughts, sanitation, and groundwater quality in Ramotswa, a town in the semi-arid southeastern Botswana. During the recent drought from 2013-2016, water shortages from reservoirs that supply the larger city of Gaborone resulted in curtailed water supply to Ramotswa, forcing people with flush toilets to use pit latrines. Pit latrines have been suspected as the cause of elevated nitrate in the Ramotswa groundwater, which also contributes to the town's drinking water supply. The groundwater pollution paradoxically makes Ramotswa dependent on Gaborone's water, supplied in large part by surface reservoirs, which are vulnerable to drought. Analysis of long-term rainfall records indicates that droughts like the one in 2013-2016 are increasing in likelihood due to climate change. Because of the drought, many more people used pit latrines than under normal conditions. Nitrate, fecal coliforms, and caffeine analyses of Ramotswa groundwater revealed that human waste leaching from pit latrines is the likely source of nitrate pollution. The results indicate a critical indirect linkage between climate change, sanitation, groundwater quality and water security in this area of rapid urbanization and population growth. A water treatment facility in Ramotswa would improve reliable access to water, reduce pit latrine use, and de-couple the community from water shortages in Gaborone.

INTRODUCTION

Water insecurity across sub-Saharan Africa (SSA) results from a complex interplay of natural and social systems (Howard & Bartram, 2010). Surface water quality and quantity are declining due to changes in climate, land use, population growth and economic activity (Jiménez Cisneros *et al.*, 2014). Groundwater supports about 75% of the SSA population as well as industry and some crop irrigation (Calow & MacDonald, 2009, Niang *et al.*, 2014, Taylor *et al.*, 2013). But its quality and quantity are threatened directly and indirectly by climate change and socioeconomic pressures, including urbanization and changes in water demand (Xu & Usher, 2006). Therefore ensuring water security in SSA under a changing climate requires an understanding of these interacting effects on groundwater (Cronin *et al.*, 2007, Famiglietti, 2014, Niang *et al.*, 2014, Taylor *et al.*, 2013).

This is a case study of the indirect impact of climate change on groundwater quality in Ramotswa, a rapidly growing, peri-urban town in the South East District of Botswana. Climate change and groundwater quality are linked by way of a coupled human and natural system (CHANS) (Liu *et al.*, 2007). I hypothesize that climate change is altering human behavior, which has implications for groundwater quality. An interdisciplinary CHANS approach was used to investigate how drought affects water supply infrastructure and sanitation access in Ramotswa, and how those changes in sanitation impact the quality of the groundwater, a source of drinking water (Figure 4.1). *The objectives of the present study are* to investigate: (1) if and how rainfall patterns have changed in the wet and dry seasons over time, (2) how changes in rainfall affect water supply and sanitation access and use in the area, (3) whether denitrification can potentially provide *in situ* bioremediation, and (4) how groundwater quality is impacted by sanitation. This is one of the first studies to apply a CHANS framework to a groundwater – climate change study and to use caffeine to trace groundwater contamination in Africa and pit latrine contamination of groundwater.

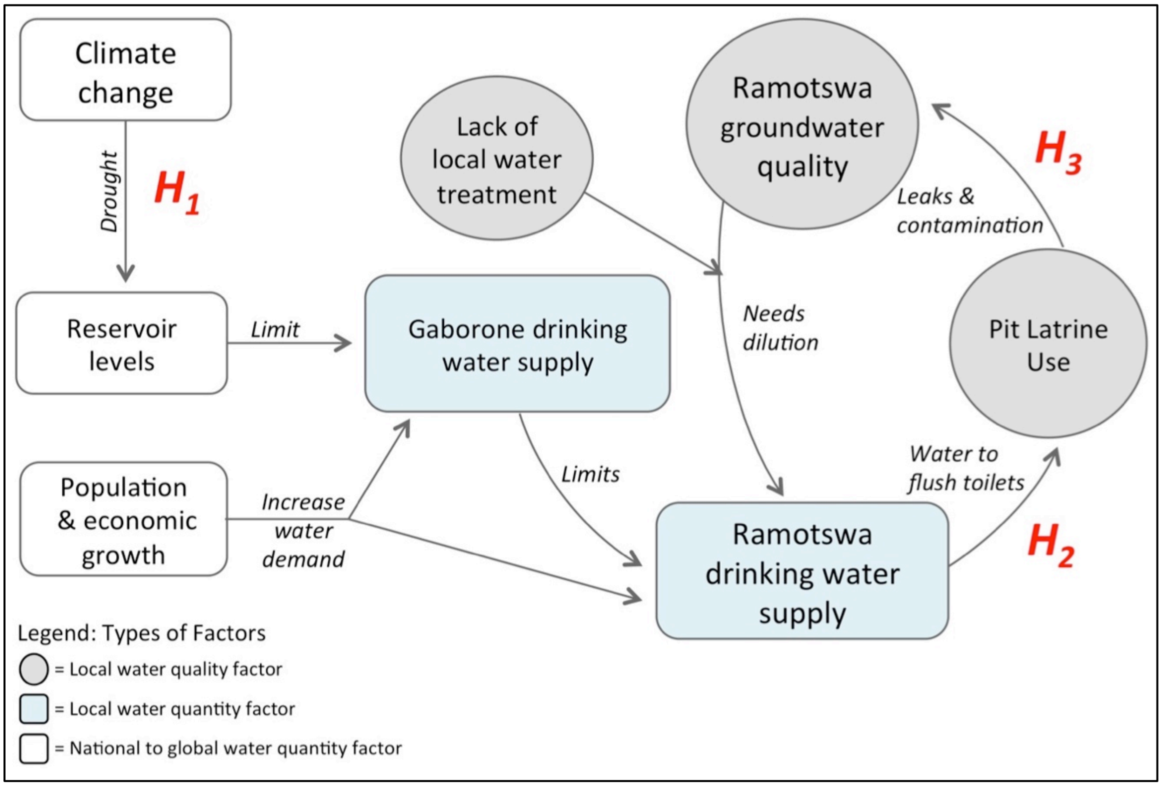

Figure 4.1. Conceptual diagram of Ramotswa groundwater coupled human and natural system (CHANS) illustrating how climate change indirectly reduces Ramotswa drinking water quantity and groundwater quality. *Red H's* represent hypotheses explained in the text.

Climate change in sub-Saharan Africa

A changing climate has been recorded across Africa, including shifts in temperature and rainfall. Over the last 50-100 years, most of southern Africa's mean, maximum, and minimum temperatures have risen, especially in the last two decades (Niang *et al.*, 2014). In this century, mean temperatures in southern Africa are projected to increase faster than the global average, especially in arid areas like Botswana; projected changes are 3 to 6°C beyond the 1986-2005 baseline by 2100 (Niang *et al.*, 2014). Between 1950 and 2000, rainfall in Botswana and neighboring countries has been declining including significant changes in the onset and duration of the wet season, growing dry spell frequencies, and greater rainfall intensity (Niang *et al.*, 2014).

Climate models project a decreasing annual mean rainfall for Botswana and Namibia, with drier and shorter wet seasons and drier dry seasons by 2100 (Niang *et al.*, 2014). Of 15 global circulation models (GCMs) simulated for Botswana, ten projected that 1^{o}C of global warming will bring less rainfall on average, potentially as much as a 12% (56mm) decrease in mean annual rainfall (Post *et al.*, 2012). Heat waves will become more likely and put the region at high risk of severe droughts (Niang *et al.*, 2014). The observed and projected changes in precipitation will likely exacerbate sub-Saharan Africa's vulnerability to water and food insecurity and further strain the livelihoods of the more than ⅔ of sub-Saharan Africans who rely on rain-fed agriculture (Connolly-Boutin & Smit, 2016).

These climate changes can have direct impacts on groundwater. In arid environments with well-drained soils, increased rainfall intensity may increase recharge as more rainfall is able to infiltrate the unsaturated zone and escape evapotranspiration (Taylor *et al.*, 2013). Changes in recharge rates may alter the rate of weathering of soil and rock materials in the subsurface, changing the concentrations of weathering-derived solutes in groundwater (Bates *et al.*, 2008). More extreme rainfall events increase erosion and transport of pollutants, and storm water may overwhelm sewage flow, threatening the quality of surrounding water bodies including groundwater (Bates *et al.*, 2008). In semi-arid environments where recharge is dominated by focused recharge beneath ephemeral surface water, increasing rain intensity (total rain volume/number days with rain) may lead to more groundwater recharge, though this may also increase microbial contamination of the aquifer (Taylor *et al.*, 2013).

Climate change can directly impact sanitation practices and infrastructure, which can have *indirect* impacts on groundwater quality. Very few studies have looked at the direct effects of climate change on sanitation, as noted in a review by Howard *et al.* (2016), but they predict that a drier climate may mean less flooding of pit latrines as well as insufficient water volume to flush toilets and operate sewage treatment systems. On the other hand, increased flooding and rainfall intensity could mean more pit latrine- and sewage treatment pond-overflow into the environment, contaminating rivers and boreholes (Howard *et al.*, 2016). Across three communities in SSA, Heath *et al.* (2012) documented several direct effects of flooding on sanitation (e.g. latrine inundation and collapse) and drought (less water for health and hygiene). The direct effects of sanitation on groundwater and human health are well understood and summarized below. Studies, such as the present one, connecting climate change to sanitation impacts on groundwater quality are scarce (Howard *et al.*, 2016).

Sanitation and groundwater quality

Rapid urbanization in developing countries frequently means that infrastructure, including sanitation, lags behind the needs of the growing population. Pit latrines are the most common means of human waste disposal in these areas, often where communities also rely on groundwater for drinking (Cronin *et al.*, 2007). Unlined pit latrines dispose of human waste via percolation to the groundwater, threatening groundwater quality and human health with pollutants like nitrate and pathogens (Cronin *et al.*, 2007, Graham & Polizzotto, 2013).

In studies of pit latrine impacts on groundwater quality, nitrate (NO_3^-) is the most commonly detected pollutant and is often found in elevated concentrations in groundwater near pit latrines (Graham & Polizzotto, 2013). Urine carries over 80% of human nitrogenous waste, with an average concentration of 8.12 g nitrogen (N) L^{-1} (Rose *et al.*, 2015). NO_3^- can be an indicator of human waste contamination. When drinking water is above 50 mg N L^{-1}, it can be a threat to human health, most notably blue baby syndrome (methemoglobinemia) (WHO, 2008) and can also cause livestock asphyxiation. In Ghanzi, Botswana, about 200 cattle died in 2000 due to presumed NO_3^- poisoning (Tredoux & Talma, 2006). High N concentrations in groundwater are also a threat to downstream ecosystems, potentially leading to eutrophication, anoxia, and fish kills (Kalff, 2002).

Denitrification has been used in aquifers for *in situ* bioremediation of NO_3^- pollution (USEPA, 2013). Denitrification is a naturally occurring, microbial process that removes NO_3^- from water. In low oxygen conditions, denitrifying microbes reduce NO_3^- into nitrous oxide (N_2O) and dinitrogen (N_2) gases (Robertson & Groffman, 2015, Seitzinger *et al.*, 2006). Heterotrophic denitrification involves several sub-reactions (one of which produces N_2O), such that complete denitrification involves:

$$5CH_2O + 4H^+ + 4NO_3^- \rightarrow 2N_2 + 5CO_2 + 7H_2O \qquad \text{(Eqn. 1)}$$

(Schlesinger & Bernhardt, 2013). Given the above stoichiometry, denitrification requires dissolved organic carbon (DOC), the oxidant, and NO_3^- in approximately a ≥ 1:1 molar ratio. Where DOC limits denitrification, bioremediation involves injecting a source of DOC into the aquifer to enhance denitrification, thus removing more NO_3^- than without the supplemental DOC (USEPA, 2013).

Discerning between human and livestock waste contamination can be a challenge.

Human and livestock stable isotope signatures for NO_3^- overlap (Fenech *et al.*, 2012), as do their gut microbial communities as measured using standard microbiological techniques (Ashbolt *et al.*, 2001). In recent years, newer tools such as antibiotic resistance, DNA fingerprinting, bacteriophage occurrence and genetic markers have been used but not yet widely tested (Fenech *et al.*, 2012). Others have employed a suite of chemicals called "emerging organic contaminants" (EOCs) including pharmaceuticals and caffeine (1,3,7-trimethylxanthine) as tracers of human contamination. These tend to persist in the environment, and detection limits continue to decrease (Fenech *et al.*, 2012, Lapworth *et al.*, 2012). Caffeine's metabolite paraxanthine (1,7-dimethylxanthine) has also been used, but not as widely. Caffeine and/or paraxanthine have been measured in groundwaters in England (Stuart *et al.*, 2014b) and Germany (Hillebrand *et al.*, 2012, Hillebrand *et al.*, 2015, Reh *et al.*, 2013), in surface waters in Switzerland (Buerge *et al.*, 2003), in surface and groundwaters in the US (Glassmeyer *et al.*, 2005, Godfrey *et al.*, 2007) and more recently in both surface waters and roof-harvested rain water catchment systems in South Africa (Matongo *et al.*, 2015, Wanda *et al.*, 2017, Waso *et al.*, 2016). The half-lives of caffeine and paraxanthine were estimated in a US estuary to be 3 to >100 days and 11 to >100 days, respectively (Benotti & Brownawell, 2009). In a German karst aquifer system the caffeine half-life was estimated at 89 days (Hillebrand *et al.*, 2015).

Indirect impacts of climate change on groundwater quality

Scientists have warned that anthropogenic impacts on groundwater quality will likely be more consequential than any direct impacts of climate change on groundwater quality (Calow *et al.*, 2010, Taylor *et al.*, 2009). Some of these anthropogenic effects may be the indirect result of climate change, where climate change alters human behavior that has an impact on groundwater, e.g. groundwater depletion due to drought and increased pumping. CHANS methods have not yet been applied in this context, but offer a powerful template for such an investigation. In fact, Sivapalan *et al.* (2012) argue it is impossible to manage or predict water availability without accounting for the feedbacks between water and human systems, because human activity has such pervasive effects on the modern water cycle. The CHANS literature demonstrates that in order to characterize today's most pressing socio-ecological issues, interdisciplinary research approaches are required to understand their complexities and develop realistic solutions (Collins *et al.*, 2011, Liu *et al.*, 2007, Millenium Ecosystem Assessment, 2005, Stevenson, 2011). In SSA CHANS has been used to study rising malaria incidence (Kelly, 2013) and floodplain management (Moritz *et al.*, 2016). Here, I combine climatology, sociology, and biogeochemistry to capture the depth of socio-ecological interactions that explain the groundwater pollution in Ramotswa. This CHANS study of Ramotswa will hopefully provide a template for socio-hydrological studies in other regions that will lead to more sustainable management and improved predictions in the face of climate change.

This study's overarching research question is, "*Does climate change impact groundwater quality in Ramotswa, and if so, how*?" Drought, water shortages, increased pit latrine use, and groundwater pollution from pit latrines potentially play a role (Figure 4.1). Specifically, this study tests the following hypotheses:

H_1: Climate change-induced droughts are becoming more frequent, which will decrease reservoir levels. Reservoirs supply the treated water that is piped into Ramotswa.

H_2: Water shortages affect sanitation behavior, increasing pit latrine use.

H_3: Denitrification has the potential to provide *in situ* bioremediation of the Ramotswa groundwater nitrate contamination.

H_4: Nitrate pollution is from human waste contamination.

Altogether these hypotheses test whether climate change is limiting reservoir water *quantity*, leading to water shortages, exacerbating the effect of increased pit latrine use on groundwater *quality*, and increasing Ramotswa's dependence on reservoir water *quantity*.

STUDY SITE

Biophysical characteristics

The town of Ramotswa (24.88^{o}S x 25.87^{o}E) is semi-arid and subtropical, about 25 km^2 in size and 20 km south of Botswana's capital, Gaborone (Figure 4.2). The peri-urban town's eastern boundary is the ephemeral Notwane (Ngotwane) River, which flows northward to the Limpopo River, and serves as the boundary with South Africa in this area. The South East District is dotted with rocky hills and ancient alluvial river plains around 1025 m above mean sea level (MAMSL) and the hills are about 1100 MAMSL (Staudt, 2003). The natural vegetation is mixed shrub and tree savanna, which is harvested for construction, firewood, and fencing (Staudt, 2003). The Ramotswa boreholes sampled, sometimes referred to as the "Ramotswa wellfield", in this study cover an area about 34 km^2 (Figure 4.2).

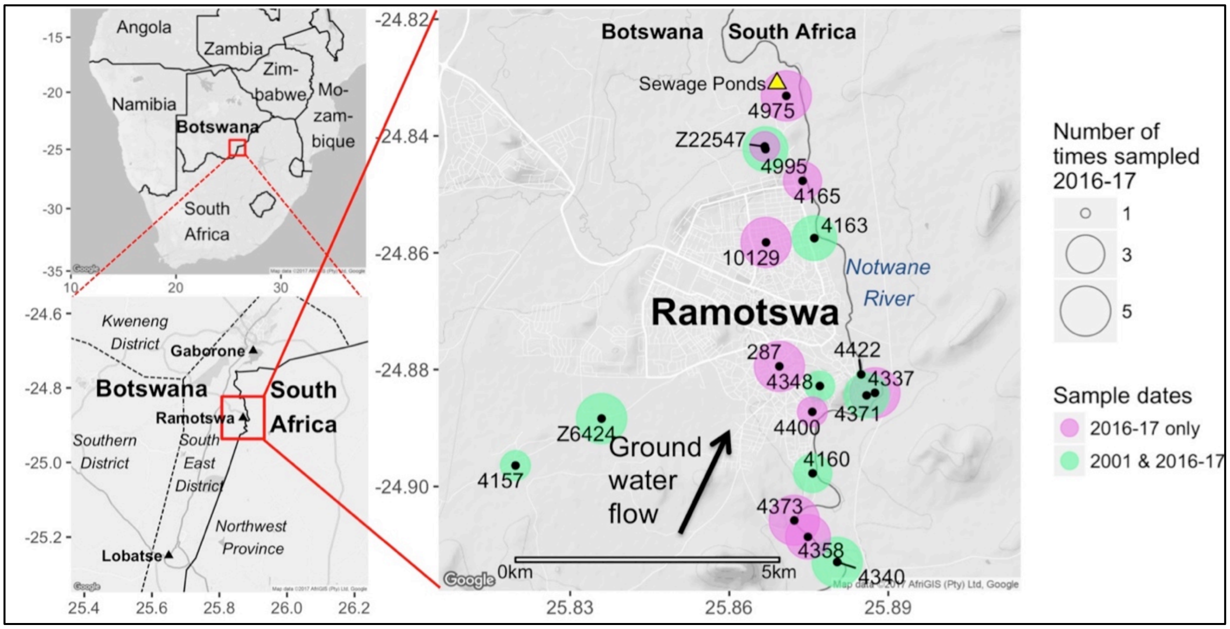

Figure 4.2. Maps of Southern Africa (*upper left*), Botswana's South East District (*lower left*) where *black triangles* represent the three weather stations used in the present study, and Ramotswa borehole locations (*right)*. Boreholes are labeled and *circle size* indicates number of times sampled in the present study. *Color* indicates whether the borehole was sampled in 2001 and this study (*green*) or only this study (*pink*). Arrow shows general groundwater flow direction (see also Figure A.4.1). *Yellow triangle* is the piped sewage network ponds.

The rainfall is highly seasonal. The wet season (summer) lasts from Oct to March and the dry season (winter) is from Apr to Sep. Therefore, the water year here is from 1 Oct. through 30 Sept. The mean annual water year rainfall in Ramotswa from 1980 to 2016 was 454 mm, 89% of which tended to fall in the wet season (data from Botswana Dept. of Meteorological Services). The majority of rainfall occurs in heavy downpours during the wet season as convectional rainfall, which, along with tree and shrub harvesting, can lead to heavy erosion and gullies in the area. Average annual evaporation from two nearby reservoirs in South Africa was 2120 mm, nearly five times the average annual rainfall (Altchenko *et al.*, 2016). Average potential evapotranspiration for all of Botswana is 1072 mm in the wet season and 573 mm in the dry season (Post *et al.*, 2012).

The geology and hydrogeology of the Ramotswa area are exhaustively described in

Altchenko *et al.* (2017). Briefly, the Ramotswa aquifer is 453 km^2, spanning both Botswana and South Africa with a portion below Ramotswa town, which supplies a portion of their drinking water (Figure 4.3). It is part of the Transvaal Supergroup, which consists of ancient carbonate

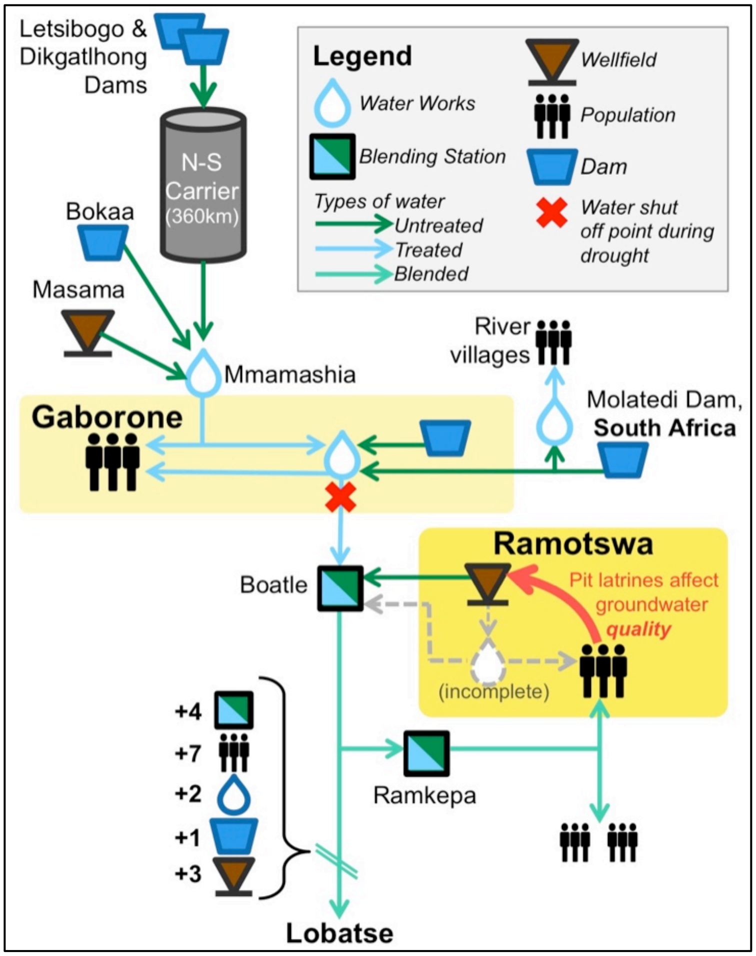

Figure 4.3. Water supply scheme for the South East District. The red arrow illustrates the coupling of water quality to water quantity and the grey dashed arrow indicates how a Ramotswa water treatment facility could de-couple Ramotswa from the Gaborone water supply, which is vulnerable to droughts. Modified from Altchenko et al. 2016. Not to scale.

and iron formations with minor amounts of silica-clastic minerals. The dolomite formations within the aquifer are referred to as the "Ramotswa Dolomite" and are the primary water-bearing units. The dominant water-bearing formations have undergone significant weathering (see below). Dolomite weathering produces high calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-) concentrations.

The Ramotswa aquifer is considered unconfined to semi-confined. In an aerial electromagnetic (AEM) survey, the Ramotswa aquifer in the area of the town was *at least* 340 m thick and, on average, 150 m thick (Altchenko *et al.*, 2017). The mean depth to the groundwater table as measured in the present study was 13.7 m below the ground surface (Table A.4.1) while in the larger Ramotswa aquifer area and over a longer time period it was 24 m (Altchenko *et al.*, 2017). The groundwater flows to the northeast (Figure A.4.1) as determined by piezometric sampling in Altchenko *et al.* (2017) and in agreement with Staudt (2003). The Ramotswa aquifer has an average specific capacity of 2.7 L s^{-1} m^{-1}, average transmissivity of 1170 m^2 d^{-1}, and a storage coefficient of 5.7 x 10^{-2} (Moehadu, 2014, Staudt, 2003). Production borehole yields range from 15 – 150 m^3/hr.

The AEM survey confirmed the complexity of the Ramotswa aquifer's hydrogeology, which is dominated by three geological processes/structures (Altchenko *et al.*, 2017). First, "karstification" or the dissolution of the dolomite by infiltrating rainwater creates preferential flow paths and underground sinkholes and caves that can store large amounts of groundwater. Second, surface and subsurface faults in the area can act as either preferential flow paths or barriers. Third, groups of deep, vertical, impermeable dykes partition the aquifer into 13 more or less well-defined dolomite compartments, potentially restricting groundwater flow but also protecting a compartment from pollution in another compartment.

Recently, Altchenko *et al.* (2017) used chloride (Cl^-) mass balance to estimate recharge rate to the Ramotswa aquifer of 19.7 (±10.7) mm y^{-1} or 4.3% of mean annual precipitation. These measurements are in agreement with other recharge estimates for this area (Gieske, 1992) . The aquifer is actively recharged and well leached; soil infiltration of rainfall is highly variable over short distances; and recharge also occurs via runoff percolation, ephemeral riverbed infiltration, and direct infiltration through outcrops (*ibid*.). The latter process of water transport is critical, as the town of Ramotswa sits on an outcrop of the Ramotswa Dolomite (Figure A.4.1). Via preferential flow paths, rain or other water near the surface can directly infiltrate the aquifer. Infiltration from diffuse recharge is <1 mm per year (Post *et al.*, 2012).

Elevated concentrations of NO_3^- have been found in arid environments, including the Kalahari desert, where it is believed to be the product of the decomposition of deposits of ancient vegetation (Heaton *et al.*, 1983, Stadler *et al.*, 2012, Stone & Edmunds, 2014). Stadler *et al.* (2012) differentiated between naturally occurring and anthropogenic NO_3^- in groundwater in the Kalahari using $\delta^{15}N$ and $\delta^{18}O$ and tritium. They showed that NO_3^- in the deeper groundwater was older in age and the NO_3^- tended to be naturally occurring, while NO_3^- in the shallower, younger groundwater tended to come from human and cattle sources. Located about 400 km east of the Kalahari District, Ramotswa's groundwater is relatively shallow and young (see results below). In a review of studies of NO_3^- pollution in groundwater across Namibia, Botswana and South Africa, the main source of NO_3^- pollution was anthropogenic activities, including pit latrines and livestock feedlots (Tredoux & Talma, 2006). Tillage and associated nitrification of organic matter can be a minor source of NO_3^- leaching. The upper soils in inland southern Africa tend to be low in N, and where inorganic N fertilizer is used, it is typically applied at low rates, though fertilizer application rates may be increasing (Tredoux & Talma, 2006).

Human dimensions of Ramotswa

Based on the most recent census in 2011, the population of Ramotswa was projected at 37,500 people in 2017 and a population density of 1500 persons/km^2 (Statistics Botswana, 2015b). It is a rapidly growing and largely residential town (Table 4.1). Between 1971 and 2011,

Table 4.1. Selected demographic and sanitation indicators for Botswana and the study area populations. Maximum values per row shown in bold.

		Botswana	Gaborone	Ramotswa	Lobatse
Demo-graphy	Population size	2,024,904	231,592	30,382	29,689
	Annual pop. growth rate (%) 2001-2011	1.9	2.5	**3.9**	-0.2
	Average household size	NA	3.1	**4.3**	3.1
	Unemployment rate 2011	20	9.2	**26.5**	12.3
Sani-tation	Access to potable water piped indoors (% households)	NA	**58**	37	42
	Access to potable water piped outdoors (% households)	NA	32	**55**	41
	Access to flush toilet (% households)	NA	**50**	38	36
	Access to pit latrine (% households)	47	3	**56**	10
	Source	*Statistics Botswana 2015a*	*Statistics Botswana 2015b*	*Statistics Botswana 2015c*	*Statistics Botswan a 2015b*

the nation's urban population grew from 9% to 64%, Gaborone being the largest urban center (Statistics Botswana, 2015a). In Ramotswa the population growth rate from 2001-2011 was 3.9% and the national average was 1.9% (Table 4.1) (Statistics Botswana, 2015b, Statistics Botswana, 2015c). Between 2001 and 2011, the populations of Gaborone and Ramotswa increased by 25% and 50%, respectively (Statistics Botswana, 2015a, Statistics Botswana, 2015b), increasing pressure on water supply and sanitation infrastructure (Table 4.1 and Figure 4.3).

Socioeconomic data illustrate that Ramotswa is a peri-urban area lagging behind in development and public services (Table 4.1). The poverty rate in 2010 was declining overall in Botswana, and in the South East District it was 13.4% compared to 6.1% in Gaborone (Statistics Botswana, 2013). In Botswana, the annual mortality rates for infants and children under 5 years are 16 and 27 deaths per 1000 infants, respectively (Statistics Botswana, 2017). Of those deaths, 6.4% of infant deaths and 8% of deaths of children under 5 years are due to "diarrhea and gastroenteritis of presumed infectious origin" (Statistics Botswana, 2017), possibly related to contaminated water.

As of 2011, more than one third of the Ramotswa households have potable water piped indoors, while about half access potable water using an outdoor pipe (Table 4.1) (Statistics Botswana, 2015b). A series of events explains the current water supply situation in Ramotswa. In the early 1980s, production boreholes were drilled in Ramotswa to supply drinking water to Gaborone and Ramotswa. When the Gaborone reservoir was completed in 1984 the Ramotswa groundwater was no longer piped to Gaborone and was only used to supply Ramotswa. In 1996 the Ramotswa wellfield was abandoned because NO_3^- concentrations exceeded the national drinking water standard, 10 mg NO_3^--N L^{-1} (Walmsley & Patel, 2011), and they lacked the capacity to treat the water (Moehadu 2014). Water was therefore piped in from Gaborone (Figure 4.3). A multi-year drought from 2013 to 2016 severely lowered the Gaborone reservoir level to <5% capacity from Dec 2014 to Mar 2016 (Figure A.4.2). Below 5% capacity the reservoir fails to produce water. In 2014, the Ramotswa well field pumps were restarted as an emergency source of water, and they continued to supply water to Ramotswa and the South East District until Tropical Cyclone Dineo hit Botswana in Feb 2017, filled the Gaborone reservoir (Figure A.4.2), and damaged the Ramotswa BHs and pumps. All Botswana water supply and sewage is managed by the Water Utilities Corporation (WUC), a parastatal organization.

NO_3^- concentrations in water from the Ramotswa boreholes had not improved since 1996 and water treatment is unavailable, so the drinking water in Ramotswa is a blend of groundwater from the Ramotswa wellfield diluted with water from the WUC's Gaborone Water Works (GWW) (Moehadu, 2014) (see Boatle blending station in Figure 4.3). The volumes of dilution water from GWW and produced from the Ramotswa wellfield over time were unavailable. Gaborone relies on supply from the Gaborone reservoir, North-South carrier, Molatedi reservoir in South Africa and other sources (Figure 4.3). When there is not enough water for Gaborone, the piped water supply from GWW is completely shut off (locally referred to as water "rationing") to Ramotswa and other towns "downstream" (south) of the GWW (see red ✕ in Figure 4.3). In addition to partially supplying Ramotswa's drinking water, the Ramotswa groundwater also contributes to the supply to the WUC's Lobatse Management Area to the south (Figure 4.3) (Moehadu, 2014).

When high groundwater NO_3^- concentrations were first measured in Ramotswa in the early 1980s, unlined pit latrines were assumed to be the source (Moehadu, 2014, Staudt, 2003, Zwikula, 2005), and a piped sewage network was initiated in Ramotswa, which is when flush toilets first came into use. However, around the same time a different government program encouraged pit latrines for sanitation in Ramotswa (Staudt, 2003, Zwikula, 2005). The piped sewage goes through a series of waste stabilization ponds north of town (downstream of groundwater flow, yellow triangle in Figure 4.2), which were expanded in the 1990s to meet population growth. They include primary and secondary anaerobic, facultative and maturation ponds, totaling 45,000 m^2 (Natacha Martin, International Water Management Institute, personal communication, 2017).

Thirty eight percent of the Ramotswa population had access to a flush toilet as of 2011 (Statistics Botswana, 2015b), the majority of which were assumed to be connected to the piped sewage network while some small fraction used septic tanks (Table 4.1) (Staudt, 2003). In a 2016 survey of 100 households in Ramotswa, it was uncommon for residents to store water to use (including for flushing) during water shutoffs, usually because they did not have a storage tank and the cost of a tank was prohibitive (Tlamelo Matsoga, University of Botswana, personal communication, 2017). Those that did store water used it to meet other household needs, not flush their toilet, and used the pit latrine. Fifty six percent of the Ramotswa population relies solely on traditional pit latrines or ventilated improved pit latrines (VIP) (Statistics Botswana, 2015b), which translates into an estimated 3,900 pit latrines in the town in 2011. As mentioned above, the Ramotswa population increased by 50% between 2001 and 2011, far outpacing sanitation and other infrastructure. How pit latrine waste is handled was uncovered in my interviews, see section 4.2 below. It is unknown how many pit latrines are lined vs. unlined.

METHODS

Changes in seasonal rainfall amount and variability

To assess whether the climate in the Ramotswa area has changed over time, daily rainfall data were combined from three weather stations in the broader area (Figure 4.2): Ramotswa (24.88^{o}S x 25.87^{o}E, established 1980), Gaborone (20 km north of Ramotswa; 24.70^{o}S x 25.90^{o}E, established 1926), and Lobatse (40 km south of Ramotswa; 25.25^{o}S x 25.65^{o}E, established 1922). These data were provided by the Botswana Department of Meteorological Services. Combining the Ramotswa data with the stations in Lobatse and Gaborone allows for analysis of a much longer time period (95 years versus 37 years) and covers a larger spatial area that includes several reservoirs that supply water to the Gaborone drinking water scheme (Figure 4.3). All three datasets are complete and extend through mid Feb 2017, except the Lobatse record is missing data for 1964 and a few months in 1978. Due to the strong seasonal pattern in rainfall, wet season (Oct-Mar) and dry season (Apr-Sep) rainfall totals (referred to hereafter as “seasonal”) were analyzed separately.

We used multiple linear regression analysis to test for trends in six rainfall metrics over time. First, seasonal totals were compared over time to see if annual (water year) volume of rain is changing. Second, number of days with rain (hereafter “rainy days”) were counted per season and compared over time. Third, rainfall intensity per season was calculated using Eqn. 2 from Pryor *et al.* (2009):

$$Season_{year}\ intensity\ \left(\frac{mm}{day}\right) = \frac{total\ rain\ (mm)}{n\ days\ with\ rain} \qquad \text{(Eqn. 2)}$$

Climate change tends to have a greater effect on temperature and rainfall extremes and variability than on averages. Variability was compared over time using the coefficient of variation (CV = standard deviation / mean) of monthly rainfall totals per season. Extreme rainfall events (droughts and floods) were measured using the upper and lower 10th percentile of seasonal rainfall totals to group extreme events (NCEI, 2017, Pryor *et al.*, 2009).

Documenting the impact of climate change on sanitation practices

To document the human behavior aspects of this study, I conducted qualitative interviews with key informants. The questions were developed to gather general information about pit latrines (history, location, types) and how water shutoffs affect people's everyday lives, including sanitation. The questions (Table A.4.3) were framed to respect sensitivity around sanitation and were approved prior to the interviews by the Michigan State University Institutional Review Board (IRB# x16-325e).

We selected three key informants for in-depth interviews: 1) a leader in the Ramotswa tribal governance, which is independent from state government and prioritizes the well being of Ramotswa citizens; 2) a WUC representative of the head office in Gaborone, whose key revenue source is payment from customers and Gaborone's water supply may be a priority over other locations; and 3) WUC Ramotswa Water Works, which is the local office that manages and prioritizes water supply and sewage in Ramotswa. These were chosen based on their contrasting roles in community leadership and resource management and to capture potentially differing perspectives and biases. The small sample size was the result of time constraints. Interviews were conducted in English, audio recorded, transcribed, and coded for thematic analysis.

Groundwater quality sampling and analyses

Existing, but sparse, water quality data were combined for production BHs from 1983-2016, a period that has a large gap in measurements between 1999-2013, with some measurements in 2005 only. This gap roughly coincides with the period when the pumps were offline (1996-2014). The only historic water quality data available for monitoring BHs comes from a baseline study conducted in 2001 by Staudt (2003). In addition, data presented here include those collected by Modisha (2017) in Aug 2016 from a subset of Ramotswa production and monitoring BHs. This sampling occurred before the onset of the wet season. New data generated in this study were collected from monitoring and production BHs on four occasions in Ramotswa: mid Oct 2016 (onset of wet season), late Nov 2016, early Jan 2017, and early Feb 2017. The wet season had peaked during Jan 2017 (Figure A.4.3). Some data on depth to water table going back to the 1980s is available however inconsistency, data gaps, and the effects of production BH pumping prohibit analysis of long term trends in the depth to water table in Ramotswa.

We were limited to sampling the existing boreholes (BHs, Figure 4.2) as new BHs were not installed for this study. There are two types of BHs: 1) Production BHs are those equipped with a pump to provide water to the water supply system and managed by the WUC, and 2) monitoring BH are those used exclusively for collecting data on the groundwater and managed by the Department of Water Affairs (DWA). They are normally welded shut and are not sources of drinking water. I also obtained permission from two farmers to sample their private BHs (BH4157 and BHZ22547), which are equipped with pumps; these data are grouped with the monitoring BHs. Fences protect production BHs, while monitoring BHs are not fenced and freely roaming livestock can access these sites. Over the four sampling events I attempted to re-sample the same BHs. Sometimes this was not possible due to inaccessibility or offline production BH equipment. Overall, I repeatedly sampled 20 BHs including six production BHs and 14 monitoring BHs (Figure 4.2). At each trip, I visited an average of 14-15 BHs. For many of the BHs, I obtained stratigraphy and casing information from BH logs archived at the Department of Geological Survey, Lobatse and published in Appendix VI of Staudt (2003) and

Staudt (unpublished) (Table A.4.1).

Samples from the monitoring BHs were collected using a Grundfos submersible centrifugal pump with an unregulated flow rate of 0.7-1.5 $m^3\ h^{-1}$, which was the same as used by Modisha (2017) and Staudt (2003) (Grundfos models MP-1 and SQ 1.2-3N, Bjerringbro, Denmark). Samples from the WUC's production BHs were obtained from a valve on the *in situ* pumps.

The following variables were measured continuously in the field while sampling with a calibrated Quanta Water Quality Sensor (Hach, Loveland, Colorado, USA): temperature, pH, dissolved oxygen (DO in mg L^{-1}), and oxidation reduction potential (ORP). The outlet of the pump tubing and the sensor were placed at the bottom of a 15 L plastic bucket that was allowed to continuously overflow. This ensured the sensor was continuously measuring water fresh from the pump (presumably equal to *in situ* water quality) and the water at the top of the bucket acted as a barrier to atmospheric gas exchange. Following the USGS (2006) protocol for groundwater sampling for water quality analyses, BHs were pumped until physical and chemical variables stabilized, with recordings every 5 min. Readings stabilized typically after 30-60 minutes of pumping, at which time the groundwater samples were collected.

An unfiltered, 500 ml sample was collected into a sterilized glass bottle for analysis of fecal coliforms, a standard indicator of fecal contamination from warm-blooded animals, including humans and livestock. Samples were analyzed within 24 hr (often within 8 hr) at the WUC Mmamashia Water Treatment Works microbiology laboratory following the ISO standardized membrane filtration method (ISO 9308-1).

A second, 350 ml sample was filtered through a new Supor 0.45 μm membrane filter for each sample (Pall Corporation, Ann Arbor, MI, USA) and stored in new plastic bottles. These samples were refrigerated and delivered to a private service laboratory in Pretoria, South Africa for the following chemical analyses that were conducted within 10 days:

1. Nitrate (NO_3^-) was measured colorimetrically using hydrazine reduction and an Aquakem 250 spectrophotometer (Thermo Scientific, Waltham, MA, USA) (USEPA 1993). NO_3^- concentrations expressed here are actually the sum of NO_3^- and nitrite (NO_2^-). NO_3^- and NO_2^- are oxidants for denitrification, see below. Chloride (Cl^-) was also measured colorimetrically using the mercuric thiocyanate method.
2. Ammonium (NH_4^+) was measured colorimetrically as free and saline ammonia (NH_3) using the salicylate method. The NH_4^+ concentration was calculated using the sample pH, temperature, and equilibrium constant between NH_4^+ and NH_3. NH_4^+ is of interest because it is an intermediate form of N between urea and NH_3 (primary forms of N in urine) and NO_3^-. Only NH_4^+ is reported here, as NH_3 was rarely detected and even then at low concentrations (<0.1 mg L^{-1}).
3. Dissolved organic carbon (DOC) was measured by UV oxidation to CO_2, which was measured using an infrared analyzer (Sievers 900 Analyzer, GE Analytical Instruments, Boulder, CO, USA). DOC is required for denitrification.
4. Total arsenic, manganese, and iron were measured by inductively coupled plasma optical emission spectrometry (ICP-OES). Arsenic is toxic and was previously observed in three monitoring BHs by Staudt (2003). Several other analytes were also measured (Table A.4.4).

Caffeine and paraxanthine (1,7-dimethylxanthine), a metabolite of caffeine, were measured in groundwater samples as indicators of human waste contamination. Caffeinated sodas, instant coffee, and black teas are popular beverages in Ramotswa (Figure A.4.4). Sample collection and solid phase extraction were conducted following Matongo *et al.* (2015). During the Nov 2016 and Jan 2017 trips only, 500 mL samples for caffeine and paraxanthine analysis were filtered in the same way as the hydrochemistry samples. Samples were stored in a refrigerator before extraction within one week. Samples were collected and extracted by someone who had not consumed caffeine in the previous five days, and stored in coolers and refrigerators not used for storing food and beverages.

Solid phase extraction for caffeine and paraxanthine was conducted at the Council for Scientific and Industrial Research (CSIR) in Pretoria, South Africa following the method in Matongo *et al.* (2015). Caffeine standard ($C_8H_{10}N_4O_2$, CAS Number 58-08-2) and paraxanthine standard ($C_7H_8N_4O_2$, CAS 611-59-6) was purchased from Sigma-Aldrich (St. Louis, MO, USA). A 10 mg L^{-1} stock standard was made by dissolving 10 mg caffeine and 10 mg paraxanthine in 1000 ml of 50:50 mix of methanol and deionized water in a flask prepared like the sample jars in a room separate from the room used for extraction, to minimize caffeine contamination. Samples were analyzed 16 weeks after extraction at Washington State University Vancouver, USA by GCMS on a 6890N chromatograph with a 5973 inert mass detector (Agilent Technologies, Santa Clara, CA, USA) in select ion monitoring mode utilizing a 15 m Rtx-35ms capillary column (Restek Corporation, Bellefonte, PA, USA). The oven program was 70^{o}C for 1 min, a 20^{o}C min^{-1} ramp to 190^{o}C, a 15^{o}C min^{-1} ramp to 210^o C, and a final ramp of 30^{o}C min^{-1} to 300^{o}C. The quantifying ions were m/z 194 and 180 for caffeine and paraxanthine respectively. Three µL injections gave a limit of quantitation for caffeine of 0.5 µg L^{-1} and for paraxanthine of

10 μg L^{-1}.

Evidence of denitrification in the aquifer was collected to determine its potential for *in situ* bioremediation (USEPA, 2013). Dissolved gas samples were collected from the groundwater for analysis of N_2O. Because gas samples were transported to the USA for analysis, they were only collected during the final sampling trip in Feb 2017 to minimize storage time between collection and analysis. Previous unpublished work has shown that N_2O concentrations in gas samples collected this way are stable for 90 days when stored in the dark at room temperature (K. Kahmark, Michigan State University Kellogg Biological Station, personal communication, 2016). Methane and carbon dioxide were also measured but data are not shown.

The gas sample collection method described in Hamilton and Ostrom (2007) was used here with a few modifications described in the methods supplement. A 30 mL water sample and a 30 mL ambient air sample were drawn into one gas tight syringe, shaken for five minutes to achieve equilibration, and 10 mL of headspace gas was injected to over-pressurize a 5.92-ml glass vial with a rubber septum (Labco Ltd, High Wycombe, UK). To ensure the sampled water was not exposed to the atmosphere, it was drawn through a narrow piece of polypropylene tubing extending from the syringe tip and inserted directly inside the end of the pump tubing or well below the water surface in the bucket. Samples were collected in triplicate at each site along with a fourth sample of ambient air. Gas samples were stored in the dark at room temperature and were analyzed at the Michigan State University's Kellogg Biological Station within 30 days on a gas chromatograph (Agilent 7890, Agilent Technologies, Santa Clara, CA, USA). N_2O was analyzed with a ^{63}Ni electron capture detector at 350^{o}C coupled to a Gerstel MPS2XL automated headspace sampler (Gerstel, Mülheim an der Ruhr, Germany). The system had a two-column back-flush setup using Restek PP-Q 1/8"OD, 2.0mm ID, 80/100 mesh, 3 m packed columns (Restek, Bellefonte, PA, USA). The oven was set to 90^oC.

Calculations of N_2O concentrations in groundwater followed those described in Hamilton and Ostrom (2007) and are the result of several steps. The concentration of N_2O dissolved in the original liquid sample is back-calculated using the calculated Bunsen solubility coefficient, Henry's Law and the Ideal Gas Law (Weiss, 1974, Weiss & Price, 1980). The ambient N_2O concentration of the air drawn into the syringe for headspace equilibration was accounted for. I estimated the concentration of N_2O dissolved in the water when it infiltrated the soil assuming it was in equilibrium with the atmosphere, and this was also subtracted from the measured N_2O concentration. Therefore, reported N_2O concentrations are the amount of *additional* N_2O the water accumulated as it flowed through the unsaturated and saturated zones.

Multiple linear regression analyses of rainfall and water quality data were conducted in R 3.3.2 (R Core Team, 2017), and coefficients and models are reported here with *adjusted* R^2 values. Plots and maps were created using the R packages ggplot2 (Wickham, 2009) and ggmap (Kahle & Wickham, 2013).

RESULTS

Changes in seasonal rainfall amount and variability between 1922-2017 in Ramotswa, Gaborone, and Lobatse

Seasonal total rainfall is decreasing significantly over time in both the wet and dry seasons (Figure 4.4a, model R^2=73%, p<0.001, Table 4.2: model 1). The *number of rainy days* is

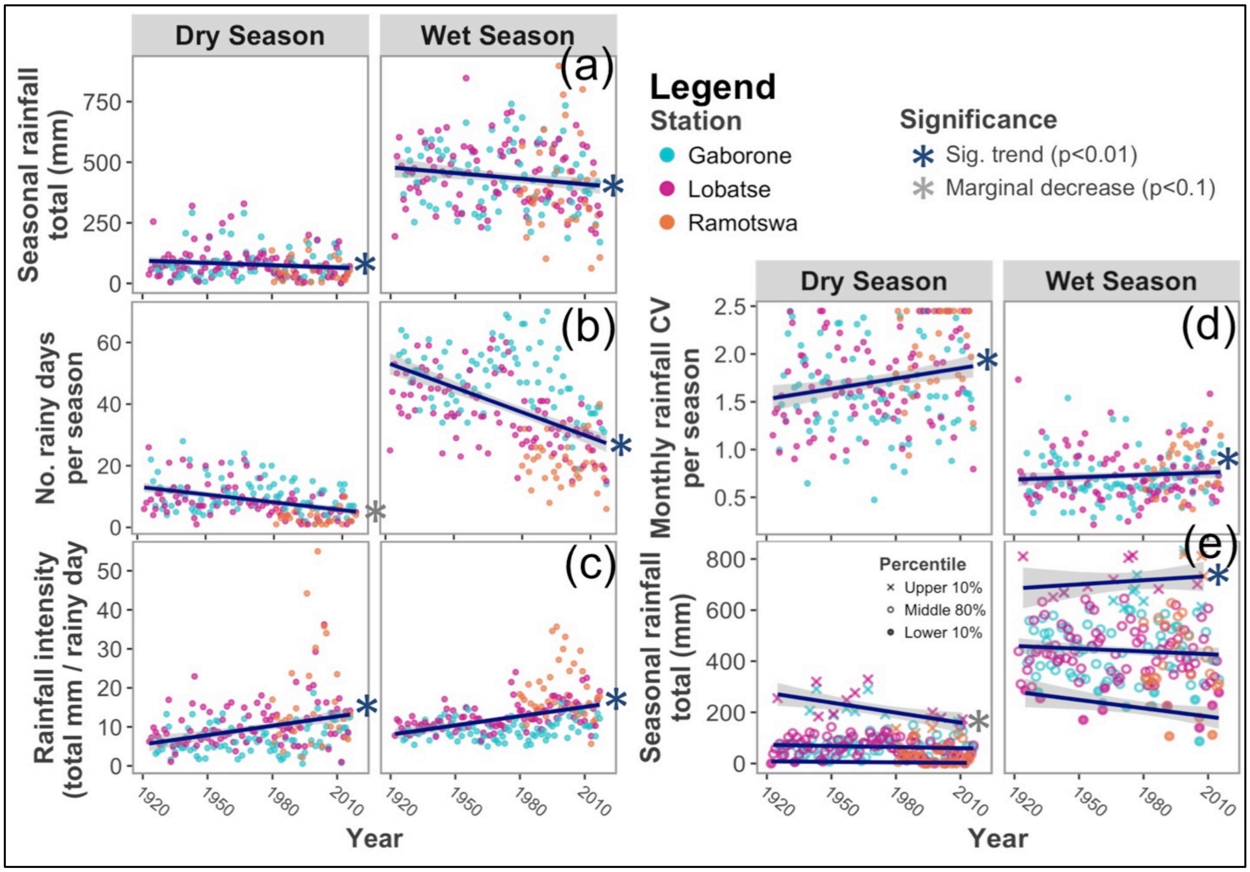

Figure 4.4. Rainfall patterns over time at Gaborone, Lobatse, and Ramotswa weather stations (*color*). Significance is indicated with a *. (a) Total rainfall in both seasons. (b) Number of rainy days. (c) Rainfall intensity. (d) Seasonal coefficient of variation (CV) among monthly rainfall totals. (e) Extreme rainfall events were grouped using the upper and lower 10th percentiles of seasonal rainfall totals (*shape*). See Table 4.2 for model results.

decreasing significantly in both seasons as well, but more so in the wet season Figure 4.4b, model R^2=81%, p<0.001, Table 4.2: model 2). The Lobatse and Ramotswa stations have, on average, fewer rainy days than Gaborone. Rainfall intensity (Eqn. 2) is increasing significantly in both the wet and dry seasons across all stations (Figure 4.4c, model R^2=35%, p<0.001, Table 4.2: model 3). Intensity at the Lobatse and Ramotswa stations are, on average, 19% and 37%, respectively, greater than at Gaborone. Because total rainfall is *decreasing*, the increase in intensity is driven by a declining number of rainy days in both seasons. Rainfall variability, measured as the seasonal coefficient of variation (CV) among monthly rainfall totals, is increasing significantly in both seasons (Figure 4.4d, model R^2=64%, p<0.001, Table 4.2: model

Table 4.2. Historic rainfall regression results.

	Estimate	SE	*p*	Adjusted R^2	Model *p*
1) Seasonal rainfall total ~ year + season				**73%**	**<0.001**
Reference level is dry season					
(intercept)	76.572	7.511	<0.001*		
year	-0.552	0.193	<0.01*		
wet season	359.565	10.469	<0.001*		
2) Number rain days ~ year * season + station				**81%**	**<0.001**
Reference levels are dry season & Gaborone station					
(intercept)	13.431	0.720	<0.001*		
year	-0.040	0.021	0.062 (*)		
wet season	30.451	0.779	<0.001*		
Lobatse station	-6.580	0.848	<0.001*		
Ramotswa station	-13.600	1.221	<0.001*		
year*wet season	-0.180	0.029	<0.001*		
3) Intensity[b] ~ year + season + station				**35%**	**<0.001**
Reference levels are dry season & Gaborone station					
(intercept)	2.700	0.061	<0.001*		
year	0.007	0.001	<0.001*		
wet season	0.435	0.066	<0.001*		
Lobatse station	0.519	0.072	<0.001*		
Ramotswa station	1.023	0.103	<0.001*		
4) CV ~ year * season				**64%**	**<0.001**
Reference level is dry season					
(intercept)	1.724	0.260	<0.001*		
year	0.004	0.001	<0.001*		
wet season	-0.995	0.037	<0.001*		
year*wet season	-0.003	0.001	<0.05*		
5) Seasonal total mm ~ year * percentile group * season				**90%**	**<0.001**
Reference levels are middle 80 percent and dry season.					
(intercept)	65.162	5.214	<0.001*		
year	-0.145	0.194	0.456		
upper 10th percentile	142.046	15.237	<0.001*		
lower 10th percentile	-60.271	15.136	<0.001*		
wet season	375.420	7.450	<0.001*		
year*upper	-1.160	0.607	0.057 (*)		
year*lower	0.080	0.510	0.875		
year*middle*wet	-0.218	0.278	0.432		
wet season, upper 10th perc.	130.839	21.970	<0.001*		
wet season, lower 10th perc.	-157.296	22.076	<0.001*		
year*upper*wet	2.056	0.892	<0.05*		
year*lower*wet	-0.804	0.764	0.294		

For all models, year is centered on the mean year.

[a] *(Intensity + 0.5)$^{1/2}$*

4). The CV is increasing more quickly in the dry season.

Rainfall extremes are also on the rise. Organizing the data by percentiles illustrates how the wettest dry seasons (upper 10^{th} percentile) are getting significantly drier over time (Figure 4.4e, model R^2=90%, $p<0.001$, Table 4.2: model 5). The wet-season upper 10^{th} percentile is getting significantly wetter over time. In other words, the extreme wet seasons are getting wetter and the wettest dry seasons are getting drier. The driest dry seasons (lower 10^{th} percentile) and the majority of wet and dry seasons (middle 80% of observations) are not changing over time. The wet-season lower 10^{th} percentile shows a drying trend, but it is not statistically significant.

In sum, rainfall metrics show the climate is becoming more extreme, with both seasons getting drier. Rainfall variability and intensity are increasing in both seasons. Altogether, these indicate an increasing probability of droughts and floods.

Interview results regarding drought-caused water shutoffs and sanitation behavior

Our interviews confirmed that pit latrines are commonplace throughout Ramotswa and have been the most common sanitation method in Ramotswa since at least the 1950s. Many of the households with a flush toilet also have a new or remnant, functional pit latrine, which they use when the water supply is shut off or when they have a large family gathering. The WUC reports that Ramotswa households continue to connect into the sewage network to the present day.

Many older homes have more than one pit latrine, some of which are abandoned or full. I learned that when pit latrines fill, a resident either pays the WUC US$50 to pump the pit latrine and truck the waste to the sewage ponds, or the resident digs a new pit latrine. Pairs of old and new pit latrines were observed in Ramotswa. It was unclear how many households choose to pump the pits or how frequently this occurs.

Sources explained that during the 2014-2016 period the water supply was shut off for several days at a time without notice due to the drought and low reservoir levels, corresponding with the reservoir capacity being at <5% (failure capacity) from Dec 2014 to March 2016 (Figure A.4.2).

It is common practice during water shut offs for those people who have flush toilets (~38% Ramotswa population, Table 4.1) to use pit latrines. People do not typically store water for flushing their toilet during water shut offs (Tlamelo Matsoga, University of Botswana, personal communication, 2017). Indeed, the Ramotswa WUC leader reported a drastic drop in flow to the sewage system during the 2014-2015 period:

> *[Water shut offs] do affect people because without those flush toilets … our sewage system is not working. Because of these water restrictions, it's only receiving very little water, which cannot keep it running. It's very visible at our [treatment] ponds…There won't be any flow from one pond to another.*

The sewage system is not fitted with a flow meter, so there are no physical data recording these changes in flow.

Similarly, a source recalled that during the water shutoffs they would "*go for about three days without water. And definitely then you would need to use the pit latrines*." These sources, with different knowledge of the community as a whole, suggest that drought-caused water shutoffs increase pit latrine usage in Ramotswa, from about 16,800 users under normal conditions to potentially 28,200 users during shutoffs, or from 56% to 93% of the population in

2011, using the data from Statistics Botswana (2015b). This view was confirmed repeatedly, though unofficially, in conversations with people in other water management positions in Botswana, residents in Ramotswa, and people living in other communities affected by water shutoffs.

In situ denitrification

High NO_3^- concentrations remain a problem in Ramotswa groundwater compared to Staudt's 2001 measurements (Figure 4.5). The highest NO_3^--N concentration measured in the

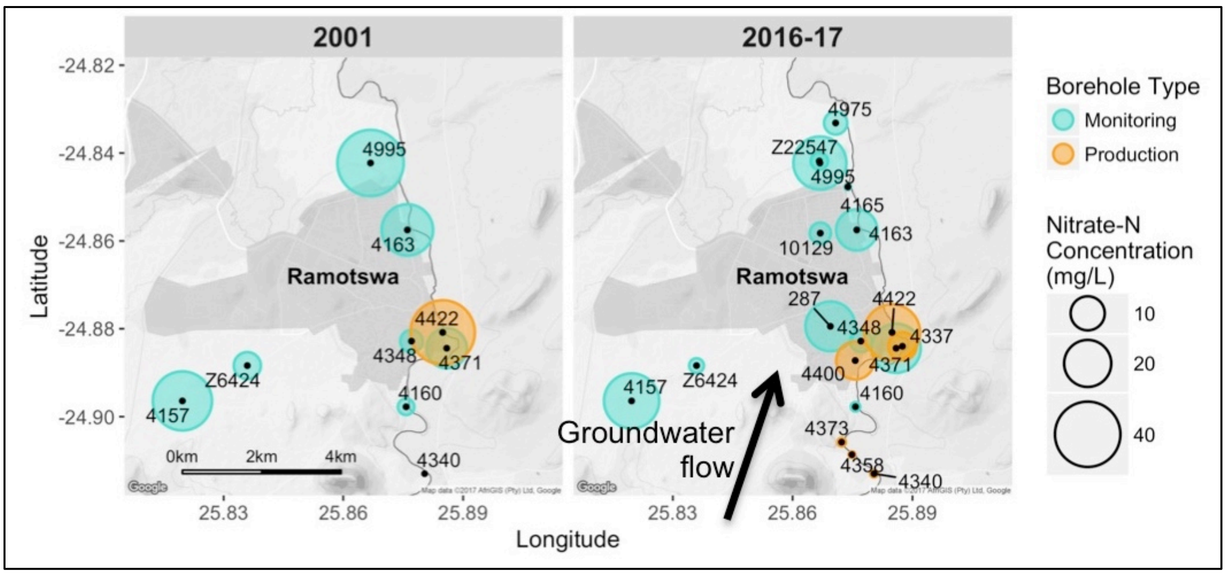

Figure 4.5. Changes in NO_3^--N concentrations in Ramotswa BHs over time and space. *Circle size* indicates BH NO_3^--N concentrations. *Shaded area* is the urbanized area, note this area has not dramatically changed in size since 2001. *Left panel* measurements made in 2001 (Staudt 2003) compared to *right panel* of mean concentration measured in this study.

present study, 29 mg NO_3^--N L^{-1}, was recorded at two sites: production BH4422 in town in Oct 2016 and private BH 4157 at the cattle *kraal* (pen) in Nov 2016 (Figure 4.5). BH4422 was unavailable for sampling after Oct. Monitoring BH4995 ranged from 23-27 mg NO_3^--N L^{-1} at four measurements between Oct 2016 and Feb 2017. These three BHs (4422, 4157, and 4995) also had three of the highest NO_3^--N concentrations in Staudt (2003) (Figure 4.5). Even though

BH4422 and BH4995 shows a decline since 2001 (both around 40 mg NO_3^--N L^{-1} then and near 30 mg NO_3^--N L^{-1} today), they are still well above the NO_3^- water quality standard. Given variability in NO_3^- concentrations and the lack of long term data (Figure A.4.5) it is unclear if the measurements reported here represent a long term declining trend. None of the BHs showed a statistically significant trend in NO_3^- concentrations over time between Aug 2016 and Feb 2017. NH_4^+-N concentrations were low, <0.6 mg L^{-1} at all BHs at all sample dates.

The molar ratio of NO_3^--N to DOC tended to be >1 and as high as 44 in the case of BH 4995, suggesting DOC is potentially limiting denitrification at certain BHs (Eqn. 1) (Figure A.4.6). The production BHs that exceeded the NO_3^--N drinking water standard, BH4422 and BH4400, also showed C limitation.

N_2O was present over and above atmospheric equilibrium concentration (~ 0.15 µg N_2O-N L^{-1}) and positively related to nitrate concentration (Figure 4.6). A linear regression of log(N_2O concentration + 0.5) by NO_3^--N concentration is highly significant ($p<0.0001$) and explains much of the variability in N_2O (R^2 =70%, Figure 4.6). BH4160 had 47.75 µg N_2O-N L^{-1} (the maximum by far). Measurements with the highest NO_3^- and N_2O were C limited (Figure 4.6).

Nitrate source tracking

Fecal coliforms were not detected in any of the *production* BHs but were detected in several monitoring BHs (Figure 4.7). The maximum detection limit of 200 colony forming units (CFU) per 100 mL, was observed at least once in BH4371, BH4995, and BH10129. High NO_3^--N concentrations did not always coincide with the presence of fecal coliforms, but the presence of fecal coliforms tended to coincide with high NO_3^--N concentrations (Figure A.4.7). Regression analysis of samples with fecal coliforms by NO_3^--N is significant (p<0.05, Table A.4.2) but only weakly explains the variation (R^2=11%).

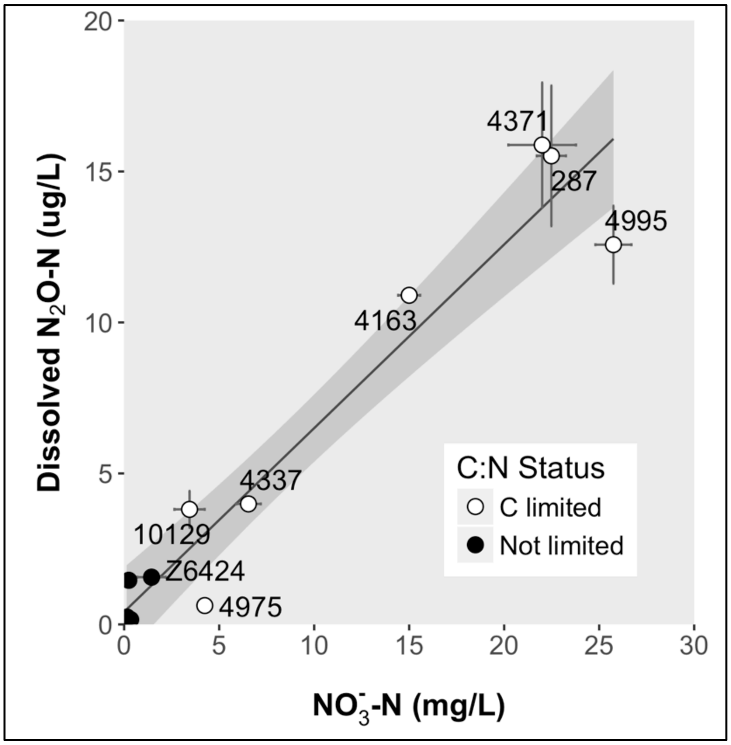

Figure 4.6. Dissolved N_2O is significantly and positively related to nitrate concentration. Error bars represent N_2O standard error among three replicate measurements on one sample date. Shaded area is the 95% confidence interval for regression analysis (*p*<0.0001 and adjusted R^2=0.70, Table A.4.2). BH 4422 and BH 4400 were inaccessible in Feb. 2017 (only time N_2O samples were collected). BH 4160 N_2O concentration was 47.75 µg N_2O L^{-1} (not shown) and was not C limited.

Caffeine and paraxanthine were present in several BHs in both Nov 2016 and Jan 2017 (Figure 4.7b, c). The detection (and non-detection) of paraxanthine at many of the same BHs as caffeine confirms the low likelihood of artificial caffeine contamination. Both compounds were measured in more wells and at slightly higher concentrations in Nov compared to Jan. The few BHs where the compounds were detected in Jan, were BHs where they were also detected in Nov (Figure 4.7b, c). Where detected, caffeine concentrations ranged from 14-56 ng L^{-1}, and paraxanthine concentrations ranged from 180 to 770 ng L^{-1}. Caffeine and paraxanthine were found in several monitoring as well as production BHs, including production BH4340, BH4358,

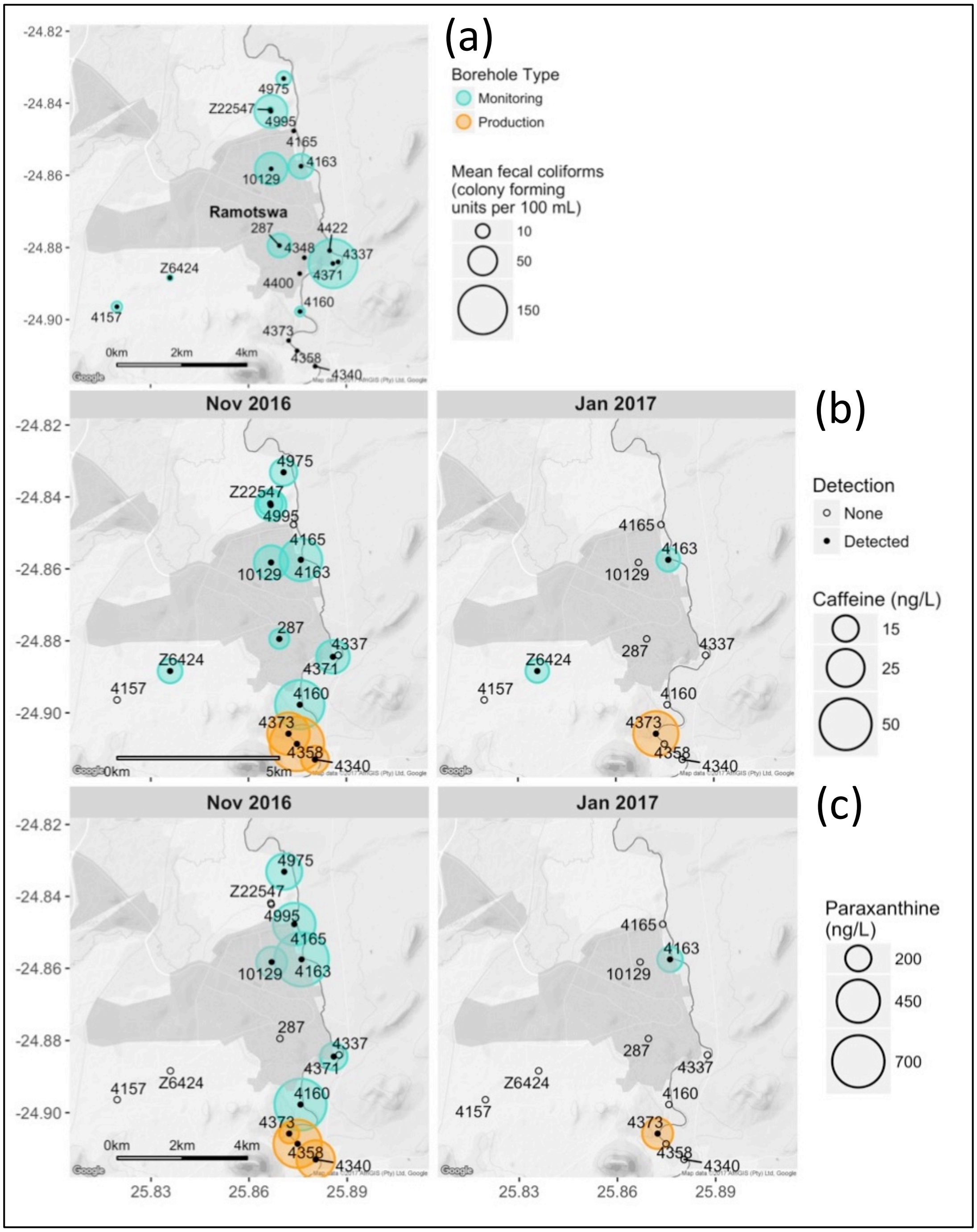

Figure 4.7. Maps of fecal contamination indicators. (a) Mean fecal coliform count, indicator of warm blooded animal fecal contamination*,* from a maximum of four measurements between the Oct. 2016 and Feb. 2017. No fecal coliforms were detected at any of the production BHs. (b) Caffeine and (c) paraxanthine concentrations as indicators of human waste contamination, measured in Nov. 2016 *(left panels)* and Jan. 2017 *(right panels).*

and BH4373, which are upstream of town. To test whether caffeine was tracing the NO_3^- pollution, I used regression analysis to explain caffeine using an interaction between NO_3^-

concentration and whether or not the sample indicated denitrification was C-limited (see below). The regression is significant ($p<0.01$) and explains 67% of the variability (Figure A.4.8, Table A.4.2).

Arsenic was not detected in any BHs, though only one BH of the three where Staudt (2001) detected arsenic was available for sampling. Manganese and iron concentrations were high at several sites (Table A.4.5).

DISCUSSION

Effect of climate change on water supply in Ramotswa

Declining rainfall and increasing variability. The analyses of the last 90 years of rainfall data strongly suggest that the South East District's climate is changing (Figure 4.4). Declines in seasonal total rainfall and number of days with rain, together with increasing variability and extremes, are likely to increase the frequency and intensity of droughts and floods, such as the most recent 2013-2016 drought. This supports $\mathbf{H_1}$: *Climate change-induced droughts are becoming more frequent* (Figure 4.4). This is in agreement with a review of historic rainfall patterns in Southern Africa (Hodnebrog *et al.*, 2016, Niang *et al.*, 2014). The climate models used in the IPCC Fifth Assessment Report project Botswana and Namibia will "very likely" (i.e., >90% probability) continue to see declines in mean annual rainfall, a delay in the onset of the wet season, and by 2100, drier and shorter wet seasons and drier dry seasons (Niang *et al.*, 2014). A delay in the onset of the wet season was not detected in the rainfall data used here.

While changes in annual total rainfall are important, changes in the variability and intensity of rainfall may have more significant influences on drought and flood frequency. The

South East District's rainfall data showed a decline in number of days with rain and increases in seasonal rainfall intensity. This is in agreement with the New *et al.* (2006) study of rainfall across southern Africa, including data from the Gaborone weather station used in the present study as well as several other rain gauges in Botswana.

Climate change impacts on Ramotswa drinking water supply. In the South East District, the water supply depends on wet season rains to fill reservoirs and provide water through the dry season. Dry season average rainfall from 1980-2016 was 47 and 64 mm in Ramotswa and Gaborone, respectively. Water levels in the Gaborone reservoir receded dramatically during the recent three-year drought, falling below 5% capacity (its failure level) from Dec 2014 through March 2016, and remaining below 20% through Jan 2017 (Figure A.4.2). This further supports **H_1**: *Climate change-induced droughts are becoming more frequent, which will decrease reservoir levels* (Figure 4.1). Here, changes in the climate and water systems that people rely on are affecting people's access to water. Increases in rainfall intensity, mentioned above, may lead to a greater fraction of rainfall running off and filling reservoirs. Heavy rainfall in Feb and early March 2017 filled the Gaborone reservoir to 100% capacity on 7 Mar 2017 for the first time in 15 years (Figure A.4.2). As the temperature is likely to increase 3.4^{o}C-4.2^{o}C by 2100 in southern Africa (Niang *et al.*, 2014), evaporation from reservoirs, already >2000 mm yr^{-1} (Altchenko et al. 2016), will likely increase with temperature, reducing the aforementioned potential increase in recharge and reservoir filling.

Drought and low reservoir levels put increasing demand on groundwater resources—a feedback from the human system as a result of changes in the water system. In the case of Ramotswa, the drinking water supply depends on treated water from the Gaborone Water

Works to dilute the locally pumped groundwater at the Boatle blending station (Figure 4.3). The water supply to the Gaborone Water Works is a patchwork dependent on pipelines, groundwater, and reservoirs vulnerable to drought. During the recent drought, when there was not enough water to supply Gaborone, the supply of water from Gaborone to dilute the Ramotswa groundwater was shut off, setting into motion a cascade of effects as discussed below.

Effect of drought and water shut offs on sanitation in Ramotswa

The key informant interviews strongly supported **H_2**: *Water shortages increase pit latrine use* (Figure 4.1). Changes in the natural system change human behavior, causing a feedback to the groundwater system. With an increasing likelihood of events like the recent three-year drought and no change in water treatment infrastructure, Ramotswa will experience more frequent disruptions in water supply, and as a result there will be more use of pit latrines (Figure 4.1). As noted earlier, water shutoffs potentially increase the number of people using pit latrines by an estimated 67% to 28,200, about 93% of the population of Ramotswa (Statistics Botswana, 2015b). Here a water *quantity* problem, drought and water shutoffs, led to a water *quality* problem, increased pit latrine use and groundwater pollution.

Groundwater quality and in situ denitrification bioremediation potential

The Ramotswa groundwater continues to exhibit NO_3^- concentrations in excess of the Botswana drinking water standard of 10 mg NO_3^--N L^{-1}. This includes two of the production BHs, 4422 and 4400, and several monitoring BHs (Figure 4.5). The concentrations on the whole do not appear to have increased or decreased significantly since the Staudt (2003) observations, despite Ramotswa's population increasing by 50% between 2001 and 2011, following a pattern of population growth dating back to the 1970s (Statistics Botswana, 2015b). There may be reasons why population growth and NO_3^- concentration are not directly correlated. Data on NO_3^- concentrations in Ramotswa are scarce and may not capture long term patterns or variation. Since approximately 2000, the newly expanding peri-urban areas of Ramotswa are connected to the sewage network and most households are believed to be connected (source: interviews); though the recent drought incentivized building pit latrines at new homes, which I observed in Ramotswa. Older households located near the sewage network continue to connect, at a cost of about US $50, which may be prohibitive to some households. Given the data available, it seems that the sewage network could be reducing the volume of human waste entering pit latrines and potentially the aquifer. But with increasing likelihoods of long term droughts, water shortages, and water shut offs, *people with flush toilets will need to use pit latrines*, short-circuiting the potentially beneficial effects of the sewage network on groundwater quality.

Relatively high N_2O concentrations suggest denitrification is occurring in the aquifer (Figure 4.6), while low DOC concentrations indicate that denitrification is C-limited (Figure A.4.6), supporting **H_3**: *Denitrification has the potential to provide* in situ *bioremediation of the Ramotswa groundwater nitrate contamination.* Jacks *et al.* (1999) also demonstrated denitrification occurrence by measuring $^{15}N/^{14}N$ ratios in Ramotswa groundwater and the leaves of non N-fixing trees with roots reaching the water table, which were both significantly enriched in ^{15}N (a sign of denitrification preferentially using up the lighter ^{14}N, leaving more ^{15}N behind in the water that is taken up by roots). The strong positive relationship between NO_3^-

and N_2O concentrations (Figure 4.6) suggests that waters with high NO_3^- probably started out along their flowpath with even more NO_3^- but have lost some to denitrification, but that not all of the NO_3^- was reduced because of low DOC. Waters with low NO_3^- may never have had much NO_3^- to begin with so they have low N_2O. Before the present study, Ramotswa groundwater had never been analyzed for DOC, but now I can show that given more DOC, *in situ* bioremediation that enhances denitrification by injecting a source of DOC could remove additional NO_3^-.

Source of NO_3^- contamination

N fertilizer, livestock waste, and human waste are potential sources of NO_3^- contamination. N fertilizer is ruled out as a contributor for several reasons. First, two of the production BHs south of town (4358 and 4340) are located in cultivated farm fields, yet their mean concentrations were consistently <1 mg NO_3^--N L^{-1} and N_2O was low as well. Second, samples with fecal coliform contamination also tended to be high in NO_3^- (Figure A.4.7), suggesting a livestock and/or human source for both. Third, synthetic fertilizer only became available to farmers in the area in the last few years as a subsidy from the government (Jacks et al. 1999 and Staudt 2003 report no synthetic fertilizer use), but NO_3^- has been high in the Ramotswa aquifer since the 1980s (Staudt, 2003).

As for livestock waste, there are no feedlots in Ramotswa where livestock waste is concentrated. Livestock waste scattered on the soil surface is commonplace throughout Ramotswa as the animals freely roam around town grazing. The likelihood of contamination from dispersed livestock waste infiltrating from the surface through diffuse recharge is low given that diffuse recharge is <1 mm per year (Post *et al.*, 2012). While 20 mm recharges per year through rapid recharge from runoff percolation, ephemeral riverbed infiltration, and direct infiltration through outcrops such as the outcrop the town sits on (Gieske, 1992). This makes unlined pit latrines more closely linked to the aquifer than diffuse livestock waste on the surface. In fact, artificial recharge from leaking pit latrines may outpace natural recharge (~20 mm yr^{-1}). With only one BH outside of town used for watering cattle (BH4157), I am unable to make conclusions about the direct impact of livestock. At this BH, NO_3^--N was high (mean concentration 15 mg NO_3^--N L^{-1}), fecal coliforms were low (5 FCU and not detected on different dates), and caffeine and paraxanthine were not detected.

Several lines of evidence suggest a human source. Fecal coliform concentrations were highest in town and consistently low at BH4157 used for watering cattle. Furthermore, BHs with low NO_3^- also tended to have low fecal coliforms (Figure A.4.7). Caffeine and paraxanthine were present in many BHs (Figure 4.7 b, c). Altogether, these support **H_4**: *Nitrate pollution is from human waste contamination*.

However, this does not explicitly identify the source of human waste. It is possible, but unlikely, that the majority of human waste comes from sources other than leaking pit latrines: other potential sources include improperly maintained or sited septic tanks, ruptures in the sewage network, or leaking settling ponds. Even though septic systems and sewage networks have been shown to contaminate groundwater with N and other pollutants (Katz *et al.*, 2011), these did not appear in Ramotswa until more recently. Pit latrines have been in use in Ramotswa since the 1950s if not earlier (source: interviews), and construction of the sewage system began in 1981 about the same time as septic systems came into use. Drinking water quality measurements of Ramotswa groundwater in 1983 showed the NO_3^- was already elevated (Figure A.4.5). The sewage settling ponds are also unlikely sources of contamination, because these are located north (downstream) of town. A study in a town 55 km north of Ramotswa, Mochudi—also located on the Notwane River, found pit latrines were the source of NO_3^- pollution of the groundwater (Lagerstedt *et al.*, 1994).

The thousands of pit latrines in Ramotswa are the most likely sources given the locations and co-occurrence of the above indicators, but the detection of caffeine in the southernmost BHs (4373, 4358, and 4340, all production BHs) is perplexing. These BHs had <0.5 mg NO_3^--N (Figure 4.7) at all sample dates and <1.5 µg N_2O-N L^{-1}, suggesting there was no NO_3^- contamination nor NO_3^- that had been removed by denitrification. Also, the presence of caffeine at these southern (upstream) locations could mean the caffeine is not coming from the pit latrines. I have a couple speculative explanations for this peculiarity.

First, these southernmost production BHs would have a large cone of depression when they are pumping, so that their chemistry represents a wider area that potentially includes recharge zones affected by human activity and pit latrines. Along this flowpath caffeine could remain in the water, but NO_3^- is denitrified to completion as N_2 so that neither NO_3^- nor N_2O are present. The caffeine could persist, even along C-limited flow paths, because denitrifying bacteria might not use caffeine as a source of DOC. Indeed caffeine is considered toxic to many bacteria (Mazzafera, 2004). Also, the conditions that enable microbial caffeine degradation are different from the conditions necessary for microbial NO_3^- removal: denitrification requires low oxygen conditions, whereas microbial degradation of caffeine seems to require aerobic conditions (Mazzafera, 2004). So, a common source of NO_3^- and caffeine contamination could exhibit NO_3^- without caffeine or vice versa along the groundwater flow path depending on microbial community and oxygen availability.

Alternatively (or additionally) the presence of caffeine in the south could be because the Notwane River carries human waste contamination when it is flowing. The river likely loses water to groundwater recharge, affecting the chemistry of these southernmost BHs located in the floodplain. Unfortunately, Notwane River chemistry data at Ramotswa are not available to test this idea. But a joint water quality report by the Departments of Water Affairs in Botswana and South Africa (2013) found that NO_3^--N was 8 mg L^{-1} after the Gaborone waste water discharges into the Notwane River (downstream of Ramotswa and the Gaborone Reservoir), which is low compared to >20 mg L^{-1} in several Ramotswa BHs reported here. Upstream of Ramotswa is Lobatse, which has a similar population size. Its wastewater effluent feeds into the Notwane Dam, 33 km upstream of Ramotswa. There are no other large settlements on the Notwane River between Ramotswa and Lobatse. Perhaps NO_3^- but not caffeine from Lobatse wastewater is removed by the time the river recharges the aquifer in Ramotswa. If the river is the source of caffeine for the southernmost BHs, then it does not explain the presence of caffeine in upland BHs like 287, 10129, or 4995—meaning, pit latrines contribute caffeine to the groundwater at least in these upland BHs.

We need a greater understanding of the role of the Notwane River in groundwater recharge in Ramotswa to assess its potential as a contamination source. However, the co-occurrence of NO_3^-, fecal coliforms, and caffeine in the sampled BHs (except for the southernmost BHs) strongly suggests human sources of contamination *within* Ramotswa, which are most likely from the thousands of pit latrines leaking into the Ramotswa Aquifer (Table 4.1).

Stepping back to the bigger CHANS view, strong linkages between Ramotswa's natural and social systems meant that changes in one led to changes in the other: changes in the climate and surface water quantity changed sanitation behavior, which increased pollution of the groundwater (Figure 4.1). This pollution, lacking local water treatment, perpetuates Ramotswa's reliance on Gaborone's drought-vulnerable water supply.

Indirect impact of climate change on groundwater quality

We have shown that human-induced changes in the climate, sanitation systems, and groundwater interact to put Ramotswa's water security at risk (Figure 4.1). The climate in the South East District of Botswana has changed significantly over the last 90 years (Figure 4.4). Water scarcity in the district is likely to increase due to changes in environmental and social conditions: the rising frequency and intensity of droughts, growing population, urbanization, and water demand. Ramotswa's dependence on Gaborone for diluting its groundwater means Ramotswa's access to safe drinking water (and water to flush toilets) is paradoxically threatened by the combination of low surface water quantity and poor groundwater quality. If water treatment of Ramotswa groundwater were available, Ramotswa water security would be de-coupled from the Gaborone water supply and its ensuing vulnerability to drought and water shutoffs (Figure 4.3: gray arrows). If pit latrines were not polluting the Ramotswa groundwater, expensive water treatment would not be necessary. Currently, more droughts will mean more water shutoffs to Ramotswa, which is when people switch to pit latrines rather than flush toilets. Therefore, climate change is indirectly impairing groundwater quality via droughts, water supply infrastructure, and sanitation. Regardless of climate change, social pressures on water supply will likely perpetuate water scarcity in the South East District, and undoubtedly exacerbate, and be exacerbated by, water quality threats (Calow *et al.*, 2010, Niang *et al.*, 2014, Taylor *et al.*, 2009). In the next section are recommendations for changes in infrastructure and governance to address water security in Ramotswa.

Recommendations

The immediate problems of pit latrines leaching into the aquifer and droughts increasing pit latrine use are significant threats to water security in Ramotswa. If Ramotswa's high annual population growth rate from 2001-2011 of 3.9% continues (Statistics Botswana, 2015b), Ramotswa will see an increase in both water demand and volume of human waste over time. Lining pit latrines should be a priority. When an unlined pit latrine is pumped, a liner could be installed. Incentives could be designed to increase the number of pit latrines that get pumped rather than abandoning full pit latrines and building new ones.

Using precious treated water to flush human waste may not be the most efficient use of water in a semi-arid environment. Path dependence on the existing investments in infrastructure and residents' preference for flush toilets (source: interviews) will likely perpetuate the current sewage system. Investment in flush toilets must be matched by efforts to improve resident's access to water to flush their toilets. The climate analysese here suggest toilets will be less and less usable with increasing frequency of droughts and water shutoffs. Captured and stored rain or grey water could be used to flush toilets, but many Ramotswa residents do not have the means for investing in such equipment. Increasing residents' capacity to flush into the sewage system should be seen as an investment in groundwater quality.

Planning for improvements in infrastructure (e.g., expanding the sewage system) requires information about the current systems. Useful spatial data that is missing includes: up to date maps of the piped sewage network, homes connected, pit latrines and their status (including lined/unlined, in-use/abandoned, etc.), and septic tanks. It would also be helpful to monitor volumes of water abstracted, depth to water table, and volumes used across the water supply scheme over time to monitor trends and manage for the sustainable use of each water source. A water treatment facility for Ramotswa's groundwater using reverse osmosis has been initialized in Boatle (site of current blending station, gray arrows in Figure 4.3) but progress has stalled for nearly a year.

If Ramotswa were able to treat the groundwater and use it for 100% of its supply, greater extractions will be required. Sustainable use of the Ramotswa wellfield depends on pumping at a sustainable rate. A 2014 review of Ramotswa's monthly wellfield abstractions by the WUC revealed that several BHs had exceeded the recommended abstraction rates (Moehadu, 2014). These over-abstractions were to make up for a failure of water supply infrastructure to Gaborone and for rising demand in another community (Moehadu, 2014). In essence, even with local water treatment, Ramotswa's water security is tied to demand and failures in infrastructure in other parts of the South East District water delivery scheme (Figure 4.3). The water supply scheme increases people's access to water, but it also makes water resources vulnerable to overuse by demand from distant communities.

The limited supply of DOC relative to NO_3^- observed in Ramotswa groundwater demonstrates that *in situ* bioremediation (ISB) using denitrification has the potential to remove more of the groundwater NO_3^- if more DOC were available (Figure A.4.6). Furthermore, the presence of N_2O dissolved in the groundwater confirmed that the microbes and conditions in the aquifer are suitable for denitrification. A vegetable oil amendment could act as a C substrate (USEPA, 2013), and this has been proposed for ISB in Ramotswa. ISB has the potential to be cost-effective and less energy intensive than traditional water treatment, however its proper implementation requires intensive knowledge of the groundwater hydraulics and geochemistry (Majone *et al.*, 2015). Many factors must be taken into consideration to test the feasibility of potentially implementing ISB in Ramotswa, including the cost (relative to the funds needed to finish building and to run the water treatment facility), sustainability, dolomite feasibility for ISB (Tompkins *et al.*, 2001), site specific hydraulic characteristics, amendment longevity, performance monitoring using tools such as stable isotopes, and effects on downstream geochemistry (USEPA, 2013).

If stakeholders want to understand how NO_3^- concentrations are responding to the complex factors involved in this CHANS and the efficacy of remediation efforts, water quality monitoring and associated funding should be a priority. If monthly sampling is too expensive, once per season, regardless of whether or not the production BHs are pumping, would still provide useful data. Further, the water quality of private BHs, which provide untreated water to many people during water shutoffs, should be monitored.

CONCLUSIONS

This work demonstrated the indirect effect of climate change on groundwater quality in Ramotswa, Botswana. Historic rainfall analyses suggested that events like the 2013-2016 drought are likely to become more frequent in Ramotswa and the South East District. The drought led to water shutoffs, inducing people with flush toilets to use pit latrines, potentially one-third of the town's population in addition to the remaining two-thirds already using pit latrines. Groundwater NO_3^- levels exceeded the drinking water standard. The presence and location of NO_3^-, fecal coliforms, caffeine, and paraxanthine in groundwater wells suggest that N fertilizer and livestock waste are not likely to be major sources of NO_3^- pollution; the most reasonable hypothesis is that human waste from pit latrines is a major source of the NO_3^-. High dissolved N_2O concentrations in the groundwater suggest *in situ* denitrification is happening, however low DOC concentrations relative to NO_3^- concentrations suggest that denitrification is C limited. Therefore, *in situ* bioremediation providing an additional C source in the aquifer could amplify nitrate removal by denitrification.

The CHANS approach allowed us to understand the water quality data in the larger context of social and natural drivers. This perspective illuminated the linkages between water supply, sanitation, and groundwater quality, which demonstrated the importance of local water treatment for improving water access and, thus, protecting groundwater quality. The CHANS framework also enabled us to connect climate change and urbanization with Ramotswa groundwater quality, which points to different potential outcomes depending on how Ramotswa and Botswana choose to manage water supplies and protect groundwater quality. Without this interdisciplinary approach, biogeochemical processes alone could not fully explain the observed patterns in groundwater quality or point to external drivers and future outcomes.

In the broader picture, this story is not unique to Ramotswa. Rapid urbanization in developing countries brings rapid increases in the number of pit latrines, often in communities that use shallow groundwater for drinking (Cronin *et al.*, 2007). The evidence presented here demonstrates the tight couplings between water quality and quantity, water supply and sanitation, and climate and infrastructure. Recognizing these interconnections could help shift the framework for water supply and sanitation. Rather than thinking about and managing water supply and sanitation separately, communities, resource managers, and policy makers can plan a water infrastructure system incorporating and addressing these interconnections—a complex task indeed. Such an integrated system that protects groundwater quality and quantity will ultimately reduce the cost of water treatment, reduce water-borne disease transmission, and strengthen the community's water security and resilience in the face of climate change and urbanization.

Finally, climate change will continue to challenge the sustainability of the water resources of Botswana's South East District. Historically industrialized countries like the US, which are responsible for the majority of past and present greenhouse gas emissions, should recognize their role in the fate of places like Ramotswa and take aggressive actions to mitigate emissions.

APPENDICES

APPENDIX A: Tables

Table A.4.1. Ramotswa borehole (BH) details. Geological and casing information from Staudt (2003).

BH	BH type[a]	Land use	Dominant formation	BH log available[b]	Well depth (m)	Water strikes (m)	Casing length (m)	Screen depth (m)	Screen length (m)	Mean[c,d] depth to water table (m)	Mean[c] NO_3^--N mg/l	Mean[c] fecal coliforms (cfu/ 100mL)
287	M	commercial, residential	Dolomite	Yes	36	-	-	-	-	22.19	22.48	32.25
4157[e,f]	M	cattle farm well, cattle watering	-	No	-	-	-	-	-	-	28	5
4160	M	grazing, near residential area	Dolomite	Yes	104	23.6	50	-	-	16.3	0.45	4
4163	M	pig farm, pit latrine	Dolomite	Yes	56	-	2.3	-	-	4.3	15	35.25
4165[f]	M	grazing	Dol., quartz, shale	Yes	100	6.7, 39.30	33	-	-	4.6	0.13	0
4337	P	residential	Dol., shale	No	118	36, 81-82	open hole	34-46, 76-100	118	-	6.54	0
4340	P	farm field	Conglomerate	No record	120	13-14, 30, 42	open hole	open hole	open hole	-	0.24	0
4348	M	farm field	Dol., chert, shale	Yes	94	76	4	-	-	14.6	3.65	0
4358	P	farm field	Shale	No	102	45	open hole	open hole	open hole	-	0.15	0
4371	M	grazing, near residential area	Dolomite	Yes	96	-	-	-	-	12.7	22	153
4373	P	pasture	Conglomerate	No record	120	40, 56, 75, 96	-	28-40, 70-89, 92-110	-	-	0.34	0
4400	P	residential	Dolomite	Yes	102	47	open hole	open hole	open hole	-	12.55	0
4422	P	residential	Dolomite	Yes	120	69	54	54	36	-	38.7	0
4975	M	grazing, sewage ponds	-	No	-	-	-	-	-	7.6	4.24	11
4995	M	near goat farm	Dolomite	Yes	150	24	16	-	-	22.0	25.75	66
10129	M	residential, school	-	No	-	-	-	-	-	8.2	3.44	62.75
Z22547[f]	M	goat farm well	-	No	120	66	-	-	-	-	2.1	1
Z6424	M	cemetery	Dolomite	Yes	150	51	69	-	-	27.7	1.44	1

[a]P=production, M=monitoring

[b]BH logs are illustrated in Staudt (2003). BH logs not recorded in Staudt (2003) were not made available from the Botswana Geosciences Institue or the Botswana Department of Water Affairs.

[c]Mean of maximum five measurements between Aug. 2016 and Feb. 2017.

[d]Not able to measure depth to water table at Production BHs and private farms outfitted with pumps (BH 4157, BHZ22547).

[e]BH4157 is referred to as WH1 in Staudt (2003).

[f]Private farm.

Table A.4.2. Regression results for N_2O, fecal coliforms, and caffeine (individually) by NO_3^-.

	Estimate	SE	*p*	Adj. R^2	Model *p*
1) Log(µg N_2O-N +0.5) ~ NO_3^--N (mg L^{-1})				**34%**	**<0.001**
(intercept)	0.733	0.228	<0.01		
NO_3^--N	0.085	0.019	<0.001		
2) Fecal coliforms (CFU) ~ NO_3^--N (mg L^{-1})				**11%**	**<0.05**
Note: Only including samples where CFU>0.					
(intercept)	15.5	20.2	NS		
NO_3^--N	2.6	1.2	<0.05		
3) Caffeine (ng L^{-1}) ~ NO_3^--N (mg L^{-1})*C status				**67%**	**<0.01**
(intercept)	-14.5	8.7	NS		
NO_3^--N	167.8	35.6	<0.001		
C limited	27.1	9.5	<0.05		
NO_3^--N * C lim.	-167.5	35.6	<0.001		

Table A.4.3. Interview questions.

	Question
1.	(Name and official title)
2.	How long have you been in this position?
3.	How long have you lived in Ramotswa?
4.	I understand that pit latrines were introduced, fairly recently, in the 1990s [we learned this is incorrect, that pit latrines have been in use since at least the 1950s]. Can you describe how they were introduced (government program, how were people convinced, more specific dates, before pit latrines open defecation)?
5.	The 2011 census report for the South East District showed the population of Ramotswa at about 30,000, with about 10% of the population have access to a flush toilet and about 15% have access to a pit latrine or VIP (own or shared). Do these numbers sound about accurate? Do you think they have they gone up or down since 2011? [These numbers were later determined to be incorrect in the census report, we now know that 38% of Ramotswa population uses a flush toilet and 56% uses pit latrines.]
6.	Does the remaining 75% or so rely on open defecation? [The above correction indicates there is very little, if any open defecation.]
7.	What are the water restrictions like in Ramotswa? (warning, duration, effects, times per month)
8.	How have water restrictions affected sanitation access in Ramotswa? (access to flush toilets, washing hands, etc.)
9.	How does season (wet season or dry season) affect sanitation access?
10.	How deep are pits dug for latrines in Ramotswa? (overall dimensions)
11.	About how long does it take for a pit to fill?
12.	When a pit latrine fills, what do people usually do?
13.	Is the ultimate goal to increase access to flush toilets? Are houses still connecting into the sewage system? What are the barriers?
14.	If you were to guess where pit latrines are having the biggest impact on groundwater / or where the most problematic latrines are located, where would that be? Can you show me on this map? Why there?
15.	What are the major constraints to improving sanitation in Ramotswa and how would you improve it? (what types of changes would you make? Priorities?)
16.	Are people in Ramotswa aware of groundwater, the nitrate in the groundwater, and the potential link between pit latrines and the nitrate in the groundwater?
17.	Do you have any data that might be useful for my project? map of flush toilets, vs. pit latrines, vs. neither? timeline of water restrictions? Numbers of households tapping into sewage system per year? Sewage system operations?
18.	Do you have any other information that I didn't ask about but that you think might be relevant to understanding the nitrate issue?

Table A.4.4. Methods for measurements of other hydrochemical analytes (data not shown, available upon request).

Analyte(s)	Method
Chloride and sulfate	Colorimetric reactions and a spectrophotometer
Conductivity	Conductivity meter
Total alkalinity	Titration
Calcium, magnesium, potassium, sodium, manganese, arsenic, and iron	Inductively coupled plasma optical emission spectrometry (ICP-OES)

Table A.4.5. Arsenic, manganese and iron concentrations.

Ion	Results
Arsenic (As)	Of the three Ramotswa monitoring BHs where Staudt (2003) measured high As in 2001 (BH4887, BH4886, and BH4165), only one, BH4165, was accessible for sampling in the present study. BH4886 has been outfitted with a data logger for monitoring depth to water table and can no longer be pumped. BH4887 is very close to the river and was flooded by the end of the October sampling week and flooded on each trip thereafter. BH4165 as well as all the other samples had no detectable As. Conductivity was high in several samples, though never exceeding the Botswana drinking water standard of 3100 uS cm^{-1}.
Manganese (Mn)	The World Health Organization's drinking water guideline for Mn is 0.4 mg L^{-1} and recommends treating water so that Mn is below 0.05 mg L^{-1} (WHO 2008). The following BHs exceeded 0.4 mg Mn L^{-1}: BH4340 (maximum 1.68 mg L^{-1}), BH4358, and BH4373. The following BHs exceeded 0.05 mg L^{-1}: BH4160, 4163, 4165, 4348, 4975, 10129, Z22547, and Z6424.
Iron (Fe)	The WHO does not provide a drinking water guideline for Fe, but the USEPA (2009) water quality standard is 0.3 mg L^{-1}, which the following BHs exceeded: BH4160, BH4165, BH4340, BH4373, and BHZ6424 (maximum 19 mg L^{-1}).

APPENDIX B: Figures

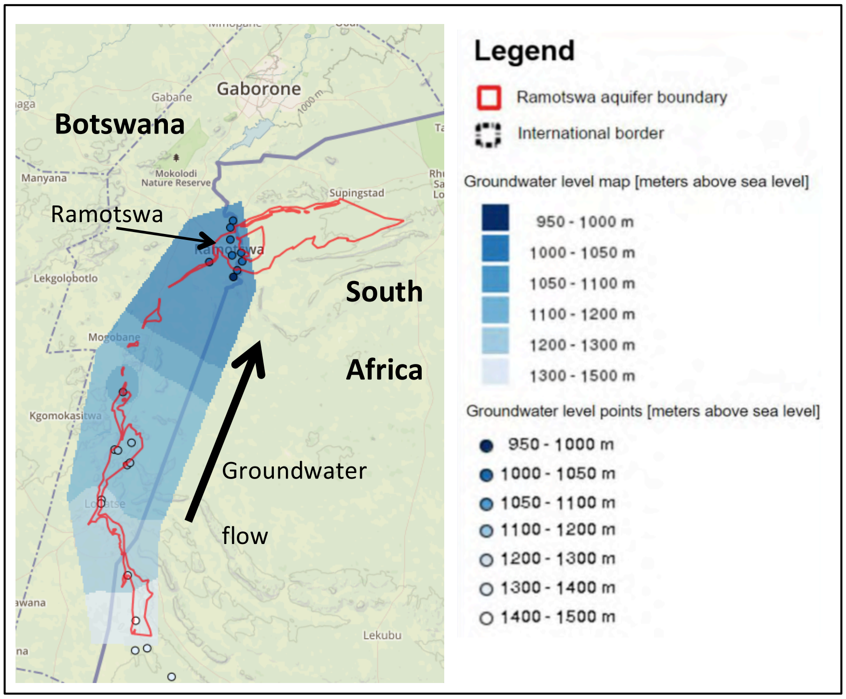

Figure A.4.1. Ramotswa aquifer outcrop boundaries (*red*) and piezometric sampling points (*circles)* in August 2016. The *blue* shading indicates groundwater level, with the interpreted flow direction shown with the *thick arrow*. From Altchenko et al. (2017).

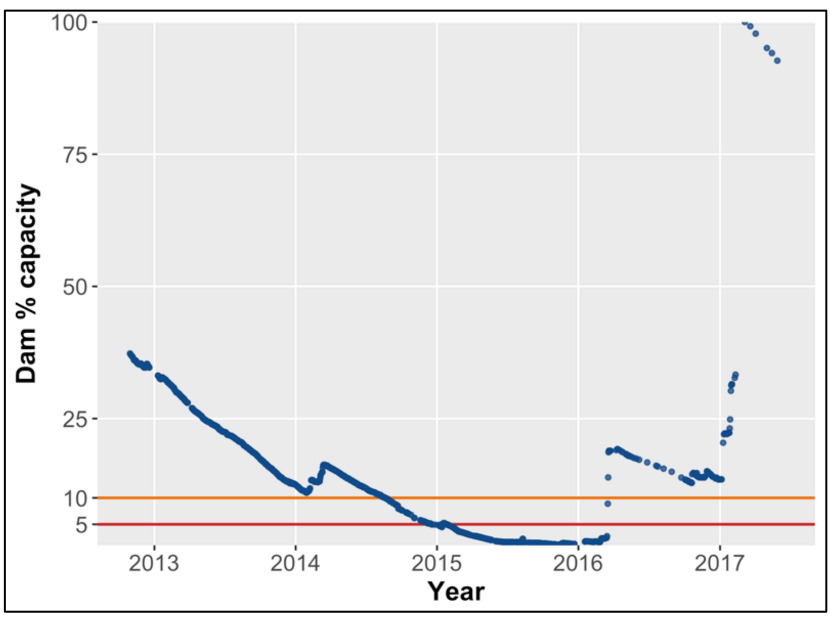

Figure A.4.2. Gaborone reservoir % capacity from 2013-2017. The *red line* marks 5% capacity, at which point the reservoir fails to produce water. Tropical cyclone Dineo hit Botswana in mid Feb 2017 and filled the Gaborone reservoir. Data from WUC.

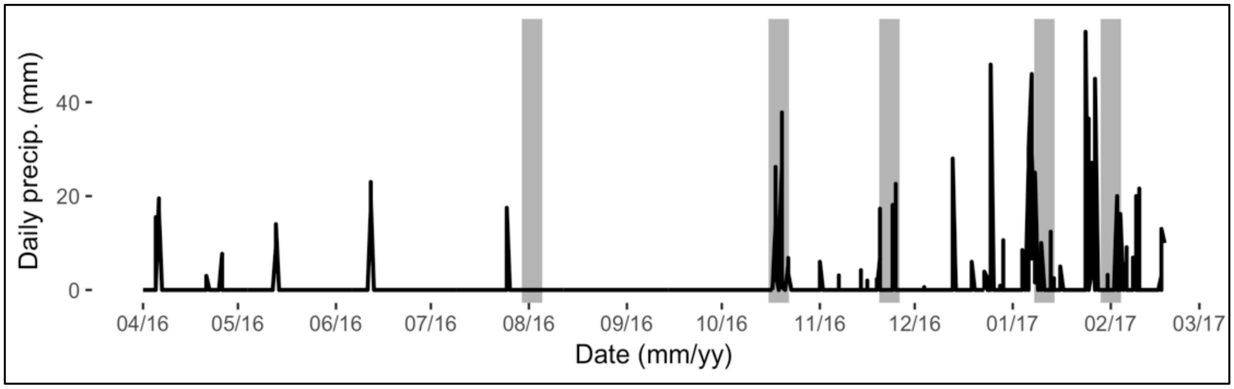

Figure A.4.3. Daily precipitation totals from Ramotswa weather station for dry season (Apr.-Sep. 2016) and wet season (Oct. 2016-Mar. 2017) of sample period. Grey bars indicate weeks when groundwater samples were collected. Results from the Aug. 2016 sampling are from Modisha (2017).

Figure A.4.4. Caffeinated beverages available in Ramotswa grocery store. (a) Soda; (b) instant coffee; (c) black tea.

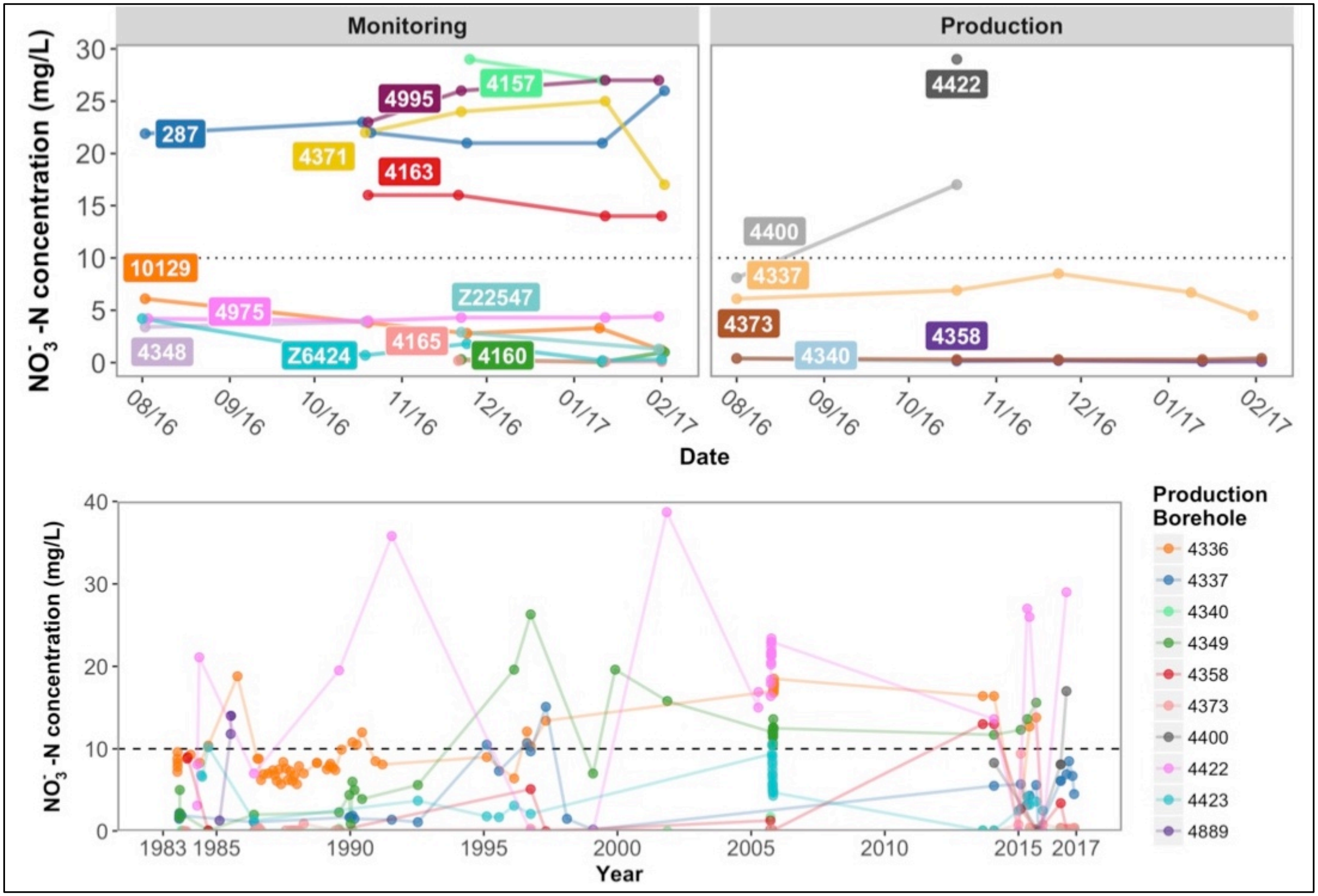

Figure A.4.5. Changes in NO_3^--N concentrations in Ramotswa BHs over time and space. (*Top*) NO_3^--N concentration variability over time in present study comparing monitoring BHs (*left*) and production BHs (*right*). The *dotted line* indicates Botswana's drinking water standard (10 mg NO_3^--N L^{-1}). Note BH4340 and BH4358 concentrations are near zero. (*Bottom*) Historical NO_3^--N concentrations in production BHs starting with earliest known measurements from 1983 (data from Modisha 2017, DWA, WUC, and present study). There are no statistically significant trends over time in either dataset.

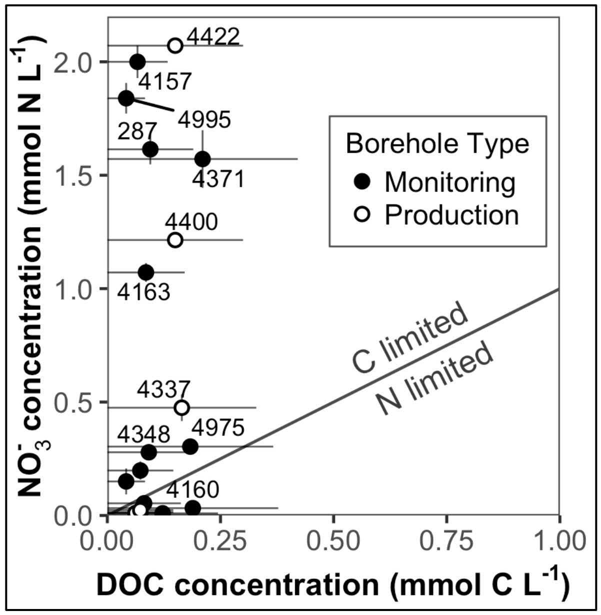

Figure A.4.6. Nitrate and dissolved organic C (DOC) concentrations at Ramotswa boreholes. The line is 1:1. X and Y error bars represent standard error among a maximum of five measurements between Aug. 2016 and Feb. 2017.

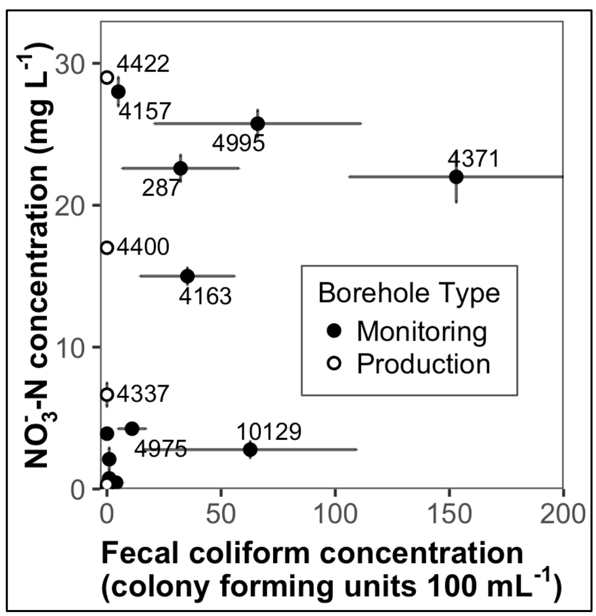

Figure A.4.7. Fecal coliform and nitrate concentrations in Ramotswa groundwater. Bars indicate standard error among a maximum of four measurements between Oct. 2016 and Feb. 2017. Regression of nitrate by fecal coliforms is significant ($p<0.05$, Table A.4.2) but weak (adjusted R^2=11%).

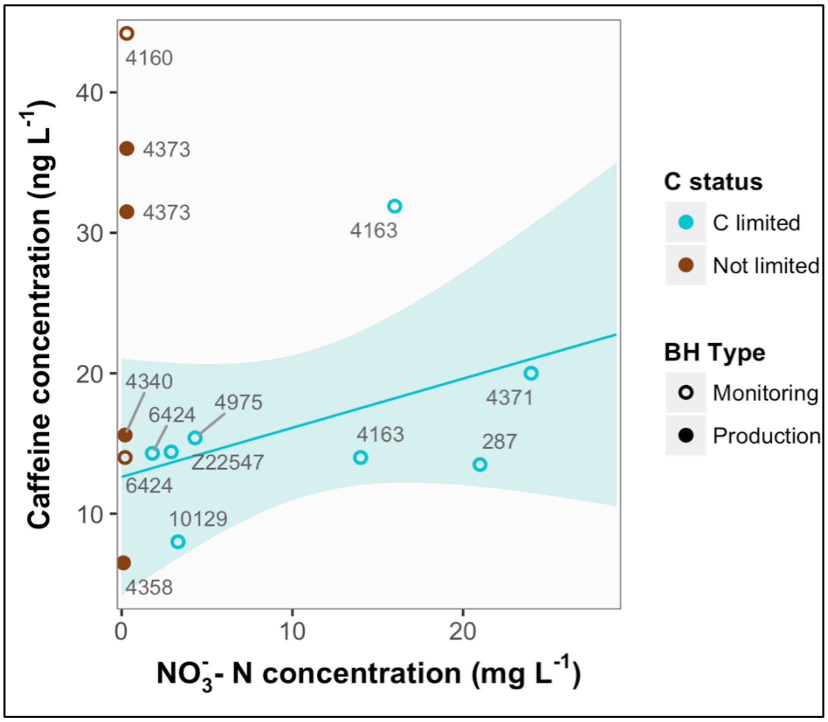

Figure A.4.8. Caffeine and nitrate concentrations in Ramotswa groundwater. Color indicates whether the sample had C-limited denitrification, i.e. mmol DOC:NO_3^--N >1. The ribbon is the 95% confidence interval for the regression of C limited samples (model p<0.01, adjusted R^2=67%, Table A.4.2).

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