Mitigating Agricultural Impacts from Field to Stream: Optimizing Biochar Field Amendments and Novel Denitrifying Bioreactors for Mitigating Greenhouse Gas Emissions

by

David Geuder

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Greenhouse gas (GHG) emissions resulting from agricultural activities are a major contributor to total emissions in Canada and around the world. The application of synthetic and animal-manure fertilizers is common practice on agricultural fields and leads to the generation of the GHGs carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O). Among these GHGs, N_2O from direct soil emissions is of great concern because of the outsized contribution of this GHG to total agricultural emissions, as well as the global warming potential which is 298 times that of CO_2. In addition to GHG emissions, the application of fertilizers to soil can result in the leaching of nutrients to groundwater and tile-drainage effluent, which will discharge to surface water and cause eutrophication and other water quality degradation impacts. There is a need for action at the field level to address these deleterious impacts of agriculture which has led to calls for the development and implementation of best management practices (BMP) that are feasible for farmers and growers. This thesis describes two components which may aid in the development of said BMPs: (1) a soil amendment experiment which compared the year-over-year GHG mitigation of differing biochar schedules, specifically focused on addressing the potential mitigation loss described in previous studies; and (2) the design and construction of a novel passive multi-component bioreactor which will be used in future research to treat tile-effluent for a variety of agricultural contaminants, including nutrients, pharmaceutical compounds, and veterinary antibiotics.

Biochar amendments have been shown to have positive impacts on soil health and crop productivity, and more recently has been found to suppress the emissions of GHGs when biochar is applied as a co-amendment with fertilizer on agricultural fields. Broadly speaking, larger biochar amendments have been linked to greater emissions reductions, however, some research

has found that this GHG mitigation decreases with time. This study examined the emissions of CO_2 and N_2O from four microplots in the Winchester area of southern Ontario, Canada following the application of liquid swine manure and biochar in different volumes on each plot. The trials took place over two field seasons and these amendment schedules were selected to observe the impact of biochar aging on GHG emissions between years. In both years the first plot (control) received no amendment, the second plot (MO) received manure only, the third plot (LVBC) received manure and a small volume of biochar each year, and the fourth plot (HVBC) received manure plus a large volume of biochar in the first year and manure only in the second year. Carbon dioxide emissions were found not to be impacted by the addition of biochar in the amendments, nor was there any observed impact of biochar aging. Nitrous oxide emissions showed reductions in the first year, with lower emissions observed for the microplot with the high-volume amendment. In the second year, however, there was no significant difference in N_2O emissions between the microplots with biochar amendments. Biochar applications contribute a large amount of carbon to the amended soil, which is reflected in the pore-water alkalinity and DOC measurements. These amendments are thought to have impacted both N and C availability for denitrifying microorganisms. These results suggest that the addition of fresh biochar in smaller volumes may provide a robust alternative to the conventional single application of large volumes of biochar while achieving the similar GHG reductions over time.

Bioreactors are effective in treating nutrient laden water and have also shown success in treating other contaminants when additional reactive materials are included in the bioreactor fill. The design and construction of this bioreactor included several novel changes that sought to address the limitations of conventional woodchip bioreactors. The addition of biochar to the fill material was included to lower the emission of N_2O gas emissions, which occur as a bioproduct

of the denitrification process. Biochar and zero-valent iron were also included to treat the effluent water to remove veterinary and pharmaceutical compounds which can be found in field amendments. These bioreactors will be used in future research at the Winchester field site.

This thesis will help inform the development of future BMPs for agricultural producers to reduce their impacts from field to stream. This thesis demonstrated that even small volumes of biochar can lower emissions by substantial amounts over time, allowing for lower costs to farmers and greater ease of application. Further research is needed to determine optimal biochar co-amendment volumes and schedules, as well as to determine the bioreactor effectiveness.

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Dedication

I dedicate this thesis to Christianne, who believed in me from the start.

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List of Abbreviations

AAFC	Agriculture and Agrifoods Canada
ABR	after bioreactor
Ag	silver
AgCl	silver chloride
AGGP	agriculture greenhouse gas program
Al	aluminum
ANOVA	analysis of variance
B	boron
Ba^{2+}	barium
BBR	before bioreactor
bgs	below ground surface
BMP	best management practice
C	carbon
Ca	calcium
$CaCO_3$	calcium carbonate
Cd	cadmium
CEC	cation exchange capacity
CH_2O	formaldehyde
CH_4	methane
Cl	chlorine
CO	carbon monoxide
CO_2	carbon dioxide

CO_2-C	carbon dioxide carbon
Cu	copper
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
Eh	redox potential
Fe	iron
GHG	greenhouse gas
GWP	global warming potential
H	hydrogen
H_2SO_4	sulfuric acid
HDPE	high-density polyethylene
HNO_3	nitric acid
HVBC	high volume biochar amendment
IC	inorganic carbon
ICP-MS	inductively coupled plasma mass spectroscopy
ICP-OES	inductively coupled plasma optical emission spectroscopy
IPCC	Intergovernmental Panel on Climate Change
IR	infrared
K_2O	potash
KCl	potassium chloride
LSM	liquid swine manure
LVBC	low volume biochar amendment
Mg	magnesium

$Mg(ClO_4)_2$	magnesium perchlorate
Mn	manganese
MO	manure only amendment
MP	microplot
N	nitrogen
N_2	nitrogen gas
N_2O	nitrous oxide
Na	sodium
NH_3	ammonia
NH_4-N	ammonium nitrogen
NO	nitric oxide
NO_2-	nitrite
NO_3-N	nitrate nitrogen
NO_x	nitrogen oxides
O	oxygen
O_2	oxygen gas
OC	organic carbon
OM	organic matter
o-PO_4	ortho phosphate
PO_4-P	phosphate phosphorus
PPCP	pharmaceutical and personal care product
PVC	polyvinyl chloride
S	sulfur

SI	saturation index
SL	suction lysimeter
SO_2	sulfur dioxide
TC	total carbon
TCD	thermo-conductivity
TDR	time-domain reflectometer
TK	total potassium
TN	total nitrogen
TP	total phosphate
wt. %	percent by weight
WTR	water treatment plant residual
Year 1	2018
Year 2	2019
Zn	zinc
ZVI	zero valent iron

Chapter 1 - Introduction

The environmental impacts of agriculture are a growing concern for governments around the world given that some practices can have negative consequences on the natural environment, such as contributing to climate change and degradation of water bodies (Parris, 2011). One critical issue associated with on-field and field-adjacent agriculture activities is the production of a substantial greenhouse gas (GHG) emissions. In Canada, the agriculture sector contributes approximately 10% of the national GHG emissions (Environment and Climate Change Canada, 2018). The majority of these emissions are methane (CH_4) and nitrous oxide (N_2O), which is concerning because the global warming potential (GWP) of these GHGs are 25 and 298 times, respectively, than that of carbon dioxide (CO_2) (Solomon et al., 2007). Worldwide, the Intergovernmental Panel on Climate Change (IPCC) has estimated that these GHG emissions from agriculture could further increase by 60% by 2030 with CO_2 also likely to increase by 10-15% (P. Smith et al., 2007). Moreover, the significant amount and impact of these emissions has led to calls for increased design and adoption of best management practices (BMP) to reduce emissions while maintaining or possibly increasing current agricultural production levels (Cole et al., 1997).

In addition to the contribution of GHG emissions, the agriculture sector has come under increased scrutiny for the deleterious impacts of soil amendments on water quality. For example, the eutrophication of streams, lakes, and large water bodies resulting from nutrient leaching and runoff of excess fertilizer has caused algal blooms, for example within the Great Lakes watershed, which occur during the summer months (Howarth et al., 2002; Michalak et al., 2013; Stumpf et al., 2012).

While manure and municipal biosolid fertilizers include nutrients for plant growth, they can also contain a variety of chemical components such as pharmaceutical compounds and veterinary antibiotics. The cumulative environmental effects of these agricultural amendments extend beyond eutrophication of watersheds, contributing to the degradation of aquatic ecosystems and have the potential to impact human health (Parris, 2011; Walters et al., 2010; Witte, 1998).

1.1 **Agricultural Contributions to GHGs**

Overall, the agriculture sector is a top contributor of GHG emissions, second only to the energy sector (IPCC, 2014). A key challenge associated with GHG emissions in agriculture is that, at the farm level, it can be difficult for individual producers to estimate their GHG contributions due to the many factors that impact emissions, such as the crop or livestock type, and agricultural practices such as amendment application rate and technique, climate, and geography (Bouwman, 1996; Eichner, 1990). In addition, there are limited "on-farm" emissions measurements, which makes it difficult for individual producers to monitor and reduce their impacts (Bouwman, 1996). As well, emissions come from a wide variety of sources. For example, the major GHG contributors from agricultural practices include enteric fermentation or livestock belching, equipment emissions from farm operations, biomass burning for land use change or remnant straw/stover, and direct soil emissions (CAST, 2011; Cole et al., 1997; Del Prado et al., 2013).

1.2 **Direct Emissions via Nitrogen Transformations**

With respect to direct soil emissions, a key process is the emission of N_2O following nitrogen transformations that occur after nutrient rich manure is applied to agricultural soils (*see* Figure 1-1). There are several pathways for nitrogen (N) losses following the application of N rich

manures, including the direct volatilization of ammonia, and the leaching of nitrate to ground or tile-drainage water (Howarth et al., 2002; Millar et al., 2014; Thangarajan et al., 2018).

Following the application of manure to fields, organic nitrogen (N) compounds are converted to inorganic N prior to plant uptake. The remaining inorganic N will proceed through nitrification or denitrification depending on factors such as soil moisture and temperature, soil oxygen availability, and soil pH (Bouwman, 1996; Firestone & Davidson, 1989). Nitrification typically occurs in more aerated soils and involves the oxidation of ammonia (NH_3) to nitrite (NO_2^-) and nitrate (NO_3-N) as well as the generation of nitric oxide (NO) and N_2O by nitrifier denitrification (Baggs & Philippot, 2010; K. A. Smith, 2017). Denitrification typically proceeds in anaerobic conditions and is the transformation of NO_3-N to nitrogen gas (N_2) via microbially mediated reduction through the intermediate products NO_2^-, NO, and N_2O (Knowles, 1982; Oertel et al., 2016). Overall, the generation of N_2O is a complex interplay of both nitrification and denitrification and the interactions of each controlling factor can be difficult to quantify (Bouwman, 1996; Cole et al., 1997; Oertel et al., 2016).

Importantly, atmospheric N that is naturally deposited on soils can result in the same nitrification and denitrification reactions that generate GHG emissions. However, anthropogenic loading of N via field amendments far exceeds atmospheric N and can lead to non-linear increases in N_2O emissions (Hoben et al., 2011).

1.3 **Mitigation of Agricultural GHG Emissions and Tile-Drainage Pollution**

Efforts to address climate change as it relates to GHG emissions can be divided into two mitigation areas, the reduction in the release of a particular contaminant, and the removal of a contaminant from the environment (WICCI, 2011). Reducing the GHG emissions caused by agricultural practices and in particular from direct soil emissions has been extensively studied

(Cayuela et al., 2014; Lentz et al., 2014; Thangarajan et al., 2018). There has been some success surrounding efforts to change farming practices, such as fertilizer application type, rate, timing, and placement (Chantigny et al., 2010; Dennehy et al., 2017; Millar et al., 2014). The use of biochar as a field amendment with fertilizer applications has positive implications for soil health and crop yield (Abel et al., 2013; Chan et al., 2007, 2008). The GHG mitigating potential of biochar was first reported by Rondon et al. (2005) and has been repeatedly demonstrated (Bamminger et al., 2014; Méndez et al., 2014; Rogovska et al., 2011). For example, a recent meta-analysis of 261 experimental treatments found that N_2O emissions were reduced by 54% with biochar additions and significant reductions in emissions could be achieved with biochar additions as low as 1-2 % (dry weight basis) (Cayuela et al., 2014). As well, due to the high carbon (C) content and apparent persistence of biochar in soils (Glaser et al., 2001), it has been proposed that the universal implementation of these amendments could offset 12% of global anthropogenic C emissions through carbon sequestration (Lehmann et al., 2006; Woolf et al., 2010).

Although the exact mechanism for lowered N_2O emissions following biochar application is not known, it is proposed that biochar may increase the rate of complete denitrification, thereby resulting in the full reduction of N_2O to N_2 (Cayuela et al., 2014). Other studies have suggested that biochar could increase aerobic respiration, thereby reducing O_2 concentrations while simultaneously providing an accessible C source to denitrifying microorganisms (Christianson et al., 2011b; Schipper et al., 2005), while others propose that biochar may act as a "electron shuttle" which facilitates electron transfer to denitrifying microorganisms (Cayuela et al., 2013; Sun et al., 2017).

In terms of water quality, nutrients from manure and biosolid applications are known to increase eutrophic conditions, degrade aquatic ecosystem, and promote excessive algae growth (Kremser & Schnug, 2002). Considerable research has been conducted on the removal of nutrients from agricultural drainage effluent. Passive bioreactors are one example. Bioreactors have been used that have employed a variety of reactive materials to target specific contaminants (e.g., Blowes et al., 1994; Christianson et al., 2011b; Saliling et al., 2007). Pure woodchip bioreactors have been demonstrated to be effective in removing NO_3-N through denitrification. However, one limitation of this method is that up to 4% of N removed is subsequently released as N_2O when the reaction does not proceed to completion (Warneke et al., 2011a). Rivett et al. (2008) identified the primary limiting factors on the denitrification process to be O_2 concentrations and the availability of electron donors such as labile organic C sources. The addition of biochar in these passive bioreactors has been proposed to allow for complete denitrification, thereby reducing the production of GHGs (Easton et al., 2015; Schipper et al., 2005).

In addition to leaching of excess nutrients from fertilizers (i.e., manure, biosolids), water quality in agricultural regions can be degraded by contaminants present in soil amendments such as pharmaceutical compounds and veterinary antibiotics. While these compounds serve specific biological and physiological functions in the organism for which they are intended, they can impact other organisms which naturally occur in the amended soils and downstream aquatic ecosystems (Fent et al., 2006; Walters et al., 2010). Additionally, these contaminants can end up in larger watersheds at an expedited rate due to tile-drainage and may have negative impacts on human health such as elevated cancer risk, reproductive impairment, and antibiotic resistance (Walters et al., 2010; Witte, 1998). The addition of biochar and zero valent iron (ZVI) (Fe^0) to

these bioreactors is one novel approach for the removal of pharmaceutical and emerging contaminants as demonstrated in laboratory scale studies (Y. Liu et al., 2014; 2019).

1.4 **Site Background**

The research site is located near the town of Winchester in southeastern Ontario (*see* Figure 1-2) on a flat 90 m long by 105 m wide field that is operated by Agriculture and Agrifoods Canada (AAFC) and the University of Guelph. The site sits within a region that is dominated by agricultural activity and is made up of a variety of experimental plots primarily used for research. The soil is composed of North Gower clay loam (Mollic Gleysol – FAO system) (Frey et al., 2015; Gottschall et al., 2016). A well defined and compacted plow pan exists at 0.2 m below ground surface (bgs) and large macropore features penetrate the soil profile down to 2 m bgs.

The research plot is divided into six 15 m wide test plots which have 0.1 m diameter plastic tile-drains that were installed in the 1980s (*see* Figure 1-3). Control structures were installed on the tile-drains in 2010 which use stoplogs to set the desired water table height in the field and minimize drainage until this height is reached. During high flow, water leaving the tiles is pumped to a nearby drainage ditch. Average monthly precipitation over the growing period, according to 30-year normals for the region, range from 83.9 mm to 97.00 mm with average daily temperatures ranging from 13.3 ^{o}C to 20.8 ^{o}C (Environment Canada, 2015).

Prior to this study, the site was on a corn-wheat-soybean crop rotation. Over the duration of the study the site was planted with corn and then wheat. Past field activities included the application of liquid swine manure and solid municipal biosolids on the field (Gottschall et al., 2016; Lapen et al., 2008a).

1.5 **Research Objectives**

The primary research objective of this thesis is to identify BMPs for the reduction of environmental degradation caused by the agricultural sector both in terms of GHG emissions and water quality. The primary component focuses on how repeated yearly applications of biochar in smaller volumes compares to larger one-time applications in mitigating GHGs. Research has demonstrated that the weathering of biochar reduces the effectiveness of GHG abatement (Spokas, 2013). This study tested the effectiveness of smaller, repeated applications in reducing GHG emissions to limit the impacts of biochar weathering. Whereas biochar has been demonstrated to contribute to the mitigation of GHGs (Bamminger et al., 2014; Cayuela et al., 2014; Rogovska et al., 2011; Rondon et al., 2005), few studies have focused on the degradation of biochar, and in particular on the comparison in mitigation potential at different volumes and temporal application rates. The outcomes of this study will help inform BMPs for the agricultural sector in determining biochar application rates and schedules especially when cost and resource availability are important considerations.

This thesis also focuses on the development of new technologies aimed at addressing water quality issues caused by agricultural practices on tile-drain waters, through the design and construction of novel multicomponent bioreactors. Specifically, recent research has proposed adding biochar to woodchip bioreactors to mitigate the GHG emissions associated with the treatment of nitrate in agricultural drainage water (Bock et al., 2015; Christianson et al., 2011b; Easton et al., 2015). Recent laboratory studies have shown mixtures of biochar and ZVI to be effective in treating pharmaceutical and veterinary compounds (Y. Liu et al., 2019). The design and construction of these novel bioreactors contributes to the longer-term goal of testing the viability of multicomponent bioreactors to treat tile-drainage water for nutrients,

pharmaceuticals, and veterinary compounds, while simultaneously reducing the N_2O emissions typically associated with this technology. Thus, this study forms the basis of developing BMPs for agricultural drainage remediation and lays the foundation for further testing and proof of concept to be carried out in future research.

1.6 **Thesis Organization**

Mitigating the contribution of the agriculture sector to climate change and water quality degradation is of utmost concern. The research in this thesis was a collaboration between the University of Waterloo, the University of Ottawa, Carleton University and AAFC as part of the Agriculture Greenhouse Gas Program (AGGP) titled "Valuing diversity in agro-ecosystems: The interplay of natural habitat, integrated BMPs, and field cropping systems on GHG emissions and carbon stocks". This thesis is one component of the broader AGGP, which is a multi-year program designed to enhance understanding of agriculture technologies and provide guidance on BMPs that can be reasonably used by farmers to mitigate GHG emissions in Canada. In pursuit of that broader goal, this thesis seeks to address the effects of agricultural practices along the field to watershed continuum. This thesis includes four chapters. Chapter One provides an introduction and overview of the thesis contents. Chapter Two describes the experimental work focused on reducing GHG emissions associated with on field manure applications and establishing BMPs for the use of biochar as a GHG mitigation technology. Chapter Three presents the design and construction of a novel remediation technology for the treatment of agricultural contaminants. Chapter Four summarizes each study and proposes future research directions.

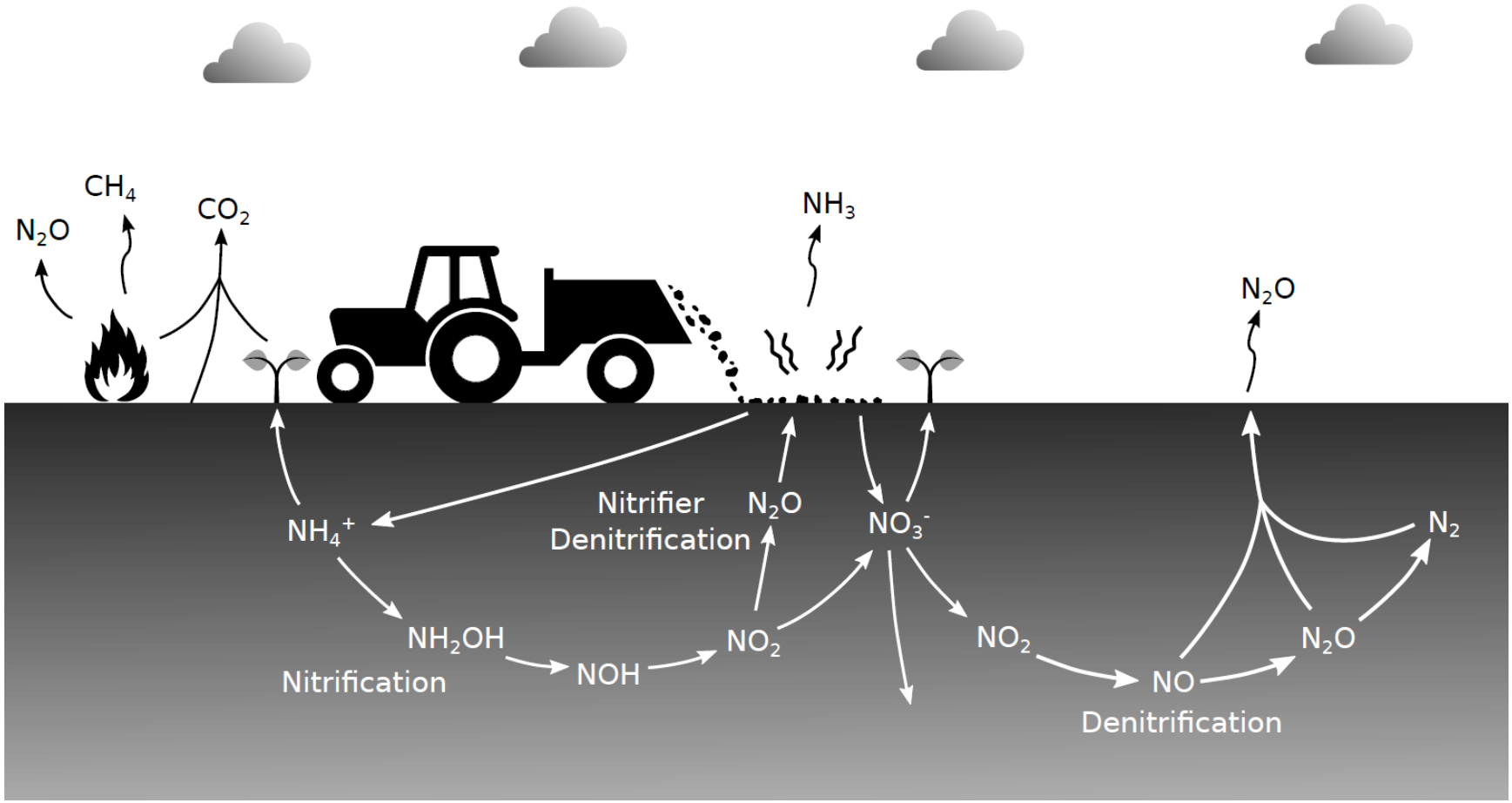

Figure 1-1: Schematic showing the N-pathways following application of N-rich manure and other pathways for GHG emissions in agriculture.

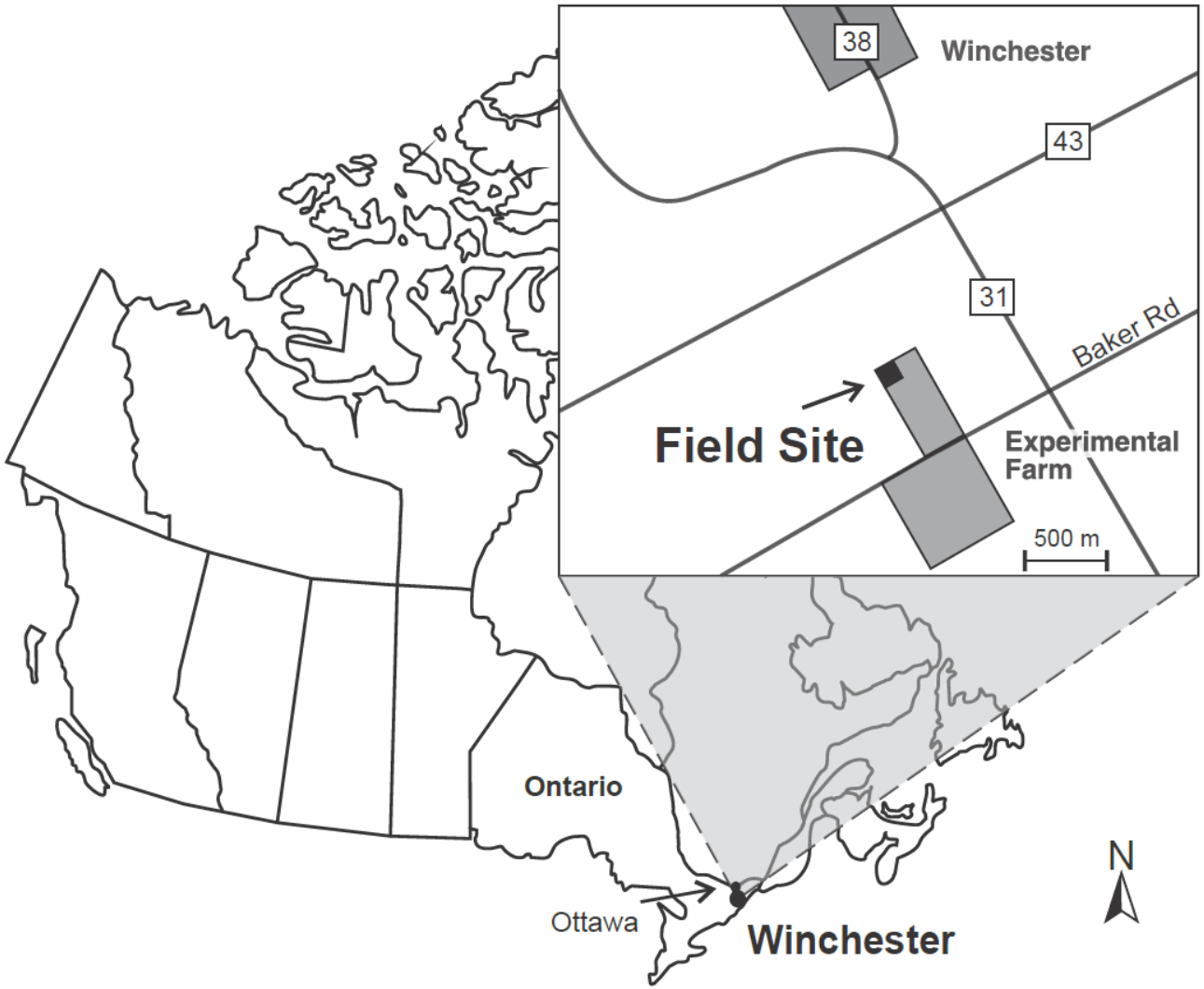

Figure 1-2: Winchester field location in relation to Ottawa, ON, Canada.

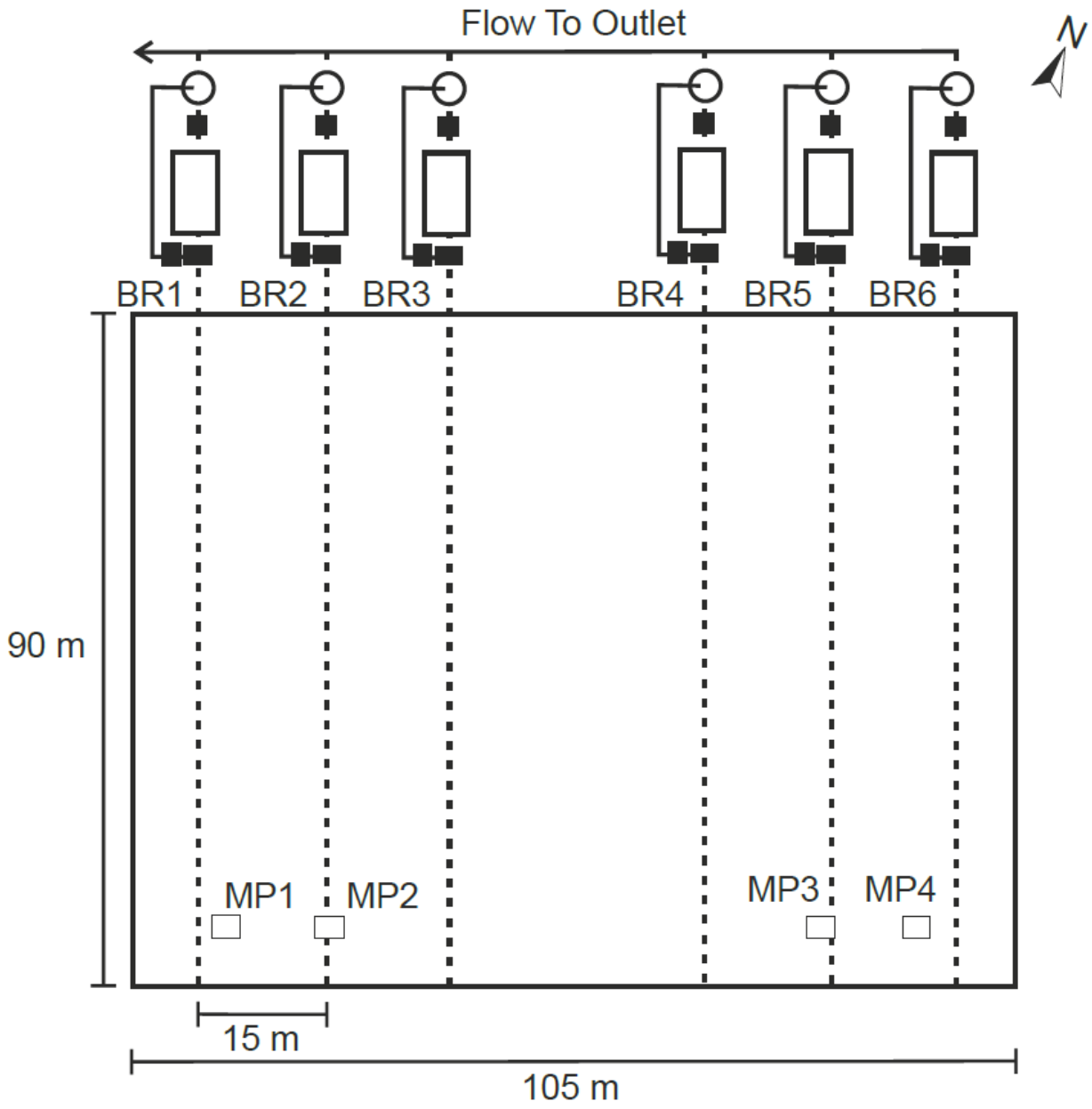

Figure 1-3: Winchester experimental field showing approximate location of microplots, tile-drains, and bioreactors.

Chapter 2 - Greenhouse Gas Mitigating Potential for two Biochar Treatment Schedules: Role of Field Aging on Mitigation Loss

2.1 **Introduction**

Agriculture is a major contributor to greenhouse gas (GHG) emissions around the world, behind only the energy sector in total emissions (IPCC, 2014). As the impacts of GHGs on global climate change are of great concern, governments are striving to lower emissions in all areas, including in agriculture (Parris, 2011). At the same time, the global reliance on agriculture continues to grow and the negative environmental consequences have become more publicly recognized, highlighting the need for strategies to address these concerns.

In Canada, it is estimated that 10% of the total GHG emissions released per year are derived from the agricultural sector, with the majority of these emissions in the form of N_2O (Environment and Climate Change Canada, 2018). These emissions are largely attributed to the use of N-rich amendments such as synthetic fertilizers and livestock manures that are widely used on farms (Cayuela et al., 2014; P. Smith et al., 2008). Nitrous oxide has a global warming potential of 298 times that of CO_2 (Solomon et al., 2007), and has increased in atmospheric concentration by ~ 54 parts per billion by volume (20%) since the industrial revolution (Ussiri & Lal, 2012). Emissions of N_2O, and other GHGs such as CO_2 and CH_4, are attributed to a variety of sources both on- and off-field. The agricultural sector has invested considerable effort in finding ways to reduce these emissions (CAST, 2011). Some success has been found in reducing GHG emissions from fertilizer applications through changes in the application types, rates, timing, and placement (Chantigny et al., 2010; Dennehy et al., 2017; Millar et al., 2014).

This study focuses on the direct emission of GHGs from agricultural fields following the application of N-rich manure amendments, with particular focus on N_2O and CO_2 mitigation. The dominant mechanisms by which N_2O is generated in soil are nitrification, denitrification, and dissimilatory nitrate reduction (Baggs, 2011; Firestone & Davidson, 1989). The contribution of each reaction differs according to soil physical and chemical conditions, with the rate of transformation controlled by microbial activity (Baggs, 2011; Butterbach-Bahl et al., 2013; Thomson et al., 2012). The generation of CO_2 is also microbially controlled, with root and faunal respiration contributing to the total emissions. Overall, the generation of both N_2O and CO_2 involves the complex interaction of several reaction pathways which are influenced by soil texture, moisture, pH, nutrient concentration, and available C, making the prediction of which process will dominate difficult (Bouwman, 1996; Cole et al., 1997; Davidson et al., 1998; Kloss et al., 2014; Oertel et al., 2016; Rastogi et al., 2002).

One strategy for decreasing the GHG emissions by the agricultural sector has been the use of biochar as a field amendment. Biochar is the carbonaceous by-product of pyrolysis, wherein some feedstock of organic material undergoes thermal decomposition in a low oxygen environment (Lehmann & Joseph, 2009). The end product is a carbon-rich material with physical and chemically recalcitrant properties that allow it to persist in soil, making it ideal for carbon sequestration (Lehmann et al., 2006). Woolf et al. (2010) estimated that the universal implementation of biochar field amendments in agriculture could offset 12% of global anthropogenic CO_2-C equivalent emissions, aided in part by the long-term persistence of biochar in soils.

In addition to carbon sequestration, biochar use has been found to have other positive impacts for both the agricultural sector and the environment: improving soil quality and crop

yield (Abel et al., 2013; Chan et al., 2007, 2008); depressing the leaching of nutrients (Major et al., 2010); and increasing habitat for soil microorganisms (Gomez et al., 2014). Biochar has been used as a soil amendment for millennia, with examples of the use of the material dating back to Amazonian tribes over 2500 years ago (Glaser et al., 2001).

This study focuses on another impact which biochar has on soils, the potential to lessen net GHG emissions when applied in combination with manure amendments. The use of biochar as a co-amendment with manure and other fertilizers was shown to reduce N_2O emissions by 54% in a recent meta-analysis of 261 experimental treatments, and may aid in addressing N use efficiency (Cayuela et al., 2014).

Biochar has been found to both increase (Ameloot et al., 2013; Case et al., 2012) and decrease (Bamminger et al., 2014; Méndez et al., 2014) CO_2 emissions, which is typically attributed to the specific physical and chemical changes imparted on the soil by the addition of biochar (Cross & Sohi, 2011; Lehmann et al., 2011). Past research has found that the addition of biochar enhanced microbial activity. Some studies have linked this microbial activity to increased CO_2 emissions due to the greater rates of soil organic matter decomposition (Kuzyakov et al., 2009). Other studies have reported decreased CO_2 emissions, which were attributed to microbial communities using C more efficiently (Bamminger et al., 2014). There is clearly a need for more research in this area to better understand the impacts that biochar additions have on CO_2 emissions following manure applications.

The impacts of biochar co-amendments on N_2O emissions are also not fully understood and are further complicated by the interaction of the three dominant pathways by which it is produced. A variety of explanations for mitigation of N_2O in biochar-amended soils include an increase in rate of complete denitrification, thereby shifting the emission of N_2O to the further

reduced N_2 (Schipper et al., 2005), and decrease of denitrification rates due to greater soil aeration (Clough et al., 2013). This mitigation of N_2O was first described by (Rondon et al., 2005), and has continued to be demonstrated since (Cayuela et al., 2014).

While the application of biochar to agriculture soils does have well founded potential for positively impacting crop yields and the environment, one major limitation identified by Spokas (2013), is the aging impact on GHG mitigation following the natural weathering of biochar in soil. That is, after a three-year trial the weathering of biochar resulted in 3- to 10-fold increases in CO_2 production, and a complete loss of N_2O mitigation. This finding has brought into question the ability of biochar co-amendments to provide a lasting solution for GHG mitigation.

This study focuses on this key limitation of biochar co-amendments to inform best management practices (BMPs) that could be realistically implemented by farmers. In particular, the aim of this study was to compare yearly, small volume applications of biochar to a one-time, large application to examine whether this year-over-year application could address the weathering effects associated with one-time biochar applications. The aim of this study is to optimize the use of biochar as a field amendment and enhance the effectiveness in GHG mitigation over time.

2.1.1 Site Description

The Winchester Agricultural Research Station is an experimental field near the town of Winchester, Ontario operated by Agriculture and Agrifoods Canada (AAFC) and the University of Guelph (Figure 1-2). The experimental field is approximately one hectare and contains North Gower clay loam soil (Mollic Gleysol – FAO system) with large macropore features penetrating the soil profile down to 2 m bgs (Frey et al., 2015; Gottschall et al., 2016).

Four microplots (MP) were sampled in two growing seasons across a 17-month period (*see* Figure 1-2). The microplots were 4 m by 3 m and were located in the southern part of the field (*see* Figure 1-3). Specifically, field sampling in Year 1 took place from May to November 2018 and in Year 2 from May to September 2019.

Air temperature (°C, 1 hr interval), atmospheric pressure (kPa, 1 hr interval), and precipitation (mm, 1 hr interval) were measured at the field site using an AAFC weather station (Station ID: 480275, AAFC) located at the northern edge of the field (45º03'44" N, 75º20'32" W). Weather data were available for the entire sampling period in each year.

2.2 **Methods**

2.2.1 Amendment Application

The application of amendment to each microplot varied depending on the plot and the year of study (Table 2-1). In both years, MP1 (control) was the control plot (control) and received no amendment in either year. MP2 (MO) received manure only in both years and MP3 (LVBC) received a mixture of manure and biochar at a low biochar rate in both years. MP4 (HVBC) received a mixture of manure and biochar at a high biochar rate in Year 1 and a manure-only application in the Year 2. Manure was applied at an application rate of 4.4 L m^{-2} (4700 gal $acre^{-1}$) which is the standard AAFC practice. The low- and high-volume biochar rates were 3 L m^{-2} (3% by vol.) and 6 L m^{-2} (6% by vol.), respectively.

Following the amendment application, the biochar was manually integrated into the top 10 cm of soil. In Year 1, biochar was added by hand to the LVBC and HVBC plot prior to the addition of manure. In Year 2, the biochar and manure were mixed prior to application on the LVBC plot (the only plot receiving biochar in Year 2). This discrepancy in application method

was due to the excessively viscous nature of the manure and high-volume biochar slurry that was applied to the HVBC plot in Year 1.

2.2.2 Field Amendment Materials and Characterization

Biochar was provided by AAFC and was the same as that used in previous work conducted by AAFC (Ball-Coelho, 2011). The "CQuest Biochar" was produced as a by-product of bio-oil production using fast pyrolysis and cellulosic feedstocks (Dynamotive Energy Systems Corporation, Richmond, BC, CAN). Fast pyrolysis involves the rapid heating of feedstock to 300 – 700 ^{o}C. and requires fine particle size feedstock like straw and stover waste (Barik, 2019). Previous analysis has shown the biochar contained 78% organic matter.

Bulk biochar samples were collected in high-density polyethylene (HDPE) containers and frozen on site (-22 ^{o}C) immediately after collection. Elemental composition (C, H, N, S, O) and ash content were analyzed by the ALS Environmental Laboratory (Tucson, Arizona, USA). C, H, and N were determined by two stage combustion followed by infrared (IR) and thermo-conductivity (TCD) detection using a LECO Truspec CHN Macro analyzer. A 100 mg sample was first combusted at 950 ^{o}C and then at 850 ^{o}C in a secondary furnace before the gas products were mixed and purged through an IR detector which measures C as CO_2, and H as H_2O. N is measured as N_2 by the TCD cell after the gas has passed through hot copper sticks, a carbon dioxide scrubber, and a water scrubber. The reporting limits for C, H, and N are 0.10%, 0.20%, and 0.10%, respectively. Sulfur was measured by combustion/infrared detection using a LECO Macro TruSpec SC832. The method follows ASTM D6316 for combustible carbon and sulfur. The sample is combusted at 1350-1550 ^{o}C and the resulting CO_2 and SO_2 gases are measured by IR cell detection. The reporting limits for C and S are 0.05%, and 0.03%, respectively. O concentrations were calculated by difference.

Manure used in this study was a liquid swine manure (LSM) from swine sows raised in "segregated early weaning" conditions. obtained from a local swine farm. The manure was sampled in HDPE bottles at the time of application and frozen on site (-22 ^{o}C) immediately after collection. In the case of the LVBC plot, in 2019 the manure + biochar mixture was sampled directly from the bucket where the slurry was made at the time of the application. Samples were shipped to A&L Laboratory Inc. (London, ON, CAN) in insulated coolers with ice packs to prevent thawing during transportation. Analyses examined dry matter, organic matter, pH, conductivity, C:N ratio, total N (TN), ammonium nitrogen (NH_4-N,) total phosphorus (TP), phosphate as P (PO_4-P), total potassium (TK), potash (K_2O), and various other chemical constituents (S, Na, Al, B, Ca, Cu, Fe, Mg, Mn, Zn). Nitrogen was determined by combustion using a LECO analyzer and the Dumas method for combustion. Ammonia was determined colourimetrically using the automated Phenate method (US EPA: method 350.1). Organic matter was measured by loss on ignition at 500 ^{o}C and the elemental composition was determined by aqua regia digestion followed by measurement using ICP-OES (EPA 6010B).

2.2.3 Microplot Layout and Installation

Measurement equipment was installed in Year 1 in August 2018 and removed prior to the harvest. Equipment was reinstalled in May 2019 for the remainder of the study. Each MP contained three static flux chambers for the measurement of GHG fluxes, and four suction lysimeters (SL) for the collection of unsaturated zone pore-water. Soil cores and pore-water were collected from each MP throughout the study. Each MP was laid out the same way and equipment was spaced to ensure access for the sampler (Figure 2-1).

The flux chambers were constructed using 16" (40.64 cm) diameter polyvinyl chloride (PVC) sewage pipe with one end beveled to reduce soil disturbance and compaction during

installation (Figure 2-2). The design was based on Rochette & Hutchinson (2005) and Van Zandvoort et al. (2017). Collars were approximately 25 cm high and were installed in the ground such that there was approximately 5 cm of head space from the soil surface to the chamber top. Lids were constructed with the same material and were insulated to prevent radiative heating inside the chamber. The lids added an additional 5 cm of head space to the chamber and were vented using 2 mm inner diameter tubing. Leakage from the chambers during deployment was prevented with memory foam glued to the lid rim and bricks placed on top to ensure a good seal. Each chamber was augmented with a 20 cm time-domain reflectometer (TDR) probe to measure soil temperature and moisture. Probes did not always function correctly, in particular at the end of the 2019 field season, so these data are incomplete.

Porous-ceramic SLs (Soilmoisture Equipment Corp., Goleta, California, USA), were installed at 20, 40, and 70 cm bgs on the MPs (*see* Figure 2-2). These depths situate the 5 cm ceramic cups within the unsaturated zone, directly above and below the plow pan (25-30 cm bgs), as well as above the tile-drain depth (~90 cm bgs). Each plot contains four SLs, one at each aforementioned depth with an additional replicate of one depth per plot (ie. SL replicate on MP 1, 2, 3, 4 were installed at 20, 40, 70, 40 cm, respectively). They were installed using a 10 cm diameter hand auger and backfilled with a silica flour slurry around the cup and bentonite clay to the ground surface. The silica slurry, as well as soaking the ceramic cup for several hours prior to installation ensured hydraulic connectivity between the soil and porous ceramic material. Each SL was capped with a vented rubber top stopper that allowed the sampler to evacuate air form the system and draw pore-water from the ceramic cup.

2.2.4 Greenhouse Gas Sampling and Analysis

Pre-application data were collected two weeks prior to the field amendment in Year 1 and seven weeks prior in Year 2. Pre-application data collection was over a shorter duration in Year 1 than Year 2 due to field access limitations.

Flux measurements were collected prior to and following each amendment application in both years. As recommended by Bouwman (1996), sampling was densest immediately following application. Sampling was typically conducted between 10:00 to 14:00 h for consistency (Van Zandvoort et al., 2017) and samples were not collected when standing water was observed inside the collars. Each GHG flux sampling event followed the procedure outlined by (Rochette & Bertrand, 2008) for non-steady state chambers and measured the diffusive flux of each gas from the soil. At time = 0 a sample was collected from directly above the soil surface within the unsealed flux chamber. Immediately following this sample collection, the chamber was sealed, and samples were taken at a five-minute interval over the proceeding 20 minutes. Following this 20-minute sampling period the chamber lids were removed and the soil within the chambers was exposed to the atmosphere until the next sampling time. Samples were collected using a 30 mL syringe and were stored under pressure in 12 mL Labco Exetainer® vials until the analysis. Prior to sampling, the vials were cleaned and prepped with an initial evacuation, followed by a helium purge and a second evacuation. To reduce the chance of moisture entering the analytical equipment and skewing the flux calculation, 2-3 mg of magnesium perchlorate ($Mg(ClO_4)_2$) desiccant was put inside each vial prior to purging.

Gas samples were analysed at the KW Neatby building (AAFC, Ottawa, ON, Canada) for GHGs (CO_2, and N_2O) using an Agilent 7890B Gas Chromatograph with a CTC PAL3

autosampler following Agilent method SP1 7890-0467. Six reference standards were used in the analysis and two standards were remeasured for every 20 GHG samples.

Flux values were calculated by plotting the concentration of the five samples collected from each collar and calculating the slope (i.e., rate of change) of the specific GHG. The linear model was used as it is less susceptible to outliers than a non-linear model (Rochette & Bertrand, 2008; Van Zandvoort et al., 2017).

Data were retained for analyses where the R^2 value was greater than or equal to 0.80. Using the calculated slope, a flux value for each collar was calculated using the following equation 2.1, where *m* is the linear slope of the measured gas values, *P* is the mean atmospheric pressure in atm during sampling, *R* is the ideal gas constant, *T* in the in-situ chamber air temperature in Kelvin, *V* is the chamber head space, *A* is the chamber surface area, and *c* is the factor to convert CO_2 to C basis and N_2O to N basis (Rochette & Hutchinson, 2005).

$$GHG\ Flux = \frac{m * P}{R * T} * \left(60 \frac{min}{hr}\right) * \frac{V}{A} * c \qquad (2.1)$$

2.2.5 Soil Cores Sampling and Analysis

Soil cores were collected within the MPs prior to and following the amendment application in each year of the study using a 2 cm JMC "Backsaver" (Newton, Iowa, USA) coring device from 0-15 and 15-30 cm bgs. Following each coring occurrence, the holes left behind were filled with bentonite clay to prevent direct infiltration of rainwater to the subsurface.

Cores were collected in duplicate and combined in soil sampling bags to provide sufficient material for laboratory analysis. Samples were frozen on site (-22 ^oC) and shipped in coolers with ice packs to the Agriculture and Food Laboratory (Guelph, Ontario, Canada) for measurement of total C (TC), TN, NH_4-N, NO_3-N, pH, and cation exchange capacity (CEC).

Elemental analysis of TC and TN were completed by combustion using a LECO CN828, as outlined in WREP-125, 4th edition (2013): Method S – 9.30. Briefly, soil samples are combusted in an O_2 environment at 950 ^oC and the subsequent gases are passed through a copper catalyst to convert CO to CO_2 which is then measured by an infra red (IR) detector. NO_x is reduced to N_2 and nitrogen is determined by a thermal conductivity detector. The detection limits for C and N are 0.02 wt. % and 0.03 wt. %, respectively.

Soil NH_4-N was extracted by a KCl extraction method and then analyzed using a Seal AQ2 discrete analyser following the colorimetric, phenate method outlined in Methods for Chemical Analysis of Waters and Wastes USEPA 600/4-79-020 (1979): Method 350.1. Briefly, 5 g of soil is mixed with 25 mL of 2.0 N KCl reagent and shaken for 30 mins. The extract is filtered, and the NH_4-N reacts with an alkaline phenol and hypochlorite solution to form indophenol blue which is measured spectrophotometrically. The detection limit for this method is 0.2 mg kg^{-1}.

Soil NO_3-N was measured following a KCl extraction and subsequent colorimetric, Cd-reduction method using a Seal AQ2 discrete analyzer, as outlined in Methods for the Determination of Inorganic Substances in Environmental Samples, USEPA 600/R93/100 (1993): Method 353.2. Briefly, following the KCl extraction the nitrate is reduced with copperized cadmium to nitrite which reacts with sulphanilamide and phosphoric acid to form a reddish-purple azo dye which is then measured spectrophotometrically. The detection limit for this method is 0.5 mg kg^{-1}.

Soil pH was determined by the saturated paste method (Hendershot et al., 1993). A saturation paste extract is generated by mixing dried soil and deionized water and the pH is measured using a standardized and calibrated pH meter.

CEC was measured using the Ba^{2+} replacement method (Rhoades, 1982). Briefly, soil sample cation exchange sites are saturated with the exchangeable cation Ba^{2+}, followed by the subsequent replacement of Ba^{2+} with NH_4^{2+}. The concentration of Ba^{2+} measured following replacement is the cation exchange capacity. The detection limit for this method is 1.0 cmol kg^{-1} (meq/100 g).

2.2.6 Suction Lysimeters Sampling and Analysis

Water samples were collected from SLs installed at three depths within the MPs before and after the amendment application in each year using dedicated tubing for each SL and a peristaltic pump. Prior to sampling, the SLs were put under tension for 24 to 48 hours, depending on the antecedent soil moisture content. Between each SL sampling, the pump tube was flushed with deionized water to prevent cross contamination of water samples. Sample volumes varied between sampling events, depending on soil moisture, but generally did not exceed 100 mL.

Bulk samples were collected in amber coloured HDPE bottles at the study site and sample splits were generated immediately after. In-field water analysis included temperature, Eh, pH, alkalinity, NH_4-N, and o-PO_4. Samples for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), anion and cation determinations were shipped in coolers on ice to the University of Waterloo, GGR Laboratory (Waterloo, Ontario, Canada) for analysis at a later date. All samples excluding pH and Eh were filtered using 0.45 µm polyethersulfone membranes.

Following bulk collection and filtering, sample splits were generated. Samples for DOC and o-PO_4 analyses were stored in amber glass bottles and preserved with H_2SO_4 at pH < 2. Cation samples were stored in HDPE bottles and preserved with HNO_3 at pH < 2. These samples

were stored at 4^{o}C prior to analysis. Anions and DIC samples were stored in HDPE bottles and amber glass bottles, respectively, and were left unpreserved but frozen immediately.

Eh and temperature were measured using a double platinum Ag/AgCl internal reference combination electrode (Orion 9678BNWP). The electrode response was checked using Zobell's solution (Nordstrom, 1977) and Light's solution (Light, 1972), and the performance was checked prior to analysis using A and B solutions (redox/ORP electrode user guide, Thermo Scientific Canada). The pH values were measured using a ROSS Ultra pH/ATC triode (Orion 8157BNUMD). This electrode was calibrated using pH standards 4, 7, and 10 which encompass the typical groundwater pH of 7. Alkalinity was measured using bromocresol green/methyl red and a HACH digital titrator with 0.08 mol L^{-1} (0.16 N) H_2SO_4. NH_3-N was analyzed following the salicylate method (HACH 10023/Clin. Chim. Acta, 14, 403, 1966), and o-PO_4 was measured following the ascorbic acid method (USEPA 365.2), using a HACH spectrophotometer DR1900.

DOC and DIC were measured using wet oxidation with heated sodium persulfate (Aurora 1030W TOC Analyser). Major anions including NO_3-N, NO_2^-, SO_4^{2-} and Cl^-, were analyzed by ion chromatography (Dionex ICS-5000, Thermo Scientific). Cations and trace elements were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES) (iCAP 6000, Thermo Fisher) and ICP-mass spectroscopy (ICP-MS) (Xseries II, Thermo Fisher).

2.3 **Results**

2.3.1 Biochar

In all samples, the C:N ratio was dominated by carbon, ranging from 68.10 to 71.74 wt. % C and 0.29 to 0.49 wt. % N (Table 2-2). The 2019 biochar + LSM mixture had the greatest N (1.22 wt. %). Organic matter was measured in the 2010 biochar at 78.90 % after the biochar was originally generated.

2.3.2 LSM

Total N in 2018 ranged from 0.50 to 0.85 % and 0.58 to 0.59 % in 2019 (Table 2-3). The NH_4-N concentration varied the most in 2018, ranging from 3830 to 7361 ppm and 3818 to 3878 ppm in 2019. All samples had nearly neutral pH, ranging from 7.83 to 7.94 in 2018 and 6.79 to 6.81 in 2019. Organic matter was low in both years, ranging from 2.1 to 2.2 % and 3.3 to 3.6 % in 2018 and 2019, respectively. The 2019 biochar + LSM sample contained the greatest C:N ratio (21:1) and the lowest pH (6.3).

2.3.3 Soil

In the upper 15 cm of soil TC, TN, CEC, and pH remained relatively constant between both years of the study, with the exception of increased TC and TN on the LVBC plot (Figures 2-3, 2-4, 2-5). In Year 1 TC, TN, CEC, and pH ranged from 1.17 to 2.21 %, 0.13 to 0.20 %, 23.0 to 26.7 %, and 5.9 to 6.3, respectively, and in Year 2 values ranged from 1.39 to 4.04 %, 0.12 to 0.20 %, 22.4 to 27.9 %, and 6.0 to 6.8, respectively. Soil NH_4-N was greater in upper soil of the LVBC plot in Year 2, but it was lower on the MO, and did not substantially change on the control and HVBC plot. Ammonium concentrations ranged from 3.21 to 18.20 mg kg^{-1} in 2018 and 1.50 to 19.10 mg kg^{-1} in 2019, with an anomalously high value recorded on the MO plot in 2018 (35.30 mg kg^{-1}), and in the LVBC plot in 2019 (97.60 mg kg^{-1}). Soil NO_3-N concentrations increased on all plots in the upper 15 cm following the application in Year 2, ranging from 2.44 to 10.70 mg kg^{-1} in 2018 and 3.60 to 29.20 mg kg^{-1} in 2019.

In the 15-30 cm interval, the TC and TN concentrations decreased, and the CEC values increased slightly from Year 1 to Year 2 (Figures 2-3, 2-4, 2-5). In Year 1 TC, TN, CEC, and pH ranged from 0.69 to 2.18 %, 0.07 to 0.19 %, 22.5 to 32.7 %, and 6.0 to 6.5, respectively, and in Year 2 values ranged from 0.57 to 1.69 %, 0.04 to 0.13 %, 24.1 to 35.7 %, and 6.2 to 6.8,

respectively. Ammonium concentrations decreased on all plots in the lower soil interval excluding the LVBC plot in Year 2, ranging from 3.46 to 23.8 mg kg^{-1} in Year 1 and 0.99 to 55.30 mg kg^{-1} in Year 2. Soil NO_3-N at 15-30 cm depth did not substantially change between years of the study, ranging from 2.17 to 10.20 mg kg^{-1}.

2.3.4 Pore-water

In both years, pore-water sampled from the SLs show near neutral pH at all depths, ranging from 6.30 to 7.89 in Year 1, and 6.76 to 7.46 in Year 2 (*see* Figures 2-6 and 2-7). On July 4, 2019 the pH values recorded in the LVBC plot increased to 8.05 at 20 cm, and 7.83 at 40 cm depth, before returning to the expected range.

In both years, the recorded alkalinity values generally increased with depth in all plots, ranging from 28 to 420 mg L^{-1} $CaCO_3$ in Year 1, and 40 to 580 mg L^{-1} $CaCO_3$ in Year 2 (*see* Figures 2-6 and 2-7). On August 22, 2018, the alkalinity measured in the control plot at 20 and 40 cm were substantially higher than any other date (328 and 256.5 mg L^{-1} $CaCO_3$, respectively), however the pore-water from these SLs returned to the normal range following this anomalous event. In Year 2, alkalinity values at 20 cm depth ranged from 40 to 130 mg L^{-1} $CaCO_3$ in the MO plot, 80 to 180 mg L^{-1} $CaCO_3$ in the LVBC plot, and 70 to 110 mg L^{-1} $CaCO_3$ in the HVBC plot. At 70 cm pore-water alkalinity values were greatest in the MO plot, ranging from 40 to 580 mg L^{-1} $CaCO_3$, and lowest in the HVBC plot, ranging from 70 to 320 mg L^{-1} $CaCO_3$.

These alkalinity data are reflected in the carbonate saturation indices (SI) where the SI values for calcite ranged from -1.36 to 0.81 in Year 1, and -1.09 to 0.12 in Year 2, with the water approaching or exceeding saturation at depth (*see* Figures 2-6 and 2-7). Similar to alkalinity, in Year 2 the samples from 70 cm depth in the biochar amended plots showed decreasing calcite SI values, while in the MO it increased. The water sample collected from the MO plot on August

22, 2018, which corresponds to an anomalously high alkalinity measurement on that date showed the greatest SI values (0.81).

Pore-water concentrations of NO_3-N in the control plot did not substantially vary with depth in both years (*see* Figures 2-8 and 2-9). In Year 1 NO_3-N concentrations were generally greatest at 40 cm depth on all amended plots, ranging from 0.48 to 22.18 mg L^{-1} NO_3-N. Pore-water at 20 cm typically ranged from 0.37 to 9.78 mg L^{-1} NO_3-N, however, after August 29, 2018 (15 days post application), the concentrations in the MO plot increased substantially to 38.73 mg L^{-1} NO_3-N. This increase was not observed on the LVBC and HVBC plots until September 26, 2018 when the pore-water concentration from this depth increased to 20.45 and 28.56 mg L^{-1} NO_3-N, respectively. In Year 2 NO_3-N concentrations in the amended plots were again generally highest at 40 cm and ranged from 0.01 to 16.69 mg L^{-1} NO_3-N. In the 20 cm level pore-water range from 0.32 to 10.10 mg L^{-1} NO_3-N until August 1, 2019, when it increased to 30.62 and 15.87 mg L^{-1} NO_3-N on the LVBC and HVBC plots, respectively. Due to insufficient sample volumes NO_3-N concentrations were not measured at 20 cm in the MO plot following the application in Year 2.

Pore-water concentrations of NH_3-N in Year 1 in the control, LVBC, and HVBC plots ranged from 0.01 to 1.79 mg L^{-1} and did not substantially change with depth (*see* Figure 2-8). In the MO plot NH_3-N concentrations briefly increased at 20 cm from August 22 to Sept 12, 2018 to a maximum of 19.70 mg L^{-1}. In Year 2 pore-water NH_3-N concentrations ranged from 0.01 to 0.44 in all plots, with the highest concentration occurring at 40 cm on June 5, 2019 in the MO plot (*see* Figure 2-9).

DOC concentration where greatest at 20 cm depth in both years and ranged from 5.6 to 33.1 mg L^{-1} as C in Year 1, and 4.5 to 19.3 mg L^{-1} as C in Year 2, excluding the anomalously

high value measured on August 22, 2018, which reached 115.5 mg L^{-1} as C (*see* Figures 2-8 and 2-9). DOC concentrations tended to decrease with depth, which is most apparent in the Year 2 data, where concentrations at the 40 cm level ranged from 3.9 to 12.8 mg L^{-1} as C, and at 70 cm from 2.7 to 9.2 mg L^{-1} as C.

2.3.5 Soil Moisture

In both years, soil moisture was measured within the top 20 cm of soil during GHG sampling events and showed generally consistent values between plots and between years (*see* Figure 2-10 and 2-11). In Year 1, soil moisture ranged from 15.4 to 32.4 % with mean values of 17.9 to 31.9 %. In Year 2, soil moisture ranged from 15.2 to 38.9 % with mean values of 16.8 to 37.1 %.

2.3.6 Greenhouse Gas Fluxes

2.3.6.1 Data removal

Prior to analyses, data quality was examined and flux values that exceeded an exclusion criterion of $R^2 = 0.8$ were retained in the data set, and remaining data removed. In 2018 this filtering of data resulted in the removal of 20 CO_2 and 17 N_2O (9% and 7% respectively) and in 2019 12 CO_2 and 17 N_2O flux measurements (4% and 6% respectively). This criterion is consistent with previously reported standards for GHG emission studies by Agriculture and Agrifoods Canada (Van Zandvoort et al., 2017).

2.3.6.2 2018 Carbon dioxide

The CO_2 flux data from 2018 showed a spike in emissions following the amendment application (Figure 2-12). A one-way analysis of variance (ANOVA) indicated that there were significant differences among the plots, $F(3, 16) = 3.50$, $p = 0.04$. Given this difference, an analysis controlling for pre-application differences was conducted by subtracting the average

emissions obtained in pre-application measurements from the post-application measurements. The results were not substantively different. The difference between the control vs. the high-volume biochar plot (HVBC) changed from marginally significant ($p = 0.07$) to significant ($p = 0.03$) when the transformation controlling for pre-application emissions was applied. For clarity, analyses were conducted and reported without controlling for the pre-application difference.

The differences in average CO_2 emissions following the addition of the manure (i.e., post-application) were examined using a one-way ANOVA. The results indicated there were no significant differences among the plots, $F(3, 52) = 1.07$, $p = 0.37$. Follow-up *t*-tests were conducted to examine specific differences between plots and again no significant differences were found (*see* Table 2-4). Analysis of short-term emissions (i.e., measurements obtained in the week immediately following the application) and long-term emissions (i.e., measurements obtained after one week had elapsed and until the end of the experiment) similarly showed no differences in CO_2 emissions among the plots ($p > 0.05$) (*see* Table 2-5). The cumulative fluxes (*see* Table 2-7) show the same sharp increase in emissions immediately after the application followed by similar increases in cumulative totals between all plots (Figure 2-13).

2.3.6.3 2018 Nitrous oxide.

The 2018 N_2O flux data showed increased emissions from the amended MPs following the application (Figure 2-14). Differences in N_2O emissions among the plots during the pre-application period were examined and the results of a one-way ANOVA indicated that there were significant differences among the plots, $F(3, 16) = 8.43$, $p < 0.01$. Given this difference, an analysis to control for pre-application differences was conducted by subtracting the average emissions obtained in pre-application measurements from the post-application measurements. The differences between the transformed and non-transformed results were not substantive, so

for clarity in the interpretations the presented results are from the analyses conducted on the post-application data without controlling for the pre-application differences. Using the transformed data changes the difference between the control vs. the low-volume biochar plot (LVBC) from significant ($p < 0.01$), to marginally significant ($p = 0.096$), and LVBC vs. HVBC plot from significant ($p < 0.01$), to non-significant ($p > 0.05$).

Following the manure application, the manure only plot (MO) cumulative flux data (*see* Table 2-7) showed the sharpest increase in N_2O emissions, and sustained increases throughout the duration of the period (Figure 2-15). The LVBC and HVBC plots had greater cumulative emissions than the control, and both biochar plots released similar total emissions at the end of the study.

The results of a one-way ANOVA indicated that there were significant differences in N_2O emissions between the plots post-application, $F(3, 52) = 34.94$, $p < 0.01$. Results of follow-up *t*-tests indicated that, there were significantly lower N_2O emissions on the control plot ($M = 45.87$, $SD = 28.17$) as compared to the manure only (MO) plot ($M = 250.75$, $SD = 102.44$), $t(26) = -7.21$, $p < 0.01$ ($d = 2.73$) (*see* Table 2-4). As well, the control had significantly lower emissions than the LVBC plot ($M = 112.47$, $SD = 46.40$), $t(26) = -4.59$, $p < 0.01$ ($d = 1.74$), but was not significantly different from the HVBC plot ($M = 62.28$, $SD = 20.64$), $t(26) = -1.76$, $p = 0.09$ ($d = 0.66$). There were significantly lower emissions on the LVBC plot, $t(26) = 4.6$, $p < 0.01$ ($d = -1.74$) and the HVBC plot, $t(26) = 6.75$, $p < 0.01$ ($d = -2.55$) as compared to the MO plot. Finally, the biochar plots were significantly different from each other, $t(26) = 3.70$, $p < 0.01$ ($d = -1.40$), with less N_2O emitted from the HVBC plot than from the LVBC plot.

2.3.6.4 2019 Carbon dioxide

Carbon dioxide fluxes measured in 2019 were highest immediately following the application and returned to the level of the control plot after one week (Figure 2-16). The final difference in cumulative emissions (*see* Table 2-7) is due to this immediate increase following application, demonstrated by the similar rate of increase in total emissions between plots after this time (Figure 2-17).

The results of a one-way ANOVA indicated there were no significant differences in CO_2 emissions among the plots pre-application, $F(3, 20) = 1.13$, $p = 0.36$. Differences between plots in the post-application data were evaluated using a one-way ANOVA which indicated there were significant differences among the plots, $F(3, 66) = 2.95$, $p = 0.04$. Results of follow-up *t*-tests indicated that, there were significantly lower CO_2 emissions on the control plot ($M = 5.16$, $SD = 2.98$) as compared to the MO plot ($M = 17.15$, $SD = 19.59$), $t(34) = -2.57$, $p = 0.02$ ($d = 0.86$), and the LVBC plot ($M = 11.25$, $SD = 10.28$), $t(33) = -2.41$, $p = 0.02$ ($d = 0.82$) (*see* Table 2-4). The difference between the control plot and the HVBC plot ($M = 9.81$, $SD = 9.55$) was marginally significant, $t(33) = -1.97$, $p = 0.06$ ($d = 0.67$). There were no significant differences between the MO plot and the LVBC or HVBC plots, and the biochar plots did not differ from each other. Supplementary analyses were conducted to examine shorter- and longer-term emissions (*see* Table 2-5). No additional differences were observed in the short term, however following the first week after application the MO plot had significantly higher emissions than the HVBC plot $t(23) = 3.47$, $p < 0.01$ ($d = -1.39$) (Table 2-5).

2.3.6.5 2019 Nitrous oxide

Emissions of N_2O in 2019 were variable across the sampling period, with the highest emissions occurring on the MO plot in the week following application (Figure 2-18). Following

this initial burst of emissions, the cumulative emissions (*see* Table 2-7) from the MO plot continued to deviate from the other MPs (Figure 2-19).

The results of a one-way ANOVA indicated there were no significant differences in N_2O emissions among the plots pre-application, $F(3, 19) = 1.81$, $p = 0.18$. An ANOVA analysis of the post-application fluxes indicated there were significant differences among the plots, $F(3, 66) = 8.45$, $p < 0.01$. Results of follow-up *t*-tests indicated that there were significantly lower emissions on the control plot ($M = 20.85$, $SD = 23.36$) as compared to the MO plot ($M = 156.71$, $SD = 121.60$), $t(34) = -4.65$, $p < 0.01$ ($d = 1.55$), and the LVBC plot ($M = 62.48$, $SD = 73.07$), $t(33) = -2.30$, $p = 0.03$ ($d = 0.78$) (*see* Table 2-4). The difference between the control plot and the HVBC plot ($M = 63.36$, $SD = 85.52$) was marginally significant, $t(33) = -2.03$, $p = 0.05$ ($d = 0.69$). As in 2018, there were significantly lower emissions on the LVBC plot, $t(33) = 2.76$, $p = 0.01$ ($d = -0.93$) and the HVBC plot, $t(33) = 2.61$, $p = 0.01$ ($d = -0.88$) as compared to the MO plot. Unlike in 2018, N_2O emissions on the LVBC and HVBC plots were not significantly different.

2.4 **Discussion**

The aim of this study was to compare yearly, smaller volume applications of biochar to a one-time, larger application. The purpose was to examine whether this year-over-year procedure could address the weathering effects associated with one-time biochar applications, which can become less effective in mitigating GHG emissions over time. Four MPs were set up without prior knowledge of the specific underlying soil conditions and experimental condition was randomly assigned. The MPs were sampled across two growing seasons in 2018 (Year 1) and 2019 (Year 2). The timing differed each year due to field access and weather restrictions. The soil conditions across the field and microplots were relatively consistent. However, the potential

impact of underlying tile-drainage was not considered as the exact location of each tile-drain was not known. Additionally, the crop planted on the field was different each year to maintain the crop rotation; no plants were grown inside of the flux chambers in either year. Each MP received the same soil amendment combination in each year (*see* Table 2-1), except for the HVBC plot, which did not receive additional biochar in Year 2.

The application method of biochar on the LVBC plot differed between Years 1 and 2 of the study. However, this change is not expected to have significantly impacted the results of the experiment because, following the applications, the biochar and manure amendments were thoroughly worked into the top 10 cm of soil using hand tools. The manure source differed in each year, typical of actual agricultural practices, which may limit the ability to directly compare results across years; however, chemically the LSM did not differ substantially between years (*see* Table 2-3). The 2018 LSM did contain greater NH_4-N, which may have contributed to the greater cumulative N_2O fluxes from all plots observed in 2018 vs. 2019.

The reduction in N_2O emissions following biochar application observed in this study are consistent with existing research, however, CO_2 emissions were not impacted by the addition of biochar. In Year 1 the HVBC plot lowered N_2O emissions by the greatest amount, but, due to the biochar weathering, performed more similarly to the LVBC plot in Year 2. The decreased mitigation potential of the aged biochar indicates that yearly applications of biochar are necessary to maintain emissions reductions.

2.4.1 CO_2 Emissions

In this study, the addition of biochar did not significantly impact measured CO_2 fluxes, nor did the biochar weathering. Emissions were similar among all amended MPs, regardless of the presence, volume, or age of biochar. These measurements are within the range of observations

from previous studies. Although several studies have found that biochar can mitigate CO_2 emissions (Bamminger et al., 2014; Méndez et al., 2014), others have found that biochar additions can increase emissions (Ameloot et al., 2013; Case et al., 2012). The application of biochar can change both physical and chemical soil conditions, which can directly and indirectly impact CO_2 emissions (Ameloot et al., 2013; Cross & Sohi, 2011; Lehmann et al., 2011).

Increased CO_2 emissions were observed on the plots that received amendments (MO, LVBC, HVBC) compared to the control plot (no amendment). No differences in CO_2 emissions, however, were observed between the MO, LVBC, HVBC plots. Specifically, there were significantly higher emissions on the MO and LVBC plots relative to the control plot in Year 2 (similar patterns were observed for the HVBC plot vs. the control in Year 2, and between the amended plots vs. the control in Year 1, but the comparisons where marginally significant ($0.1 > p > 0.05$)).

Carbon dioxide is generated via microbial, root, and faunal respiration, which can be impacted by many factors such as soil moisture, texture, temperature, pH, nutrient concentration, and available C (Davidson et al., 1998; Kloss et al., 2014; Rastogi et al., 2002). The absence of biochar impacts on emissions reflects this complex relationship between soil environment and microbial communities which generate CO_2. The addition of biochar does not have a singular effect on CO_2 generation in soils (Anders et al., 2013; Davidson et al., 1998).

The impact of biochar on CO_2 soil emissions is not fully understood and can have neutralizing effects on CO_2 emissions. In some instances, the addition of biochar has been found to positively impact microbial activity, which increases CO_2 emissions via the decomposition of soil organic matter (Kuzyakov et al., 2009). However, other studies describe microbial communities using C more efficient following the addition of biochar, which in turn reduces the

soil CO_2 emissions (Bamminger et al., 2014). Further, the high C content means the addition of biochar to soil will increase the C:N ratio and decrease microbial activity (Atkinson et al., 2010). The 2019 biochar + LSM amendment which was applied to the LVBC plot had a C:N ratio of 21:1 (*see* Table 2-3). These opposing processes may explain why a major impact on CO_2 emissions was not observed following the application of biochar amendments.

In both years, CO_2 emissions were greatest immediately following amendment application. Increased emissions were observed for approximately one week before returning to the pre-application baseline. This observation is consistent with previous research which found similar short-term releases of CO_2 following the application of soil amendments (Jones et al., 2011). This effect may be due to the increased soil moisture and aeration following the application and incorporation of a liquid manure, which can impact microbial activity by facilitating O_2 diffusion within biochar, thereby increasing respiration (Banerjee et al., 2016; Case et al., 2012; Jones et al., 2011). In both years, no substantial increases in soil moisture were observed following the amendment applications (*see* Figure 2-10 and 2-11). Short-term emissions may also be caused by enhanced soil enzyme activity due to the high concentration of NH_4-N in the LSM amendment (*see* Table 2-3), which can lead to increased CO_2 production (G. Liang et al., 2015). Where the precipitation events and flux measurements align more closely, such as in late July and August of 2019, no substantial spikes in CO_2 emissions are present, indicating that it is likely the combination of increased aeration and NH_4-N following amendment incorporation are responsible for the short-term emissions.

The addition of fresh biochar to the LVBC plot in Year 2 of this study did not affect CO_2 emissions, when compared to the aged biochar plot (HVBC), or when compared to the LVBC plot across years (*see* Figure 2-20). The cumulative flux values for Year 2 did show greater

reductions in CO_2 emissions compared to Year 1. Specifically, in Year 2, the percent difference between the LVBC and HVBC plots compared to MO were 32% and 50% lower, respectively (*see* Table 2-7), as opposed to 10% and 1% higher in Year 1. Closer examination of the data suggests that this may be due to an anomalously large flux value measured on the MO plot on July 10, 2019. Thus, this study found that CO_2 emissions were likely caused by a combination of increased soil aeration, and NH_4-N concentration from the physical incorporation of the amendments, rather than by biochar volume or age.

2.4.2 N_2O Emissions

Significant differences between plots in terms of N_2O fluxes were observed in this study. Specifically, the inclusion of biochar in the field amendment led to significant N_2O emissions reductions as compared to MO, in both years. The N_2O emissions reductions occurred immediately after the biochar application and emissions returned to the baseline (i.e., comparable to the control plot) more quickly than was observed on the MO plot.

In Year 1, the percent difference of cumulative N_2O emissions from the LVBC and HVBC plots were 88% and 121% lower than the MO plot, respectively. Further, lower short- and long-term emissions were observed on the HVBC vs. LVBC plot. The percent difference between emissions from the HVBC plot were 45% lower than that of the LVBC plot. These results were expected because it is well established that N_2O emissions decrease with increased biochar application rates (Cayuela et al., 2014). The N_2O emissions from the HVBC plot were reduced to nearly the same level as the control plot, which had no manure or biochar amendment (cumulative emissions percent difference was 12% higher on HVBC plot).

Following the initial spike in N_2O emissions after the amendment application each plot tends to maintain a stable level of elevated emissions, with the major exception of the MO plot

starting in late August 2018 (*see* Figure 2-14). This large secondary spike in emissions coincides with a sharp increase in the NO_3-N concentration in the pore-water at 20 cm depth that is not seen on the other amended plots until later in the fall (*see* Figure 2-8).

In Year 2, the HVBC plot did not receive any additional biochar, thus allowing for the comparison between fresh and aged biochar. The results were similar to Year 1 with both HVBC and LVBC plots outperforming the MO plot in terms of N_2O emissions reductions, however in this year the biochar plots did not significantly differ. There was an initial spike in N_2O emissions following the amendment application which was quickly followed up by a secondary spike that likely occurred due to precipitation event on July 11, 2019 (*see* Figure 2-18). Another spike occurred around the beginning of August 2019 which was also likely caused by a large precipitation event that occurred on July 28, 2019 which saturated the soil and introduced conditions for denitrification to occur.

The use of biochar as a field amendment has been found to reduce N_2O emissions typically associated with nitrogen rich manure applications (Agegnehu et al., 2015; Bamminger et al., 2014; Cayuela et al., 2014; X. Liu et al., 2012; Rondon et al., 2005; Van Zwieten et al., 2013). There are some exceptions, primarily in studies where the biochar feedstock was an animal-manure or food waste which created high N biochars following pyrolysis (Singh et al., 2010; Spokas & Reicosky, 2009; Van Zwieten et al., 2010). The biochar used in this study contained 70.20% carbon, 6.70% ash, and 0.33% N (*see* Table 2-2) which are all within the common ranges for biochar used in agricultural greenhouse gas studies (Spokas & Reicosky, 2009), so all subsequent N_2O emissions are assumed to have come from other sources.

As the production of N_2O is a microbially driven process, any impact that biochar has on microbial communities is expected to be important, regardless of the specific pathway (Cayuela

et al., 2014; Lehmann et al., 2011). Due to the high porosity of biochar, microbes are expected to have greater habitat for growth, which may stimulate increased activity (Atkinson et al., 2010; Pietikäinen et al., 2000). However, some biochar has been found to produce or contain microbial inhibitors such as ethylene and polycyclic aromatic hydrocarbons, which reduce microbial activity and can lead to reduced N_2O emissions (Quilliam et al., 2012; Spokas et al., 2010). Due to the powdered texture of the biochar used in this study it was not possible to collect aged biochar from the field for comparison.

Past research has found physical and chemical changes imparted on soil with the introduction of biochar. The large porosity of biochar impacts soil aeration and hydrology (Atkinson et al., 2010; Rogovska et al., 2011). Increased aeration introduces more O_2 to the soil, thereby inhibiting denitrification (Clough et al., 2013). Biochar can also impact N_2O emissions via pH shifts, due to the alkaline nature of many biochars (Cayuela et al., 2014; Clough & Condron, 2010). As soil pH increases, the N_2O:N_2 ratio would decrease due to elevated N_2O reductase activity which favors the production of benign N_2 gas (Clough et al., 2013; Firestone et al., 1980). No substantial pH changes were observed in the soil cores or pore-water samples across the duration of this study (*see* Figures 2-3, 2-6, 2-7).

The amount of N in soil plays a key role in the formation of N_2O. Therefore, the impacts of biochar additions on nutrient availability has been proposed as a significant factor controlling N_2O emissions (Butterbach-Bahl et al., 1997; Skiba et al., 1998). Total N in the LSM applied did not substantially differ between years, and excluding the LVBC plot, no substantial increase in soil N was observed in the 0-15 cm interval between both years. Importantly, the increase in average TN on the LVBC plot between years was not accompanied by an increase in N_2O emissions from this plot. Soil NH_4-N concentrations were over 1300 mg L^{-1} higher in Year 1

than in Year 2 (*see* Table 2-3) which may explain why N_2O emissions were generally greater on all amended plots in Year 1.

In addition to having a high cation exchange capacity, biochar can also adsorb anions (Barnes et al., 2014; Clough & Condron, 2010; Major et al., 2009). This ability to adsorb both NO_3-N and NH_4-N can reduce the amount of inorganic-N available in the soil for microbes to utilize, thereby reducing N_2O production (Cayuela et al., 2014; Christianson et al., 2011b; Clough et al., 2013). Soil CEC did not change substantially during this study; however, soil NO_3-N concentrations did increase upper 15 cm of soil on all plots between Years 1 and 2, and soil NH_4-N increased substantially in the LVBC plot (*see* Figures 2-3, 2-5). It should be noted, this increased soil NO_3-N and NH_4-N did not translate to higher cumulative N_2O emissions in Year 2 (*see* Figure 2-19) indicating that biochar may be adsorbing these inorganic N species to a greater extent on the fresh biochar of the LVBC plot, thereby making it unavailable for denitrifying bacteria.

Carbon plays an important role in N_2O production as the process of denitrification relies on C as an electron donor (Groffman et al., 1999; Knowles, 1982; Morley & Baggs, 2010; Rivett et al., 2008). Some research has found that the availability of C impacted the denitrification product ratio [N_2O /(N_2O+ N_2)] shifting it towards greater N_2 production (Miller et al., 2008). Further, when the C:N ratio in soil is high N can become temporarily immobilized, resulting in lowered N_2O emissions (Baggs et al., 2000; Cayuela et al., 2014). In 2019 the Biochar + LSM amendment applied to the LVBC plot had a C:N ratio of 21:1 (*see* Table 2-3), and from Year 1 to Year 2 the total C in the near surface soil increased substantially, while in the other plots soil TC did not change over the same period (*see* Figure 2-4).

Increased complete denitrification, which results in the production of N_2, has been found following the application of biochars containing labile C, which is readily used by soil microorganisms (B. O. Clarke & Smith, 2011; Clough et al., 2013; J. L. Smith et al., 2010). While some biochar contains labile C, it is not considered an important source. Rather, biochar can interact with labile organic C present in the soil, or from additional amendments such as manures (Joseph et al., 2010; B. Liang et al., 2010). The biochar used in this study contained 78.9 % organic matter after it was initially produced so could be contributing both OC and IC to the soil. In Year 2 the increase in soil TC in the upper interval of the LVBC plot is mirrored in the increased soil OC and IC at this depth (*see* Figure 2-4) and demonstrates the presence of the fresh biochar which was incorporated in this plot. This fresh biochar may have contributed the C needed as an electron donor for denitrifying microorganisms while temporarily immobilizing N, resulting in decreased N_2O emissions.

In both years in all plots the pore-water alkalinity tended to increase with depth and approached or exceeded saturation with respect to calcite at 70 cm bgs (*see* Figures 2-6, 2-7). The opposite was observed for the DOC concentration, which was generally highest at 20 cm (*see* Figure 2-8, 2-9). These trends are consistent with expected site soil conditions, which tend to have greater organic matter content above the plow pan (0.2 m), and more inorganic mineral sources of carbon deeper in the profile (Frey et al., 2013; Hussain et al., 2019). In Year 2 the pore-water alkalinity values measured at 20 cm bgs in the LVBC plot were higher than in all other plots which corresponds to the increased soil IC in this plot. Water collected at 20 cm depth would have the most contact with the fresh biochar as it infiltrated through the upper tilled soil before encountering the compacted plow pan which presents conditions for preferential lateral flow (Frey et al., 2013). Below the plan pan macropore flow dominates downward water flow

that infiltrates beyond this layer and will typically be drained quickly by the underlying tile-drains (Frey et al., 2013; S. I. Hussain et al., 2019).

Thus, while the precise process by which biochar mitigates N_2O emissions remains unclear, the results from Years 1 and 2 in terms of general emission reduction are consistent with other studies (Cayuela et al., 2014; X. Liu et al., 2012; Rondon et al., 2005; Spokas, 2013). Further, the year-over-year design of the current study also allowed for examination of the effects of biochar weathering on the effectiveness in reducing N_2O emissions (Spokas, 2013).

In Year 1, N_2O emissions from the HVBC plot were significantly lower than the LVBC plot (i.e., percent differences of cumulative emissions between the biochar plots and the MO were 121% vs. 88%) (*see* Table 2-7). By comparison, the reduction in emissions were comparable in Year 2, narrowing the cumulative emissions difference between the HVBC and LVBC plots over the full study (*see* Figure 2-21). The percent differences of cumulative emissions were 76% lower than the MO plot for the HVBC plot and 77% lower for the LVBC plot. The Year 2 results represent a noticeable decline in emissions reduction of 45% difference between the HVBC and MO plots. Past research has suggested that this loss of mitigation may be caused by the loss of sorption capacity on the weathered biochar, or possibly leaching of organic compounds that act as microbial inhibitors (Spokas, 2013).

2.4.3 Conclusions, Implications, and Limitations for BMPs

This study aimed to aid in the development of BMPs that can be implemented to reduce agricultural contributions to GHG emissions, specifically in the area of biochar as a field co-amendment. This current study examined year-over-year applications of biochar as a field amendment to determine if the losses associated with biochar aging could be overcome. After

two years, GHG mitigation of a high-volume biochar application was reduced to the same level as a biochar application that was half the volume.

This study found that CO_2 emissions spiked immediately after the amendment applications, which were attributed to the combination of increased soil aeration and NH_4-N. However, the addition of biochar did not significantly impact CO_2 emissions over the study period and emissions also did not differ with the application of fresh biochar in lower volumes compared to a single higher volume application. The observation that CO_2 emissions did not differ significantly across the amended plots suggests that biochar additions may impact more than one mechanism controlling CO_2 emissions, potentially cancelling each other out and resulting in no substantial change in emissions. This finding is consistent with other studies demonstrating mixed effects where increased emissions are typically attributed to increased soil organic matter decomposition (Kuzyakov et al., 2009) and decreased emissions to more efficient microbial C use (Bamminger et al., 2014).

Significant N_2O emissions reductions were observed in this study following the application of biochar as co-amendment, along with a pronounced biochar aging effect, where the mitigation of emissions by a single application of biochar, performed equally to a fresh yearly application of smaller volumes. In this study, the addition of biochar co-amendment was thought to have primarily impacted the N and C availability in the near surface soil layer, leading to decreased N_2O emissions on both biochar amended plots. Increased soil inorganic N in Year 2 did not result in greater emissions which may be due to the high ability of biochar to adsorb and make unavailable this N source for denitrifying bacteria (Barnes et al., 2014; Clough & Condron, 2010; Major et al., 2009). The high C content introduced with the addition of biochar also likely played a role in N_2O mitigation. The high C:N ratio of the Biochar + LSM could shift

denitrification towards N_2 gas generation, and immobilize N which is needed for the reaction to occur (Baggs et al., 2000; Cayuela et al., 2014; Miller et al., 2008).

The addition of fresh biochar on the LVBC plot was found to have brought the two biochar amended plots towards equal N_2O mitigation after two years. Although additional research is needed to identify the mechanisms controlling this mitigation loss, and to assess whether this downward trend would continue, the mitigation loss of such a substantial amount in only two years indicates small, year-over-year applications may be an alternative to conventional large, one-time applications.

In addition to addressing the impacts of biochar aging, this application schedule has further implications which may increase the uptake of this BMP. Namely, the application of small biochar volumes may help farmers overcome the prohibitive cost of biochar, as well as address the concern surrounding the application process, which can be arduous when working with large volumes of biochar (Major, 2010; Smith P. et al., 2014; Sohi, 2012).

Using biochar at the industrial agriculture scale can quickly become untenable for farmers who must consider the trade-offs of carbon sequestration and biochar cost, particularly when the GHG mitigation benefit may not persist. This research highlights the possibility of using smaller volumes at a yearly rate which opens up the possibility for farmers to purchase less biochar, or potentially produce biochar using waste straw and stover leftover following harvest. Further, smaller volumes of biochar may help to address the issues associated with application such as loss of dust fractions and dealing with overly viscous manure and biochar slurries (Major, 2010; Verheijen et al., 2010). Lower volumes of biochar may be more easily incorporated in the broadcast spreaders tanker, which has the added benefit of reducing the amount of passes a farmer needs to make during the application.

Although the findings of this study are promising, there are several limitations worth noting. While key comparisons are between plots within years (i.e., comparing LVBC and HVBC plots to each other in the same year) and the results are generally consistent with the existing literature, future research should attempt to standardize conditions between years. For example, factors such as the sampling period, biochar application method, and source of liquid swine manure should be held constant to aid comparison across years. Further, because this study was conducted over two field seasons, it can not be concluded that the LVBC plot has outperformed the HVBC plot because after two seasons they are essentially equal in terms of overall emissions reductions, and the cumulative volume of biochar added to each plot was equal after two years. An additional field season is necessary to clarify if the decline in GHG mitigation on the HVBC plot would continue, and if there would be additive effects of the multi-year applications on the LVBC plot. Using chip sized biochar which could be recovered from the soil following each year would allow more precise examinations of the weathering processes taking place and help elucidate the cause behind the loss of emissions mitigation. Taken together, this study provides a foundation for additional research aiming to develop BMPs that help reduce GHG emissions yet are accessible for farmers.

Table 2-1: Microplot amendment schedule.

Microplot	Treatment (Year 1 – 2018)	Treatment (Year 2 – 2019)
Control	No amendment	No Amendment
Manure Only (MO)	Manure amendment only	Manure amendment only
Low-Volume Biochar (LVBC)	Manure + low (3 % vol) biochar amendment	Manure + low (3 % vol) biochar amendment
High-Volume Biochar (HVBC)	Manure + high (6 % vol) biochar amendment	Manure amendment only

Table 2-2: Mean elemental analysis of biochar and biochar/liquid swine manure from Winchester experimental microplots. Where no standard deviation is present the value represents the measurement of a single sample. * reported value is calculated based on the C:N ratio and the total N value. -- not measured

	Biochar	Moisture	Ash	C (total)	H (total)	N (total)	O (calc.)	S (total)
			Moist. Free	Moist. Free	Moist. Free	Moist. Free	Moist. Free	Moist. Free
Sample	% vol.	wt. % (SD)	wt. % (SD)	wt. % (SD)	wt. % (SD)	wt. % (SD)	wt. % (SD)	wt. % (SD)
Biochar 2010	100	--	--	43.61*	--	0.49	--	--
Biochar 2019	100	4.14 (0.08)	6.70 (0.57)	70.20 (1.73)	3.65 (0.13)	0.33 (0.04)	19.12 (2.03)	< 0.03 (na)
Biochar + LSM 2019	3	78.73	8.94	68.32	4.03	1.22	17.34	0.14

Table 2-3: Mean elemental analysis of liquid swine manure from Winchester experimental microplots. Where no standard deviation is present the value represents the measurement of a single sample.

Sample	Dry Matter % (SD)	TN % (SD)	NH_4-N ppm (SD)	TP % (SD)	S ppm (SD)	OM % (SD)	C:N	pH (SD)
LSM 2018	3.13 (0.06)	0.64 (0.19)	5209.67 (1887.75)	0.08 (0.01)	263.90 (11.36)	2.17 (0.06)	2:1	7.88 (0.06)
LSM 2019	4.55 (0.21)	0.59 (0.01)	3848.00 (42.43)	0.11 (0.00)	494.50 (5.23)	3.45 (0.21)	3:1	6.80 (0.01)
Biochar + LSM 2019	21.90	0.64	3018.00	0.13	603.70	23.50	21:1	6.30

Table 2-4: Mean post-application GHG flux values for Winchester microplots for 2018 and 2019 field seasons. Significant ($p < 0.05$) p-values from independent sample t-tests are bolded. Control: No manure or biochar. MO: Manure-only. LVBC: Manure + low-volume biochar. HVBC: Manure + high-volume biochar in 2018, Manure-only in 2019.

Year and Micro-Plot	Micro-Plot Comparison	CO_2			N_2O		
		Mean (SD) (kg C ha^{-1} day^{-1})	*p*-value	Effect Size (Cohen's *D*)	Mean (SD) (μg N m^{-2} hr^{-1})	*p*-value	Effect Size (Cohen's *D*)
2018							
Control	Control	6.87 (2.02)	--	--	45.87 (28.17)	--	--
	MO	15.99 (16.80)	0.054	--	250.75 (102.44)	< **0.001**	2.73
	LVBC	17.99 (26.45)	0.129	--	112.47 (46.40)	< **0.001**	1.74
	HVBC	15.98 (17.82)	0.068	--	62.28 (20.64)	0.091	--
MO	LVBC	17.99 (26.45)	0.813	--	112.47 (46.40)	< **0.001**	-1.74
	HVBC	15.98 (17.82)	0.999	--	62.28 (20.64)	< **0.001**	-2.55
LVBC	HVBC	15.98 (17.82)	0.816	--	62.28 (20.64)	**0.001**	-1.40
2019							
Control	Control	5.16 (2.98)	--	--	20.85 (23.36)	--	--
	MO	17.15 (19.59)	**0.015**	0.86	156.71 (121.60)	< **0.001**	1.55
	LVBC	11.25 (10.28)	**0.022**	0.82	62.48 (73.07)	**0.028**	0.77
	HVBC	9.81 (9.55)	0.058	--	63.36 (85.52)	0.050	--
MO	LVBC	11.25 (10.28)	0.277	--	62.48 (73.07)	**0.009**	-0.93
	HVBC	9.81 (9.55)	0.172	--	63.36 (85.52)	**0.013**	-0.88
LVBC	HVBC	9.81 (9.55)	0.674	--	63.36 (85.52)	0.974	--

Table 2-5: Short- and long-term post-application CO_2 flux values for Winchester microplots for 2018 and 2019 field seasons. Significant ($p < 0.05$) p-values from independent sample t-tests are bolded. Control: No manure or biochar. MO: Manure-only. LVBC: Manure + low-volume biochar. HVBC: Manure + high-volume biochar in 2018, Manure-only in 2019.

Year and Micro-Plot	Micro-Plot Comparison	Short-Term			Long-Term		
		Mean (SD) (kg C ha^{-1} day^{-1})	*p*-value	Effect Size (Cohen's *D*)	Mean (SD) (kg C ha^{-1} day^{-1})	*p*-value	Effect Size (Cohen's *D*)
2018							
Control	Control	7.42 (2.29)	--	--	6.56 (1.93)	--	--
	MO	30.20 (22.27)	0.052	--	8.09 (3.78)	0.295	--
	LVBC	34.46 (41.57	0.185	--	8.84 (2.95)	0.070	--
	HVBC	30. 76 (24.08)	0.063	--	7.77 (3.68)	0.396	--
MO	LVBC	34.46 (41.57	0.845	--	8.84 (2.95)	0.647	--
	HVBC	30. 76 (24.08)	0.971	--	7.77 (3.68)	0.857	--
LVBC	HVBC	30. 76 (24.08)	0.867	--	7.77 (3.68)	0.507	--
2019							
Control	Control	7.73 (4.65)	--	--	4.18 (1.25)	--	--
	MO	40.26 (26.27)	**0.026**	1.72	8.26 (2.32)	**< 0.001**	2.19
	LVBC	22.08 (13.86)	0.059	--	6.74 (2.91)	**0.008**	1.16
	HVBC	21.03 (11.36)	**0.042**	1.53	5.13 (2.18)	0.188	
MO	LVBC	22.08 (13.86)	0.208	--	6.74 (2.91)	0.161	--
	HVBC	21.03 (11.36)	0.171	--	5.13 (2.18)	**0.002**	-1.39
LVBC	HVBC	21.03 (11.36)	0.899	--	5.13 (2.18)	0.139	--

Table 2-6: Short- and long-term post-application N_2O flux values for Winchester microplots for 2018 and 2019 field seasons. Significant ($p < 0.05$) p-values from independent sample t-tests are bolded. Control: No manure or biochar. MO: Manure-only. LVBC: Manure + low-volume biochar. HVBC: Manure + high-volume biochar in 2018, Manure-only in 2019.

Year and Micro-Plot	Micro-Plot Comparison	Short-Term			Long-Term		
		Mean (SD) (kg C ha^{-1} day^{-1})	*p*-value	Effect Size (Cohen's *D*)	Mean (SD) (kg C ha^{-1} day^{-1})	*p*-value	Effect Size (Cohen's *D*)
2018							
Control	Control	32.41 (10.48)	--	--	53.36 (32.53)	--	--
	MO	213.50 (91.74)	**0.002**	2.77	271.44 (107.22)	< **0.001**	2.75
	LVBC	133.93 (70.83)	**0.013**	2.01	100.54 (23.27)	**0.003**	1.67
	HVBC	57.95 (31.42)	0.123	--	64.69 (13.43)	0.348	--
MO	LVBC	133.93 (70.83)	0.163	--	100.54 (23.27)	< **0.001**	-2.20
	HVBC	57.95 (31.42)	**0.007**	-2.27	64.69 (13.43)	< **0.001**	-2.71
LVBC	HVBC	57.95 (31.42)	0.060	--	64.69 (13.43)	**0.001**	-1.89
2019							
Control	Control	26.86 (33.50)	--	--	18.54 (19.45)	--	--
	MO	275.46 (167.23)	**0.012**	2.06	111.04 (59.10)	< **0.001**	2.10
	LVBC	73.84 (78.26)	0.252	--	57.74 (73.87)	0.077	--
	HVBC	106.10 (141.45)	0.258	--	45.56 (46.76)	0.068	--
MO	LVBC	73.84 (78.26)	**0.040**	-1.54	57.74 (73.87)	0.057	--
	HVBC	106.10 (141.45)	0.122	--	45.56 (46.76)	**0.006**	-1.22
LVBC	HVBC	106.10 (141.45)	0.667	--	45.56 (46.76)	0.634	--

Table 2-7: Cumulative GHG fluxes and percent differences for Winchester microplots for 2018 and 2019 field seasons. Control: No manure or biochar. MO: Manure-only. LVBC: Manure + low-volume biochar. HVBC: Manure + high-volume biochar in 2018, Manure-only in 2019.

Year and Micro-Plot	Micro-Plot Comparison	CO_2		N_2O	
		Cumulative Flux (kg C ha^{-1})	% diff.	Cumulative Flux (µg N m^{-2})	% diff.
2018					
Control	Control	2.54 $x10^2$	--	5.74 $x10^4$	--
	MO	4.57 $x10^2$	-57	2.65 $x10^5$	-129
	LVBC	5.05 $x10^2$	-66	1.03 $x10^5$	-57
	HVBC	4.63 $x10^2$	-58	6.49 $x10^4$	-12
MO	LVBC	5.05 $x10^2$	-10	1.03 $x10^5$	88
	HVBC	4.63 $x10^2$	-1	6.49 $x10^4$	121
LVBC	HVBC	4.63 $x10^2$	9	6.49 $x10^4$	45
2019					
Control	Control	1.42 $x10^2$	--	1.80 $x10^4$	--
	MO	4.57 $x10^2$	-105	1.16 $x10^5$	-146
	LVBC	3.30 $x10^2$	-79	5.13 $x10^4$	-96
	HVBC	2.73 $x10^2$	-63	5.22 $x10^4$	-98
MO	LVBC	3.30 $x10^2$	32	5.13 $x10^4$	77
	HVBC	2.73 $x10^2$	50	5.22 $x10^4$	76
LVBC	HVBC	2.73 $x10^2$	19	5.22 $x10^4$	-2

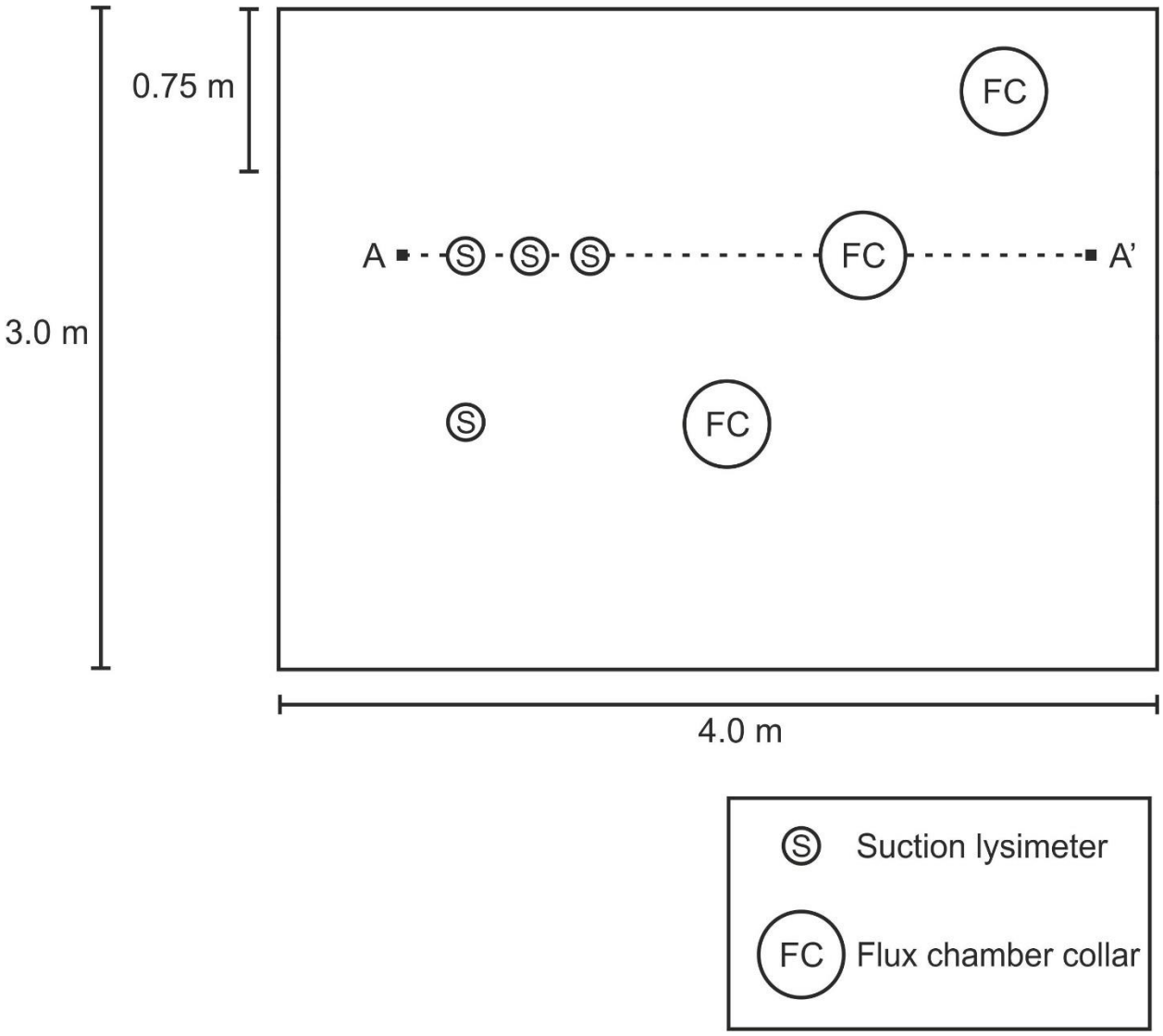

Figure 2-1: Microplot dimensions and equipment layout with cross section A-A' shown.

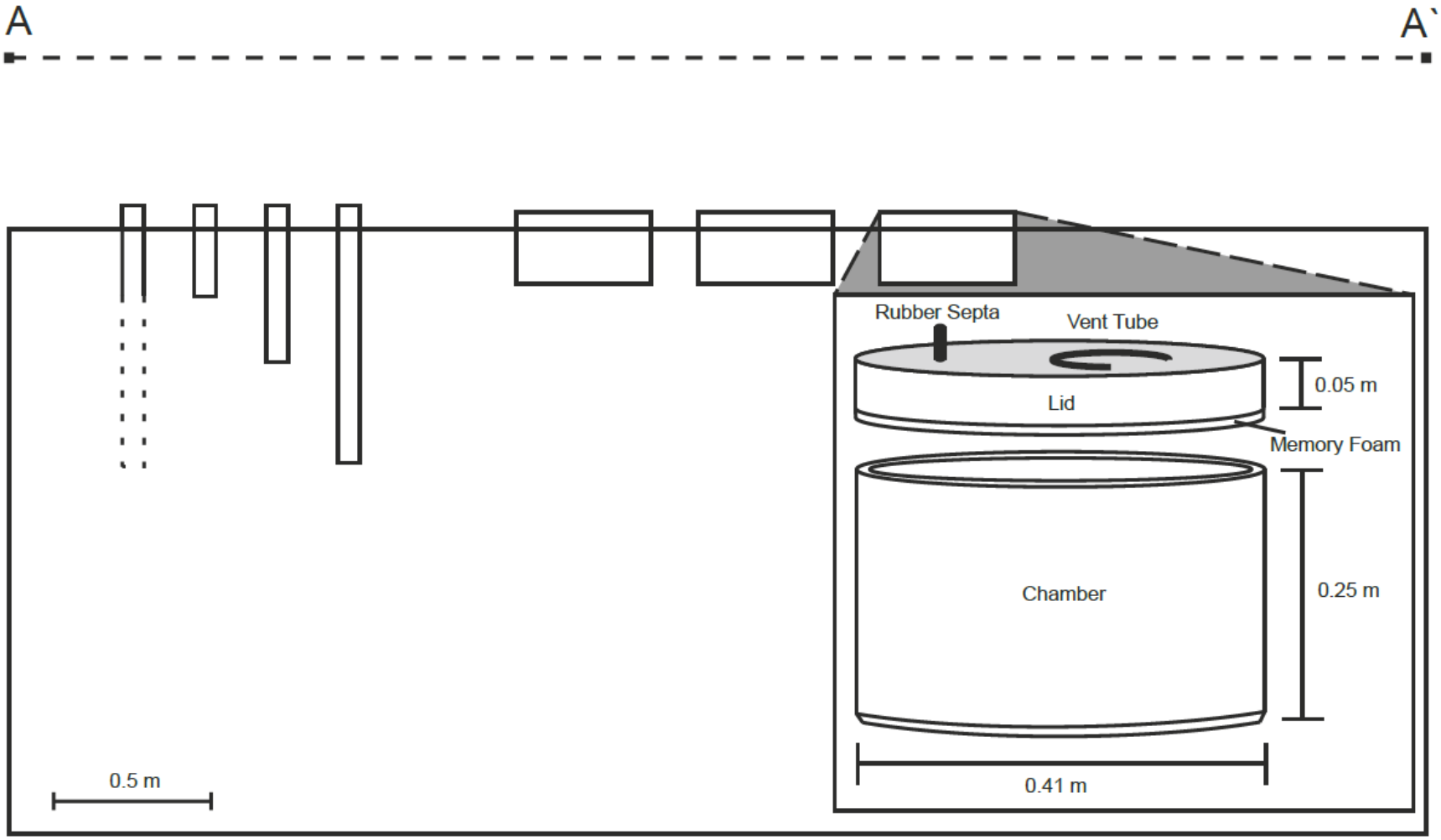

Figure 2-2: Cross section through A-A' (Figure 2-1) showing installation depths of suction lysimeters, and flux chambers. Inset image shows the design of the flux chambers.

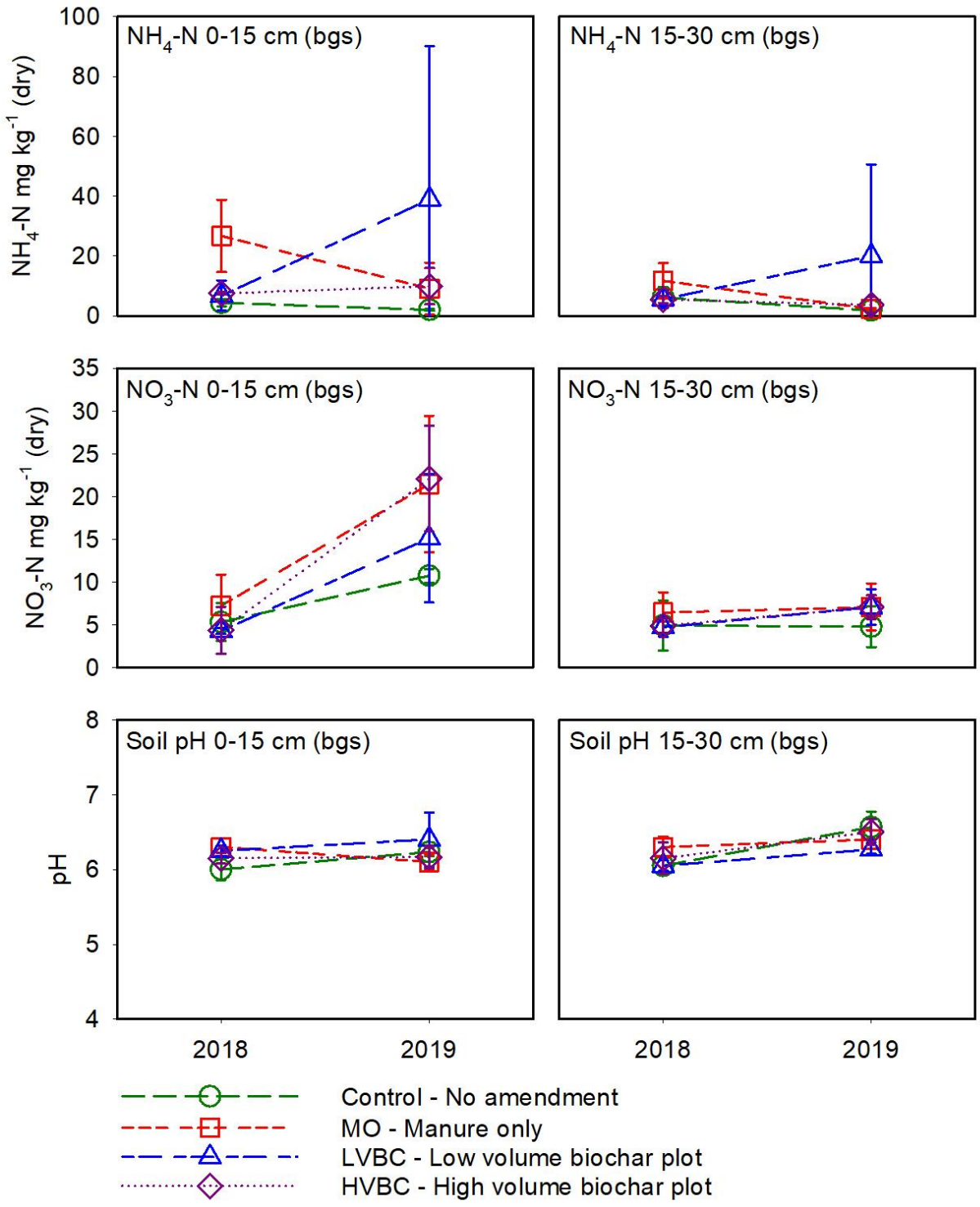

Figure 2-3: Mean post application soil NH_4-N, NO_3-N, and Soil pH data from the Winchester microplots.

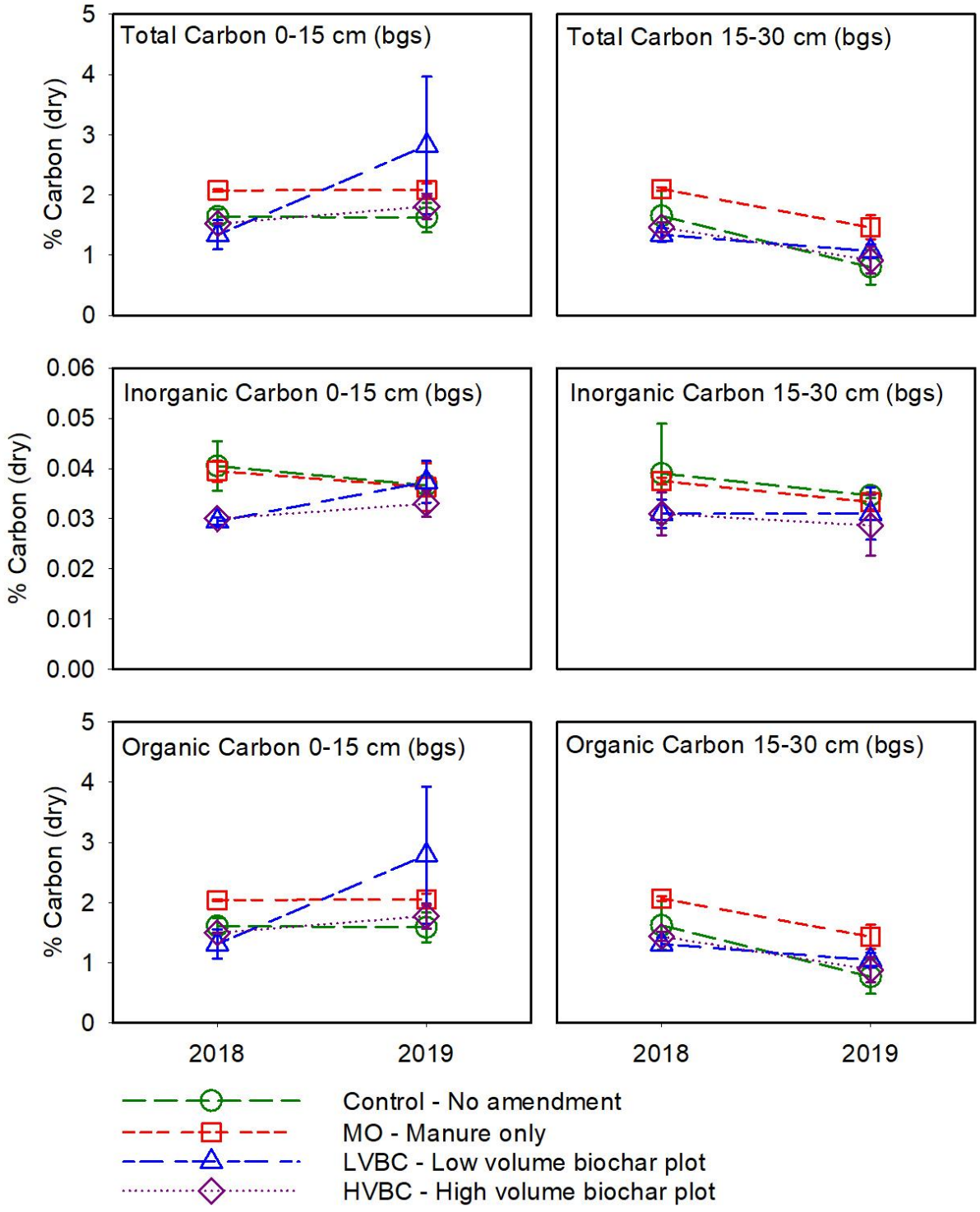

Figure 2-4: Mean post application soil TC, IC, and OC data from the Winchester microplots.

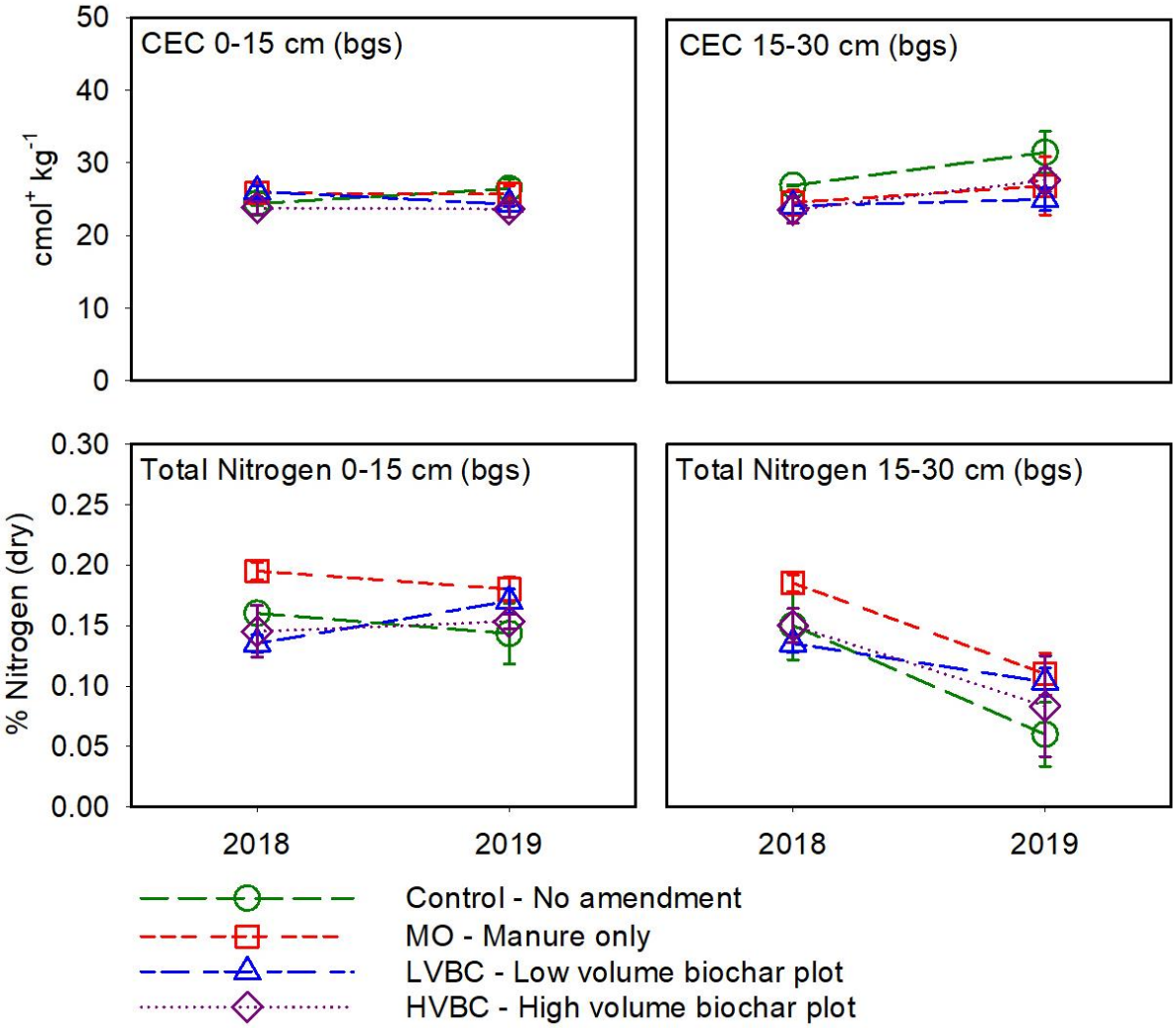

Figure 2-5: Mean post application soil CEC, and TN data from the Winchester microplots.

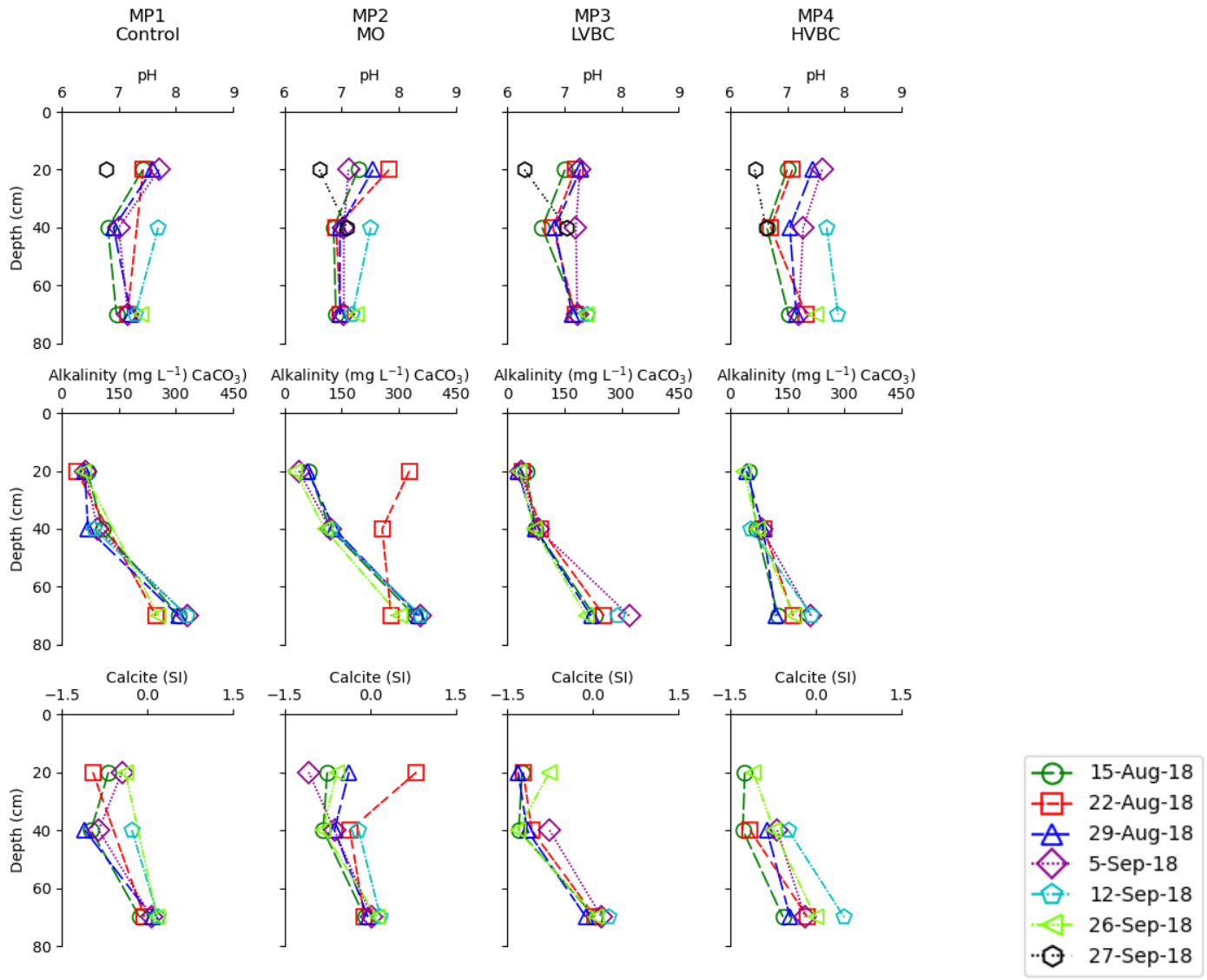

Figure 2-6: 2018 pore-water pH, alkalinity, and calcite SI data from the Winchester microplots.

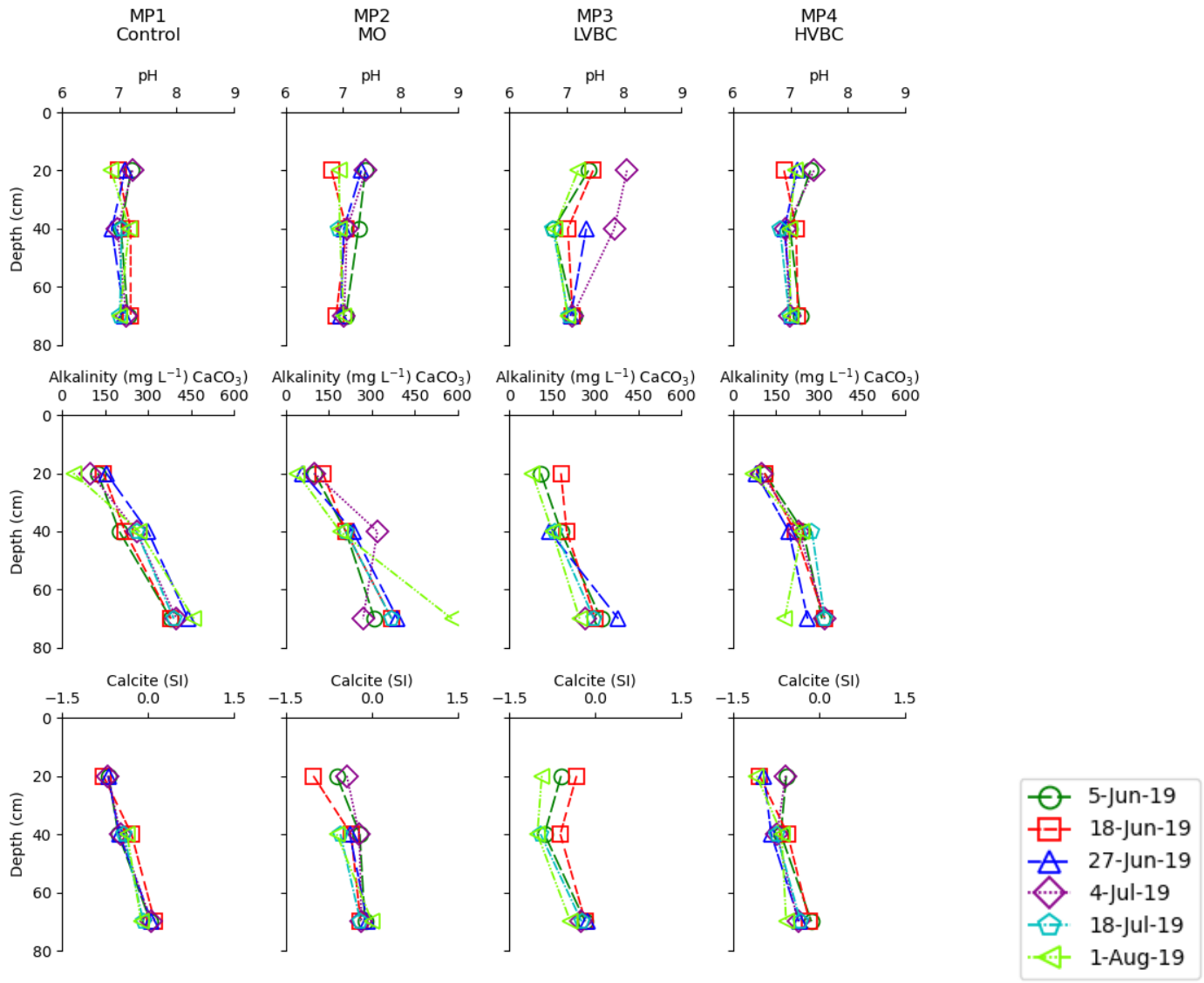

Figure 2-7: 2019 pore-water pH, alkalinity, and calcite SI data from the Winchester microplots.

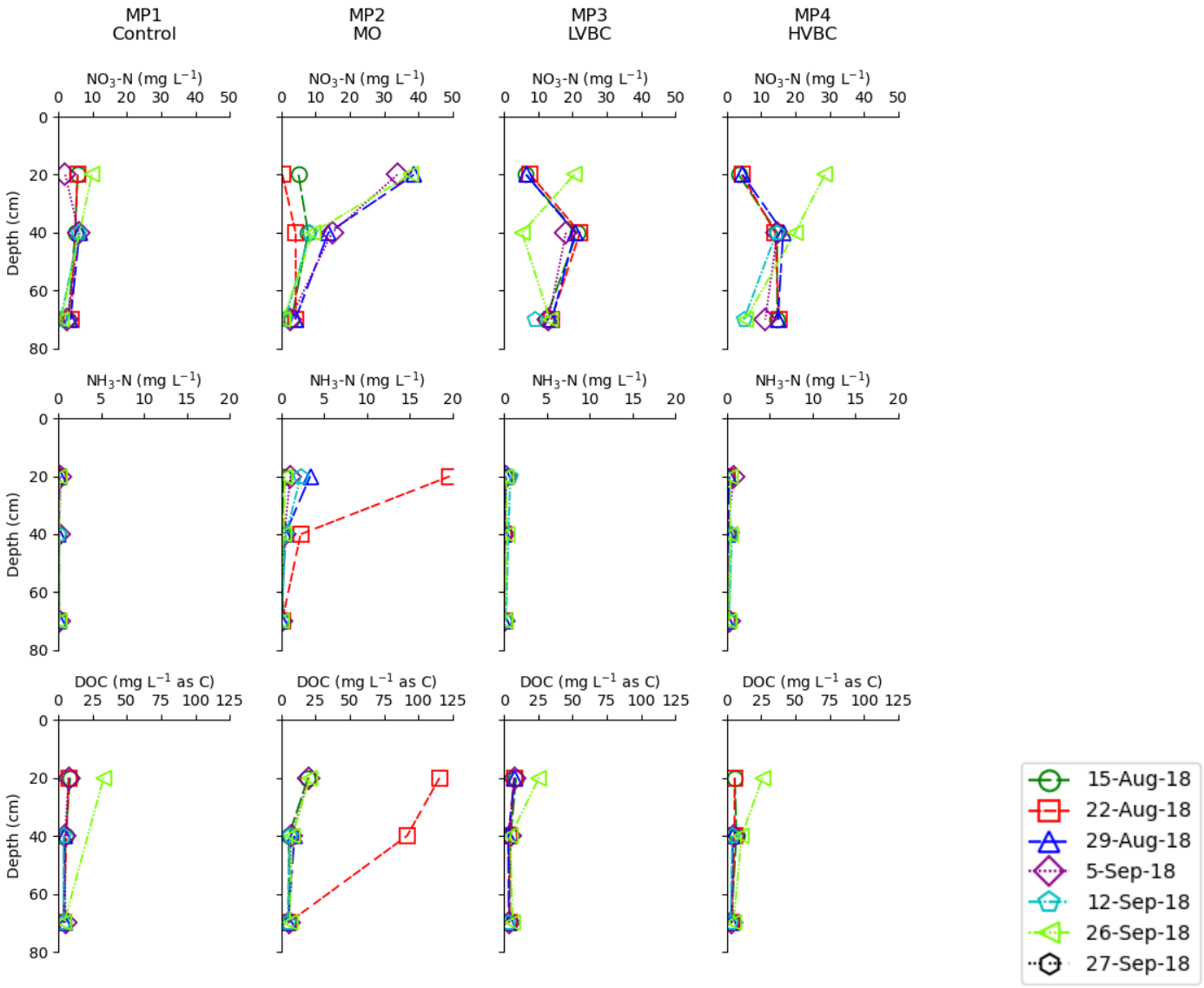

Figure 2-8: 2018 pore-water NO_3-N, NH_3-N, and DOC data from the Winchester microplots.

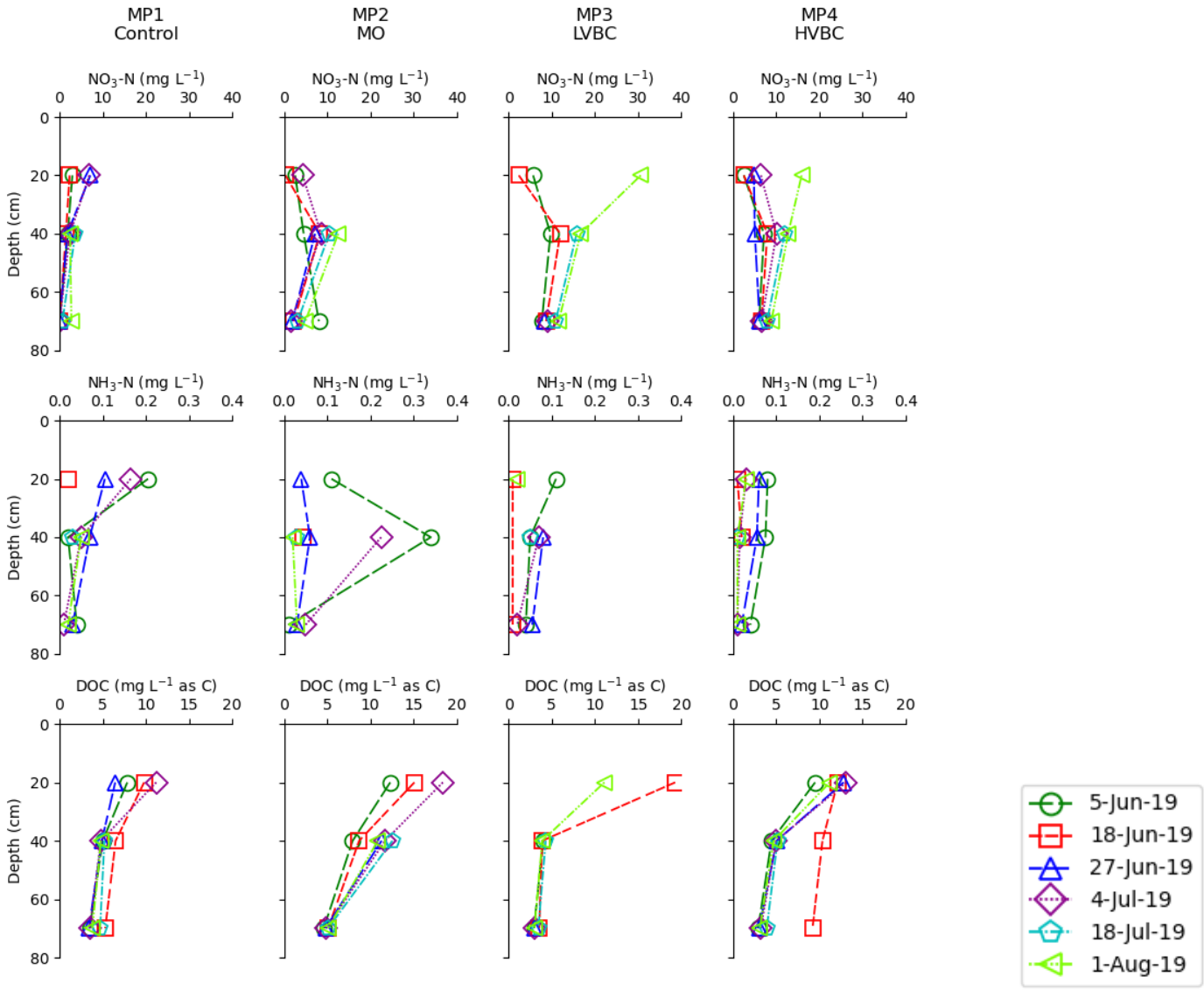

Figure 2-9: 2019 pore-water NO_3-N, NH_3-N, DOC data from the Winchester microplots.

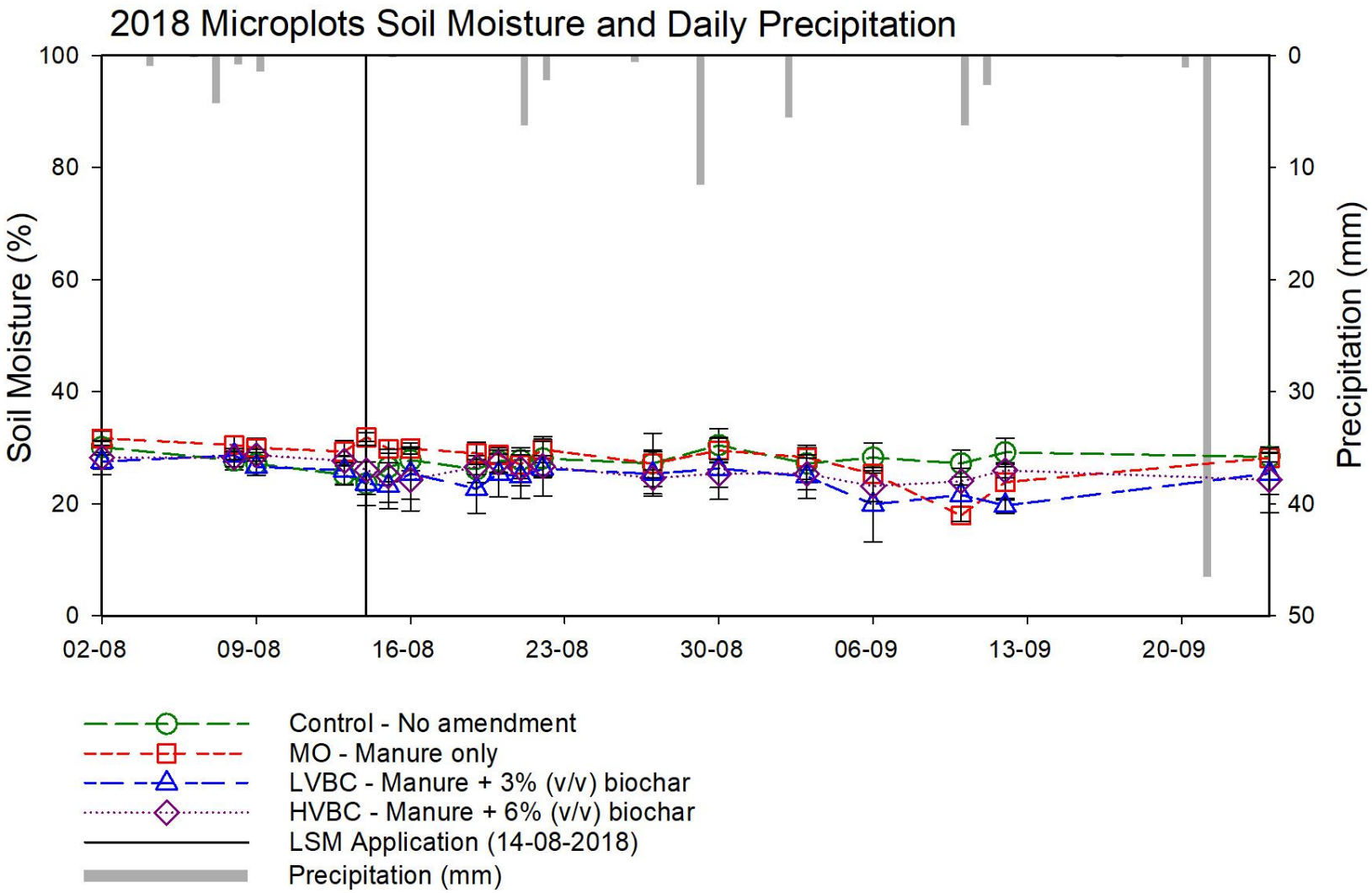

Figure 2-10: Mean daily soil moisture and daily precipitation from the Winchester microplots during 2018 sampling season. Dates are DD-MM.

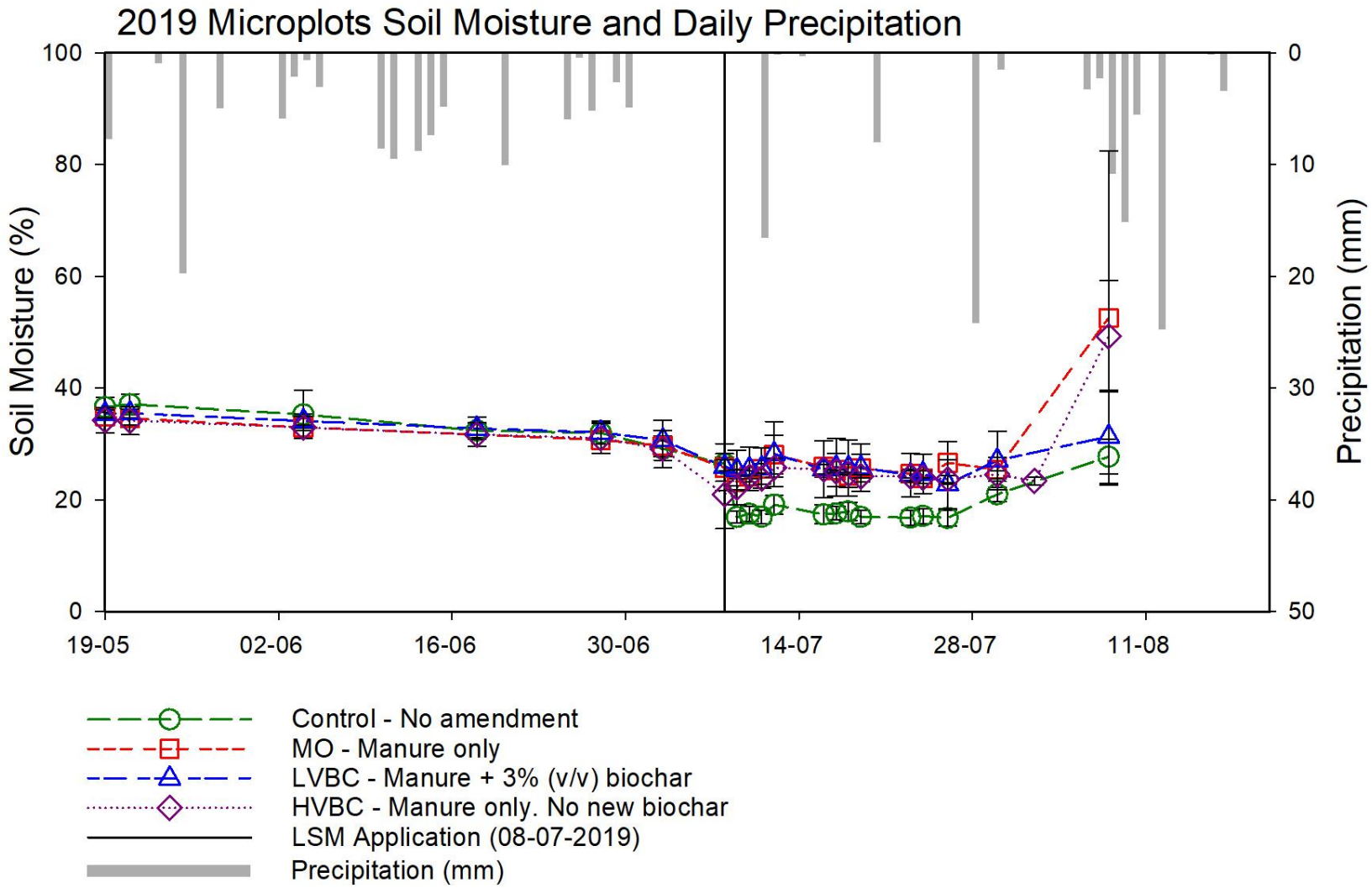

Figure 2-11: Mean daily soil moisture and daily precipitation from the Winchester microplots during 2019 sampling season. Dates are DD-MM.

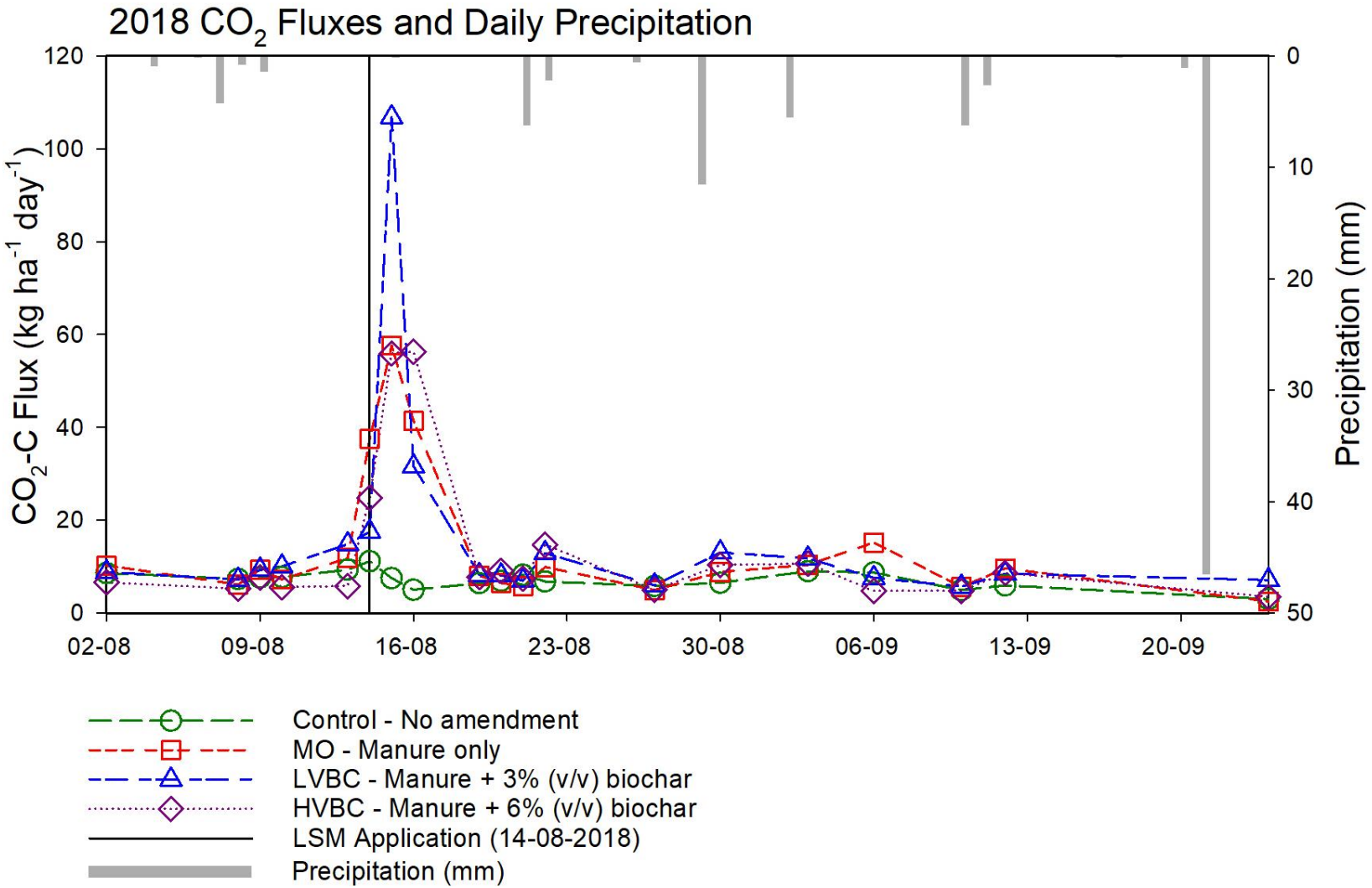

Figure 2-12: Mean daily CO_2 emissions (R^2 >= 0.8) and daily precipitation from the Winchester microplots during 2018 sampling season. Dates are DD-MM.

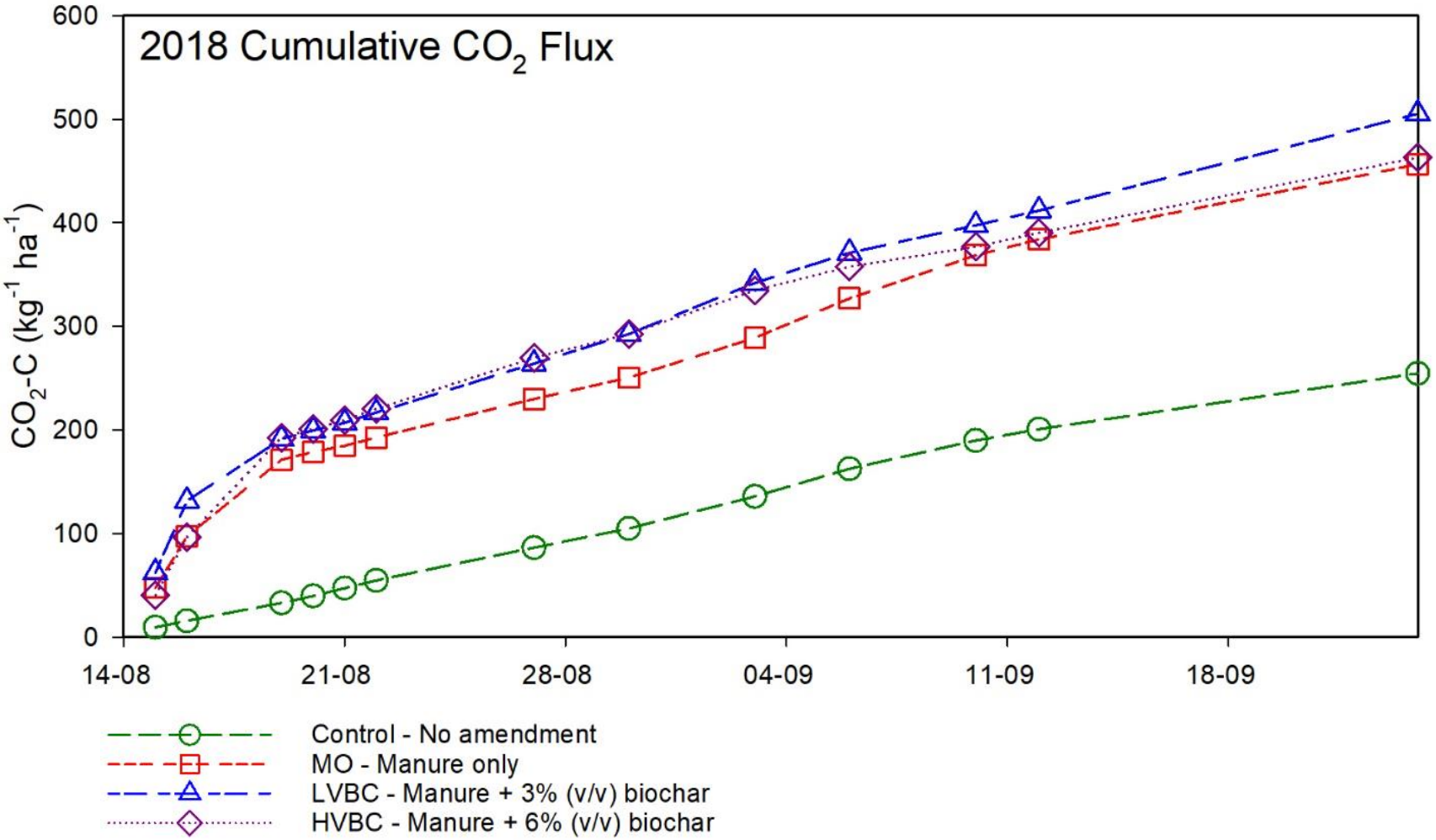

Figure 2-13: Cumulative CO_2 emissions from the Winchester microplots during 2018 sampling season. Dates are DD-MM.

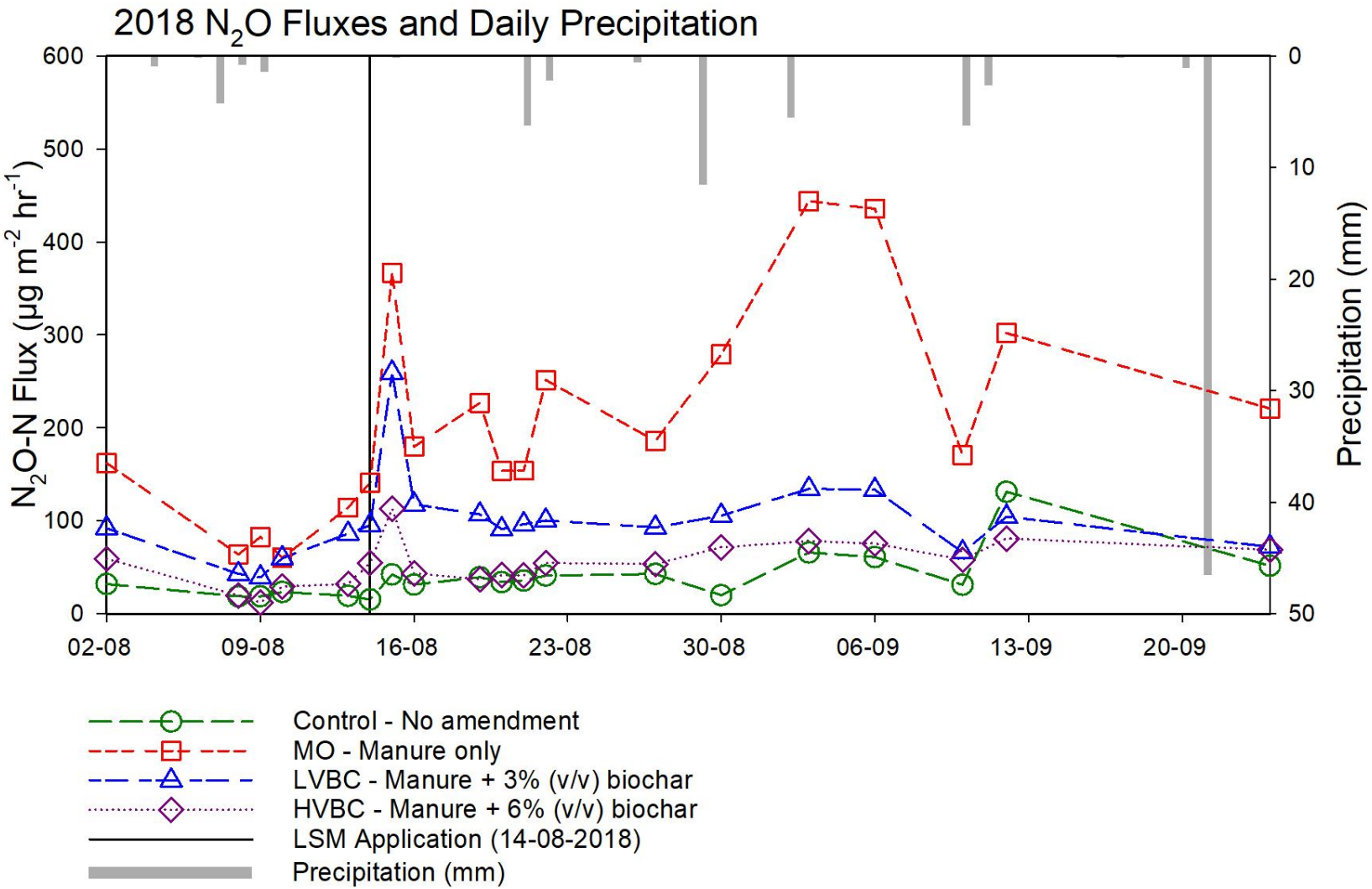

Figure 2-14: Mean daily N_2O emissions (R^2 >= 0.8) and daily precipitation from the Winchester microplots during 2018 sampling season. Dates are DD-MM.

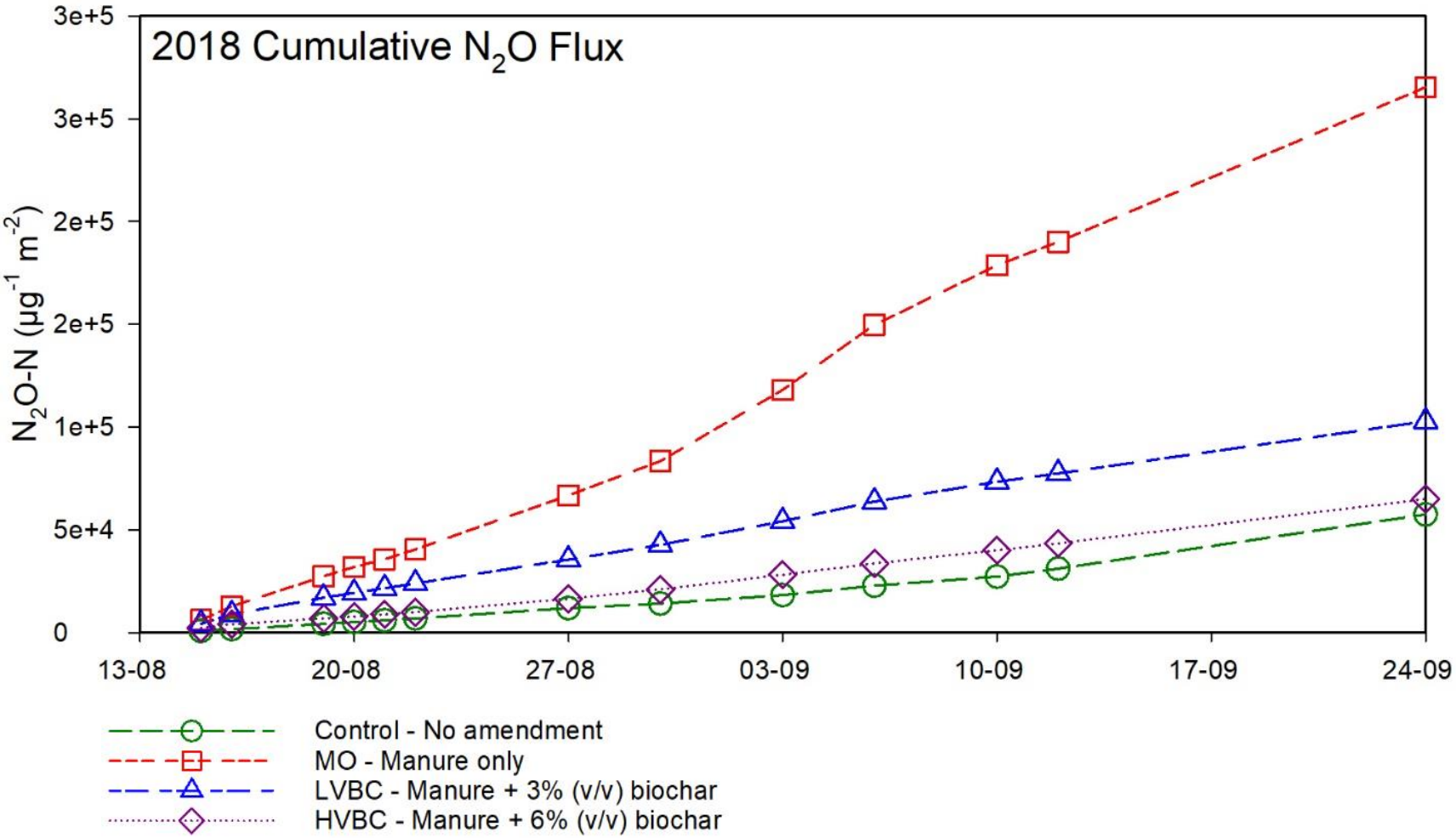

Figure 2-15: Cumulative N_2O emissions from the Winchester microplots during 2018 sampling season. Dates are DD-MM.

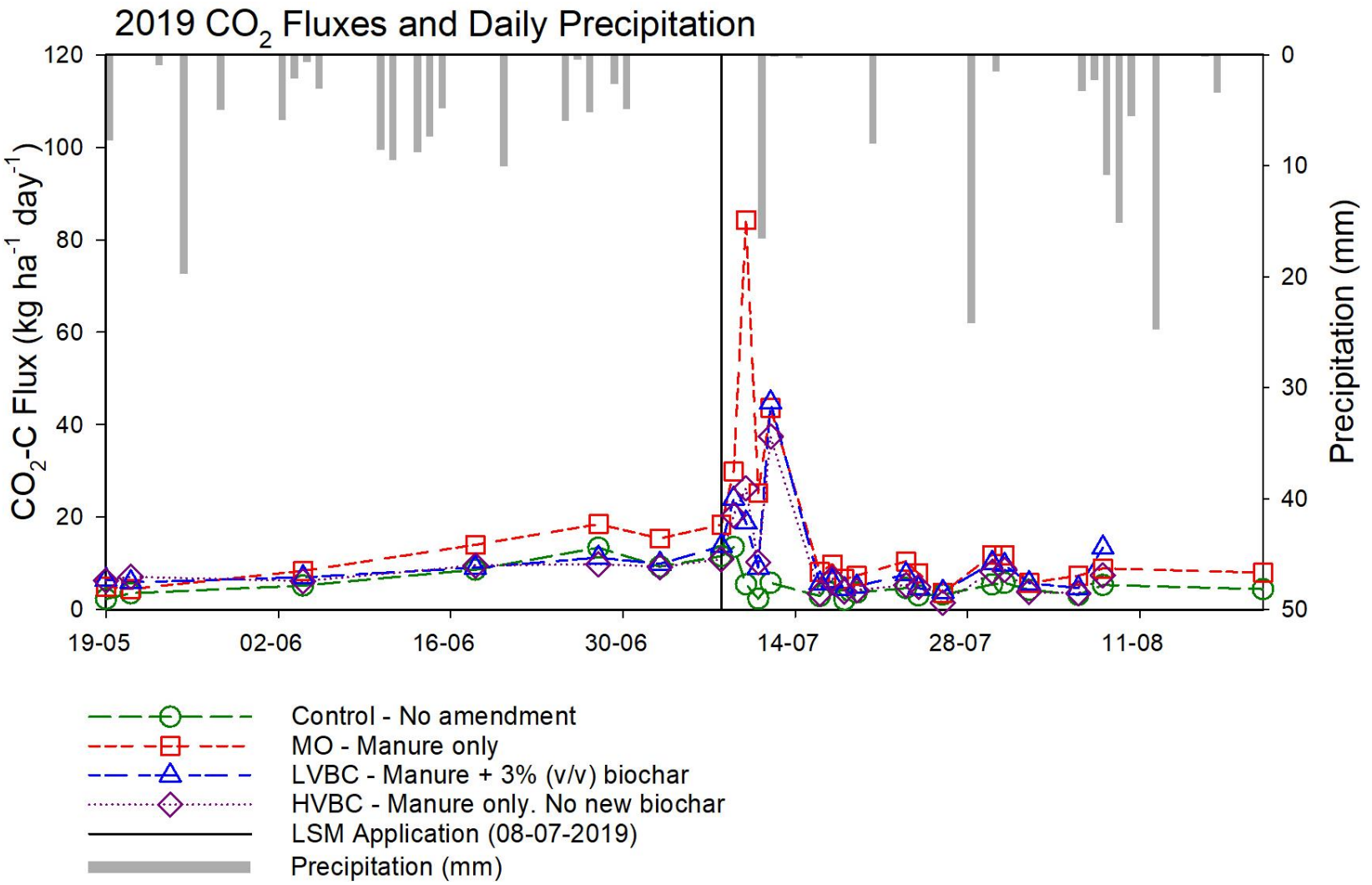

Figure 2-16: Mean daily CO_2 emissions (R^2 >= 0.8) and daily precipitation from the Winchester microplots during 2019 sampling season. Dates are DD-MM.

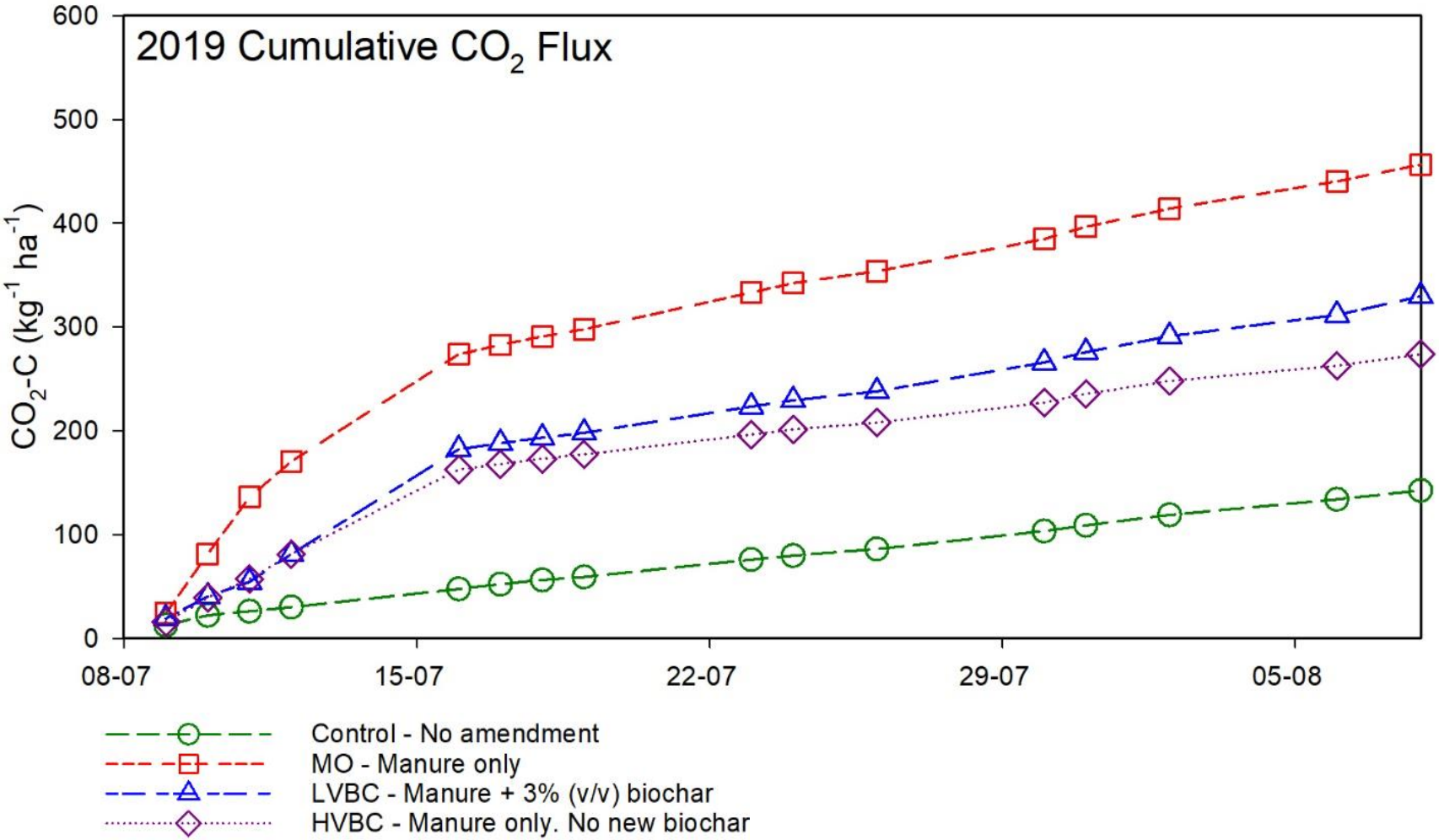

Figure 2-17: Cumulative CO_2 emissions from the Winchester microplots during 2019 sampling season. Dates are DD-MM.

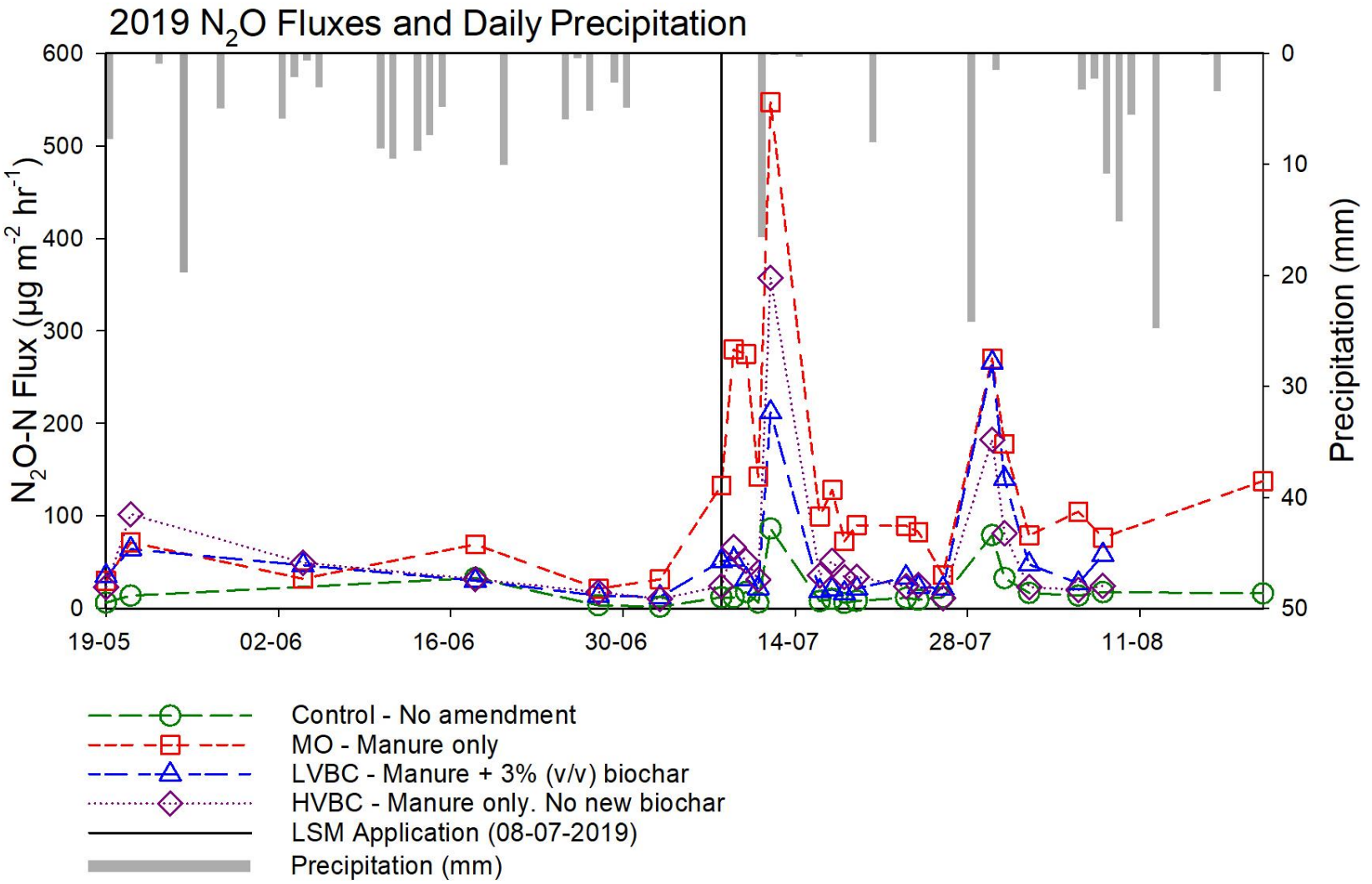

Figure 2-18: Mean daily N_2O emissions (R^2 >= 0.8) and daily precipitation from the Winchester microplots during 2019 sampling season. Dates are DD-MM.

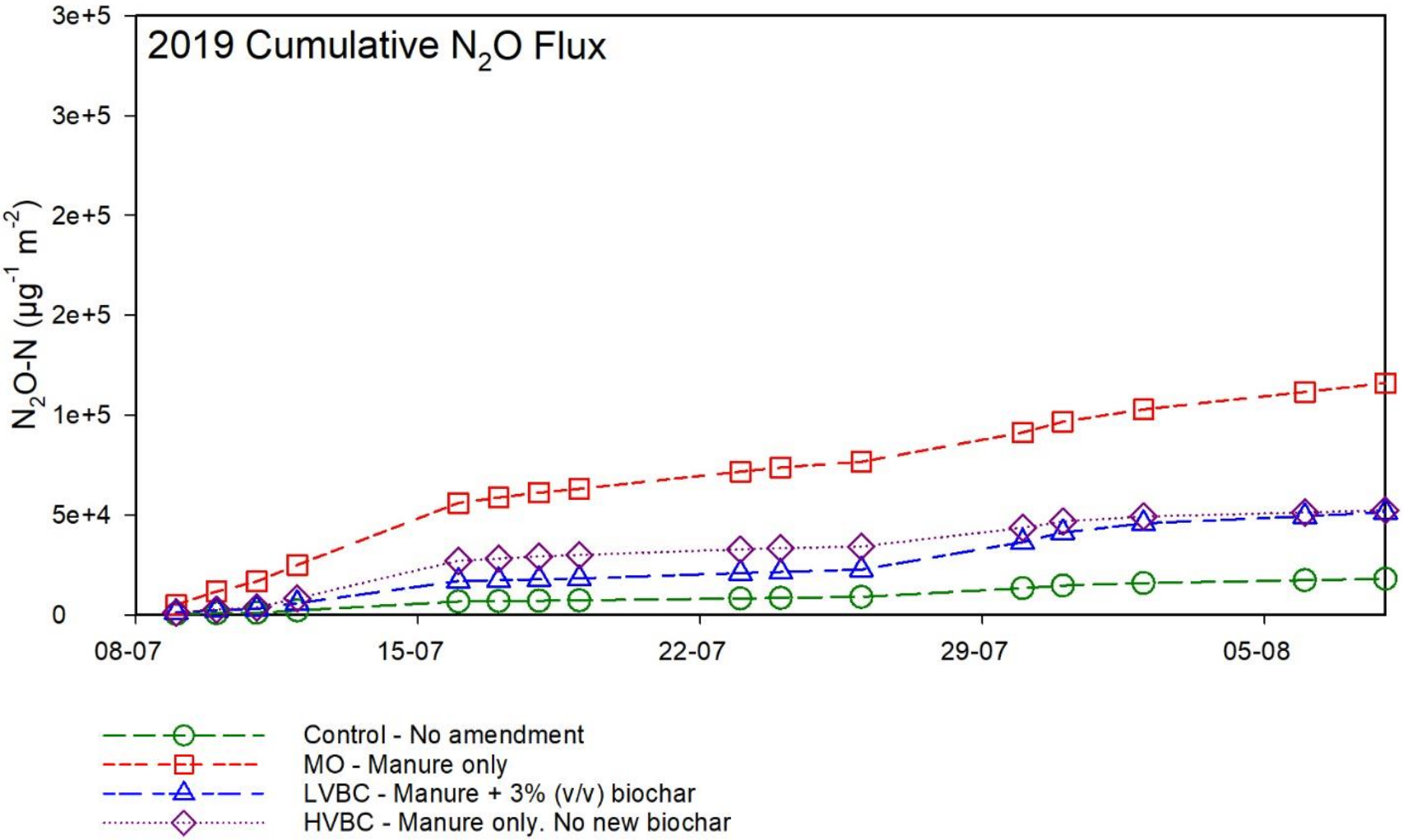

Figure 2-19: Cumulative N_2O emissions from the Winchester microplots during 2018 sampling season. Dates are DD-MM.

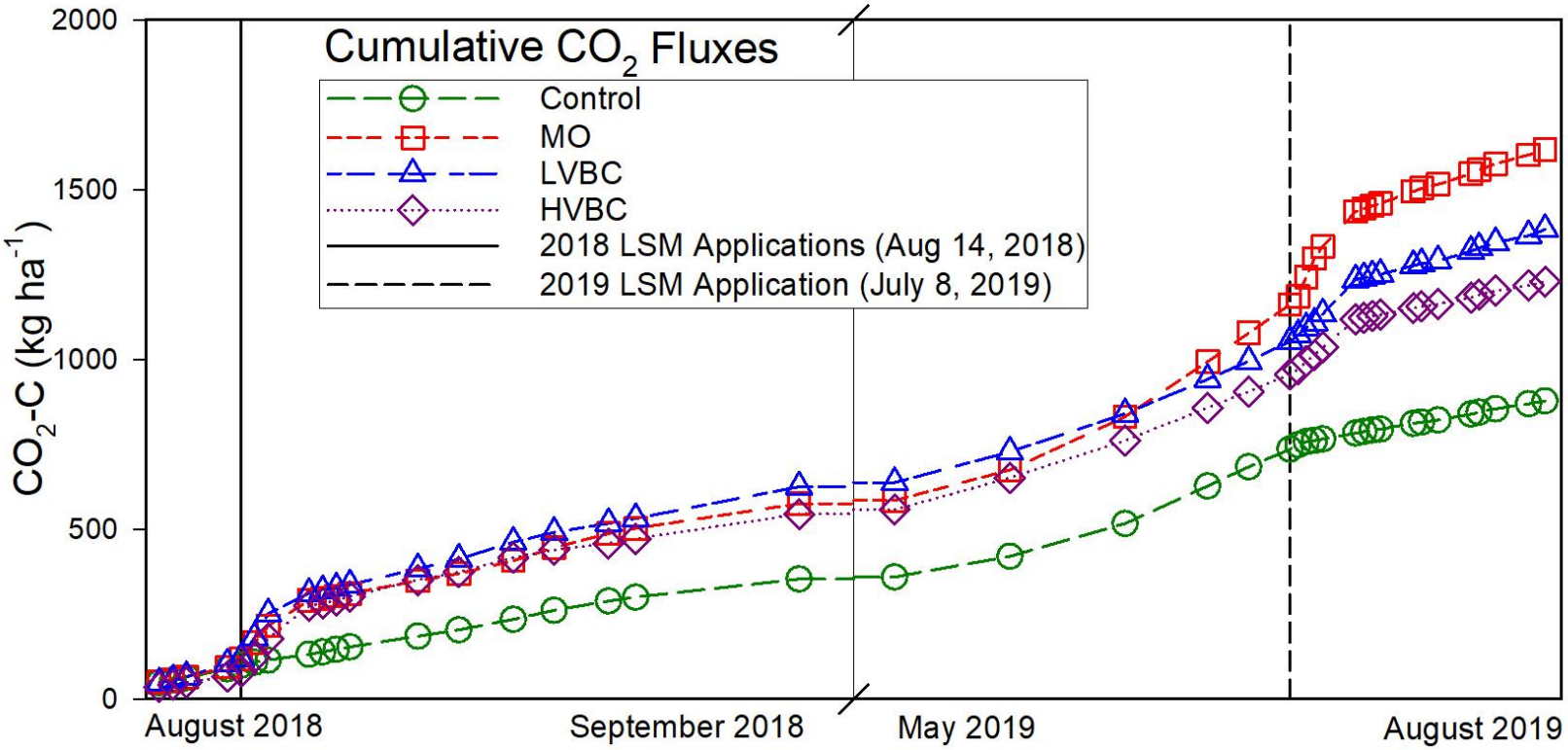

Figure 2-20: Cumulative CO_2 fluxes from the Winchester microplots during the 2018 - 2019 sampling seasons.

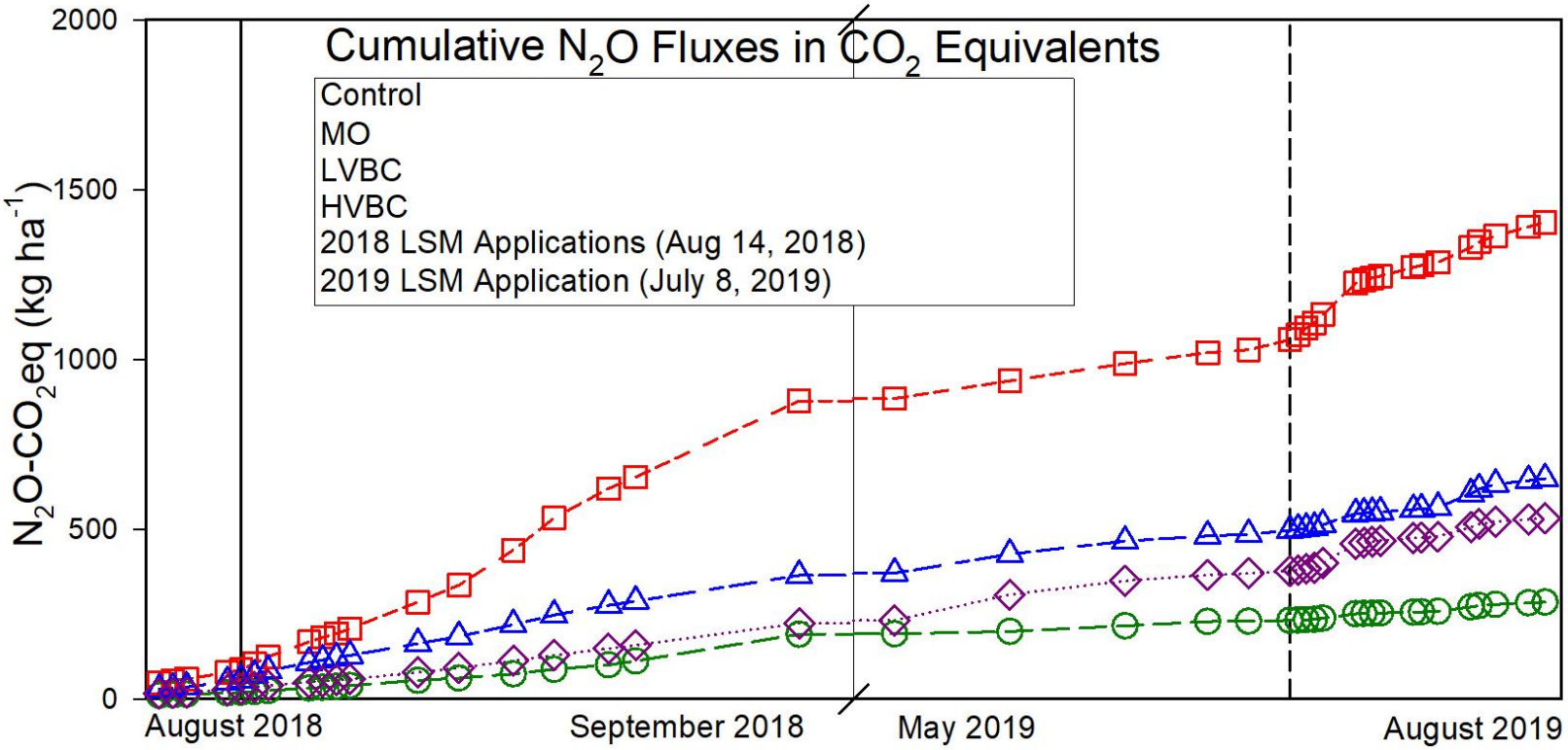

Figure 2-21: Cumulative N_2O fluxes expressed as CO_2 equivalents (conversion factor of 298 used) from the Winchester microplots during the 2018 - 2019 sampling seasons.

Chapter 3 - Design and Construction of Multi-component Bioreactors for the Treatment of Nutrients and PPCPs while Reducing N_2O Emissions

3.1 Introduction

Surface water contamination caused by agricultural practices is of growing concern for governments, community stakeholders, and environmental organizations (Addy et al., 2016; Howarth et al., 2002; Kremser & Schnug, 2002). The application of field amendments, such as synthetic fertilizers and animal- and human-waste derived fertilizers, contributes significant amounts of contaminants to surface water bodies through the leaching of these contaminants to groundwater, especially when plant demands are exceeded (Dinnes et al., 2002; Schipper et al., 2010). For example, the algal blooms in Lake Erie that occur during the summer months have been attributed to agricultural intensification in the watersheds which discharge into the lake. These blooms illustrate the deleterious impacts of nutrient loadings on aquatic ecosystems (Michalak et al., 2013; Stumpf et al., 2012). Excessive levels of the nutrient nitrate (NO_3-N) can also impact human and aquatic health and are related to hypertension, methaemoglobinaemia (in infants), and fish die offs (Ayres, 1997; Blowes et al., 1994; Galloway et al., 2003). In addition to the contribution of nutrients, human- and animal-derived waste has the potential to release pharmaceutical compounds and veterinary antibiotics that are present in the diets and vaccinations of the fertilizer/amendment sources (Boxall, 2012; B. O. Clarke & Smith, 2011). These contaminants can negatively impact soil fauna and downstream ecosystems and have been linked to elevated cancer risk, reproductive impairment, and antibiotic resistance (Ding & Peijnenburg, 2013; Fent et al., 2006; Sanchez et al., 2011; Walters et al., 2010; Witte, 1998).

Further exacerbating this contamination is the widespread use of tile-drainage in agricultural fields. This is especially common in Southern Ontario, Canada where approximately

45% of crop land has tile-drainage (Kokulan, 2019). It is used in regions where field access is limited in early and late seasons due to the high water content in the soil and provides a way for farmers to lower the water table in their fields (Christianson et al., 2012). In general, it involves the installation of perforated pipe, typically 1 m bgs, along the length of the field where it directs tile-effluent into adjacent drainage ditches. The rate at which tile-drainage removes water from agricultural fields far exceeds the speed of natural groundwater flow and has been found to increase the amount of nutrients and other pollutants which enter streams and rivers, and eventually larger water bodies (Christianson et al., 2012; Kellman, 2005). Thus, field wide application of fertilizers is often thought of as a non-point source of pollution, but tile-drainage collects the contaminated water and discharges it at narrow pipe ends. The point-source nature of the tile-drainage pollution allows for the potential use of smaller, more localized methods to treat large areas. This study will focus on the design and construction of novel multi-component bioreactors to be used to address the issues associated with agricultural field applications.

3.2 **Background**

3.2.1 Nitrate Contamination

When nutrients such as NO_3-N exist in excess of plant demands in agricultural settings, they can leach downwards to shallow groundwater and transported to surface waters; this latter process can be enhanced through the use of tile-drainage networks. The concentrated tile-discharge can have a wide range of impacts on water quality, aquatic ecosystems, and human health (Ayres, 1997; Billen et al., 2013; Diaz, 2001; Howarth, 2008), particularly because the pollutants can shortcut the naturally slower groundwater transport and accompanied transformation processes (Kellman, 2005). In tile-drained regions in North America, nutrient rich waters make up a sizable amount of the baseflow of rivers (Moorman et al., 2010); NO_3-N concentrations can exceed 15

mg L^{-1} during the year (Baker et al., 1975; Gast et al., 1978) and end-of pipe-solutions are necessary.

Nitrogen removal from contaminated waters is well studied; however, many promising technologies such as selective ion exchange, reverse osmosis, and nanotechnologies (e.g., nanotubes) have limited feasibility in agricultural settings due to the prohibitive costs and large scales of farm operations (Blowes et al., 1994; Schipper et al., 2010; Tyagi et al., 2018). These methods may also require post-treatment and specific disposal, can be sensitive to other contaminants, and may require significant upkeep to avoid system decline (Tyagi et al., 2018). Large scale and lower cost remediation methods such as constructed wetlands, pond systems, and land disposal have also been used in agricultural settings (Cameron & Schipper, 2010). These methods rely on anaerobic denitrification to facilitate the removal of NO_3-N from contaminated water. However, they require large amounts of land that otherwise could have been farmed, potentially limiting uptake by farmers.

Another technology that has been proposed for use in treating agricultural drainage is denitrifying bioreactors, or biofilters. Similar to the larger footprint methods, bioreactors utilize anaerobic denitrification to remove NO_3-N (e.g., Gibert et al., 2008; Greenan et al., 2006). They typically use a porous, organic carbon (OC) based fill material, making them more economical than other treatment methods. Further, bioreactors are installed at field edges where tile-drainage effluent exits to drainage streams, limiting the total footprint (Cameron & Schipper, 2010).

Past research examining the effectiveness of bioreactors has used a variety of reactive materials to facilitate denitrification. Removal rates range from 2–22 g N m^{-3} d^{-1} (Schipper et al., 2010) and can approach 100% with longer residence times (Woli et al., 2010). For example, Blowes et al. (1994) used a porous medium composed of sand and OC, including tree bark,

woodchips, and leaf compost, to treat agricultural runoff containing NO_3-N. Vogan (1993) used wood and wheat straw, Volokita et al. (1996) used cotton, and Greenan et al. (2006) used wood, cardboard, and corn husks. Although each of these materials offers certain advantages (e.g., maize cobs remove the greatest amount of NO_3-N; (Warneke et al., 2011a), woodchips are the most commonly used material due to widespread availability, low cost, and long-term stability (Bock et al., 2015). Further, woodchip denitrification systems are effective in removing NO_3-N from contaminated water for a decade or longer due to the anaerobic conditions within the bioreactors which slows woodchip degradation (Moorman et al., 2010; Robertson et al., 2000).

Denitrification involves the stepwise reduction of NO_3-N to molecular nitrogen gas (N_2) by facultative, anaerobic, heterotrophic microorganisms (Averill & Tiedje, 1982; Knowles, 1982; Rivett et al., 2008). In denitrifying bioreactors, a C source (e.g., woodchips) acts as the electron donor and NO_3-N is the preferred electron acceptor (Schipper et al., 2010). Equation 3.1 illustrates the anaerobic requirement in the general reaction for denitrification (Robertson et al., 2000).

$$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 5CO_2 + 3H_2O + 4OH^- \quad (3.1)$$

In this reaction, OC (denoted in the generic form: CH_2O), is the electron donor and N_2 is generated as a reaction by-product. Effective removal of NO_3-N from tile-water requires that denitrification proceeds rapidly which occurs after O_2 concentrations are sufficiently depleted by facultative microbes (Brock et al., 1984; Christianson et al., 2011b). This reaction requires that the bioreactor is fully saturated and has anoxic conditions, and the redox potential (Eh) favors NO_3-N reduction (Bock et al., 2015; Easton et al., 2015).

Oxygen concentrations and the availability of electron donors such as OC are the greatest limiting factors on the denitrification reaction (Rivett et al., 2008). However, temperature, pH,

and NO_3-N concentrations can also limit denitrification (Seitzinger et al., 2006; Warneke et al., 2011a). Under these conditions, when the denitrification reaction does not proceed to completion, a series of intermediate products can be generated instead, such as nitrite (NO_2^-), nitric oxide (NO), and nitrous oxide (N_2O) (Kampschreur et al., 2009).

Since the initial development of bioreactors, there have been concerns about the negative by-products or "pollution swapping" (Addy et al., 2016, p. 874) within a normally functioning bioreactor system (Healy et al., 2012; Moorman et al., 2010; Warneke et al., 2011b). Specifically, one issue with woodchip bioreactors is the generation of N_2O gas, which is an intermediary product of denitrification and a potent greenhouse gas (GHG). In several studies, less than 1% of the total NO_3-N removed from the treated water was accounted for by N_2O emissions (David et al., 2016; Elgood et al., 2010). However, (Warneke et al., 2011a) found this product of NO_3-N removal to be up to 4.3%, and Feyereisen et al. (2016) found N_2O production rates as high as 7.5% at low temperatures.

The current study introduces biochar into a conventional woodchip bioreactor to mitigate N_2O emissions and promote complete denitrification. Biochar is the carbonaceous by-product of pyrolysis, where some feedstock of organic material undergoes thermal decomposition in a low O_2 environment (Lehmann & Joseph, 2009). Studies have demonstrated that biochar as a soil and field amendment can lower the mobility of nutrients such and NO_3-N in soils (Bock et al., 2015; Clough & Condron, 2010) and can lower N_2O emissions (Chapter 2; Agegnehu et al., 2015; Bamminger et al., 2014; Cayuela et al., 2014; X. Liu et al., 2012; Rondon et al., 2005; Van Zwieten et al., 2013). Biochar is proposed to impact denitrification in soils by increasing cation exchange capacity, soil aeration, soil C and impacting microbial communities (Cayuela et al., 2014). Based on these findings in soil, biochar has been added to denitrifying bioreactors (Bock

et al., 2015; Christianson et al., 2011b; Easton et al., 2015). It has been proposed that these biochar additions could increase aerobic respiration, thereby reducing the O_2 concentrations while simultaneously providing an accessible C source to denitrifying microorganisms (Christianson et al., 2011b; Schipper et al., 2010). However, results have been mixed. In laboratory studies, Bock et al. (2015) and Easton et al. (2015) found biochar additions resulted in reduced N_2O emissions from woodchip bioreactors. Christianson et al. (2011b) found no effect and Bock et al. (2018) found that biochar additions increased N_2O emissions. Given these disparate findings, it is important to further examine the addition of biochar to denitrifying bioreactors, particularly in field scale experiments.

3.2.2 Pharmaceutical Compounds

The release of contaminants, such as pharmaceutical and veterinary-antibiotic compounds, into agricultural tile-drainage is a recurring issue around the world given the widespread use of human- and animal-derived waste products in the form of fertilizer amendments (Burkhardt et al., 2005; R. M. Clarke & Cummins, 2015; Du & Liu, 2012; Kay et al., 2005; Kim et al., 2005; Lapen et al., 2008a). These widely varying contaminants, referred to as pharmaceutical and personal care products (PPCPs), are considered any chemical substance which is used by or administered to humans or agricultural livestock with the purpose of enhancing health and growth, or for cosmetic and fragrance purposes (R. M. Clarke & Cummins, 2015; Yang et al., 2011).

Pharmaceutical and personal care products are regularly overused in both human populations and agricultural practice (Du & Liu, 2012; Martin et al., 2015). Consequently, these compounds are not fully absorbed, which leads to the excretion of between 30-90% of the unaltered compounds along with their metabolites (Halling-Sorensen et al., 1998; Heberer, 2002;

Phillips et al., 2004; Winckler & Grafe, 2001). These compounds then persist in the sewage sludge (biosolids) and animal-manure that is produced (Boxall, 2012; B. O. Clarke & Smith, 2011) and can be released to the environment when amendments are applied to agricultural soils where they can have unintended impacts on other organisms which naturally occur in the amended soils and downstream aquatic ecosystems (Fent et al., 2006; Khachatourians, 1998; Walters et al., 2010). Further, even with the typically low concentrations of these PPCPs in agricultural drainage, when present in larger watersheds these compounds can have negative impacts on human health such as elevated cancer risk, reproductive impairment, and antibiotic resistance (S. R. Smith, 2009; Walters et al., 2010; Witte, 1998). Pharmaceutical and personal care products have been traced from applications on agricultural soils to surface waters (R. M. Clarke & Cummins, 2015; Kinney et al., 2012), and tile-drainage can expedite this travel (Lapen et al., 2008b).

The practice of applying biosolids on agricultural fields is common around the world because it can provide essential nutrients and organic matter to soils at low cost (B. O. Clarke & Smith, 2011; Edwards et al., 2009), while simultaneously presenting an opportunity to recycle this difficult to dispose of material (CEC, 1986; European Commission, 2020; Wu et al., 2012). For these reasons, the removal of PPCPs from agricultural drainage is of increasing concern.

Given the widespread use of tile-drainage systems, the contaminants within field amendments that are not taken up by plants or degraded in soil can discharge rapidly to nearby surface waters via unblocked tiles (Edwards et al., 2009; Lapen et al., 2008b; Qin et al., 2015). Controlled drainage is increasingly used to slow this process, by employing stop log gates to restrict the discharge of tile-effluent until a desired threshold is met (Gilliam et al., 1979). This method can reduce the net export of nutrients to surface waters (Drury et al., 1996; Wesström &

Messing, 2007). However, the effectiveness of this method has not been widely explored as it relates to PPCPs.

Typically, removing PPCPs from water requires treatment processes such as reverse osmosis, nanofiltration, advanced oxidation, and microbial treatment (Ahmed et al., 2017; Bo et al., 2015). However, in field scale agricultural practices these methods are limited by prohibitive costs and slow treatment (Grassi et al., 2013). Recently, the use of zero valent iron (ZVI) (Fe^0), biochar, and water treatment plant residuals (WTR) in passive systems has been identified as an effective alternative for the removal of pharmaceutical and emerging contaminants in laboratory (König et al., 2016; Y. Liu et al., 2014, 2019), and field scale studies (Gottschall et al., 2016). The strongly reducing nature of ZVI and some of the corrosion products like green rust makes this material effective for treating a variety of organic compounds (Devlin et al., 1998; Elsner et al., 2004). Similarly, biochar can also be effective in removing a variety of pharmaceutical compounds due to the high C content, porosity, and sorption potential for nonpolar organic compounds (Jung et al., 2015; Scherer et al., 2000; Williams et al., 2015). The high aluminum content of WTR and other industrial waste products can effectively treat pharmaceuticals through aluminum oxide adsorption (Hussain, 2013). These compounds have potential for an alternative treatment of PPCPs, especially due to the relatively low cost and ease of procurement. Further, Y. Liu et al. (2019) recently showed that the combination of ZVI and biochar is more effective than either ZVI or biochar alone in the treatment of pharmaceutical compounds.

3.2.3 Purpose of Study

The current study focuses on the development of new technologies aimed at addressing the water quality issues caused by agricultural practices on tile-drain waters. This study proposes supplementing woodchip bioreactors with ZVI, biochar, and WTR to treat tile-drainage effluent

for nutrients and PPCPs while also mitigating emissions of N_2O common in woodchip bioreactors. The design and construction are described to inform future research that tests the effectiveness which may inform the development of best management practices for farmers.

3.3 **Design and Construction**

3.3.1 Bioreactor design

The bioreactors in this study were installed in Fall 2018 using the existing controlled tile-drain infrastructure at the Winchester field site described in Gottschall et al. (2016) and were designed to treat 20% of the peak flow rate of 2 L s^{-1}. The modified design installed for this study incorporated a baffle-system that was included to limit preferential flow pathways through the bioreactor, which can result in decreased residence time and water contact with the reactive material. Additionally, the inflow and outflow depths from the bioreactor were raised to form a "bathtub" effect that maintained saturation of the reactive materials during low flow. Denitrifying bioreactors rely on biological processes which require anoxic, saturated conditions, long residence times, and contact with organic material to remove NO_3-N. Therefore, increasing residence time, contact, and maintaining saturation may increase the removal rate (Christianson et al., 2011a; Van Driel et al., 2006).

The bioreactors measure 2.44 x 1.22 x 1.52 m, with a total internal volume of 4.52 m^3 (*see* Figure 3-1a). The hydraulic gradient along the length of the bioreactor is set using stop log gates in the "before bioreactor" control structure (BBR) and the "after bioreactor" control structure (ABR), which allows for simple adjustments to the flow rate to find the "optimum range" (p. 2741) for contaminant removal (Christianson et al., 2011a). The bypass system will divert excess flow around the bioreactor, directly to the outflow side (*see* Figure 3-1b) to maintain a minimum residence time during peak flow events. Maintaining saturation of the

reactive material during low- and no-flow times is necessary to keep atmospheric O_2 from entering the bioreactor where it reduces removal efficiency (Robertson et al., 2000). A saturated state was achieved by installing the inflow and outflow pipes above the base of the bioreactor, forming a bathtub-like system. Further measures to exclude atmospheric O_2 included the installation of U-shaped water traps at the inflow and outflow of each bioreactor and covering the reactive materials with a pure woodchip layer to allow for tension saturation above the set water table.

Three baffles were installed forming four "stages" along the length of the bioreactor. Baffle #1 is a hanging baffle which forces flow under a 0.1 m high gap and separates stage 1A and 1B. Baffle #2 is 0.5 m high and extends from the base of the bioreactor forcing water over top of it from stage 1B to 2A. Baffle #3 is a hanging baffle with the same specification as baffle #1 and separates stages 2A and 2B. Baffles #1 and #3 were installed with an angular limestone gravel (2 cm) cage beneath each to separate the reactive materials, as well as to discourage the development of preferential flow paths between each stage. Each stage within the bioreactor has the same dimensions, measuring 0.61 x 1.22 x 1.52 m and 1.13 m^3 in volume.

Within the bioreactor four multilevel piezometers, two water level piezometers, one multiprobe, and one suction lysimeter were installed (*see* Figure 3-1a). The multilevel piezometers were installed in each stage and were constructed using 1-inch PVC pipe, screened at the base using 90 µm Nitex screen material with an additional five mini-piezometer sampling points, each 15-20 cm apart starting at the base (*see* Figure 3-2). The mini-piezometers were constructed using 1/4-inch (inner diameter) high density polyethylene tubing and 90 µm Nitex screen material. The water level piezometers were installed in stages 1A and 2B and were constructed using 1-inch PVC pipe which was screened at the base with 90 µm Nitex screen

material (*see* Figure 3-2). The Decagon devices INC. 5TE ECH2O probe was installed between stage 1B and 2A. It measures volumetric water content, temperature, and electrical conductivity. One porous ceramic suction lysimeter (Soilmoisture Equipment Corp., Goleta, California, USA), was installed in stage 2B. In addition to these sampling points within the bioreactors, both the BBR and ABR control structures can be manually or automatically sampled using Teledyne ISCO auto samplers.

3.3.2 Materials

The study design consists of three treatment bioreactors as well as an additional replicate of each (*see* Table 3-1). Within the treatments the reactive material mixtures vary in each stage of the bioreactor, with each containing some combination of woodchips, ZVI, biochar, WTR, and gravel aggregate.

The biochar used in the bioreactors was sourced from Biochar Now LLC., Loveland, CO, USA. It is produced by the slow pyrolysis of shredded woody materials in portable kilns which meet EPA standards for clean air. These bioreactor systems use biochar chips ranging in size from 3 to 25 mm. Biochar Now LLC. reports a surface area of 400 $m^2\ g^{-1}$ and a water holding capacity of 5.6 g water g^{-1} biochar. The ZVI used in this study was obtained from Connelly-GPM INC., Chicago, IL, USA. The granular iron size ranges from 0.15 to 2.36 mm with a reported average density of 2.4×10^3 kg m^{-3}. Water treatment plant residual was sourced from the R. C. Harris Water Treatment Plant in Toronto, ON, CAN. Past research using this material reported an aluminum content of 146000 μg g^{-1} (Gottschall et al., 2016). The woodchips used in the bioreactors was obtained from a local source and composed of primarily hardwood material ranging in size from <1 cm to 5 cm. To increase hydraulic conductivity and promote distributed flow throughout the bioreactor stages, clean gravel was mixed with the reactive materials. The

gravel was sourced from a quarry near the study site and is made up of small (1 cm) angular gravel limestone aggregate. During installation, a subset of each material and mixture was collected and stored for future analysis.

3.3.3 Construction

The bioreactors were constructed between August and November 2018. Prior to installation, the multilevel piezometers and water level piezometers were constructed at the University of Waterloo. The reactive materials were mixed on site using a skid-steer loader and excavator in a large roll-off bin. Materials were measured by volume in the specified proportions. The bioreactor frames were built with the specified dimensions on site prior to installation using untreated SPF lumber. They were lined with a rugged plastic tarp/sheeting that formed the bathtub to hold the reactive materials.

An excavator was used to dig each bioreactor pit to the specified depth, which placed the top of the bioreactor frame level with the ground surface. The frames were placed in each pit and adjustments were made to ensure they were level prior to connecting the plumbing from the BBR and ABR control structures. A U-shaped trap was created with non-perforated pipe on the inflow and outflow sides of the bioreactor. The plumbing was then inserted through the lining material at the specified depths and was sealed to the tarp material using a thick roofer's tar tape. Inside the bioreactors the non-perforated pipe was connected to a T-shaped section of perforated pipe, which distributed the in-flow and collected the out-flow tile-water across the width of the bioreactor. The aim of these T-distributors was to discourage the development of preferential flow paths. These distributors were secured at the specified depths using steel strapping to minimize movement during material compression.

The sampling instruments were placed in the specified locations during filling and were held in place as the reactive material mixtures were loaded with a grain conveyor auger. The bioreactor stages were filled in sequential order from BBR to ABR while the areas surrounding the bioreactor were simultaneously backfilled with soil. Following the addition of the pure woodchip layer above each of the other stages, a geotextile fabric (Marfil 30) was place on top to prevent soil and roots from entering the system. This fabric was covered by a layer of plastic sheeting before topsoil was added to level the bioreactor with the surrounding ground surface. After the bioreactors were installed, the control structures were adjusted such that a hydraulic gradient of 20 cm along the length of it was established.

3.3.4 Future work

An uncharacteristically dry summer in the Winchester region resulted in minimal flow throughout summer, 2019. Early spring flow occurred prior to the application of the field amendment and there was no flow again until late autumn, 2019. Due to the bathtub design of the system, saturation was maintained during this time (confirmed by water level measurements in piezometers). Future research examining the effectiveness of these systems should focus on monitoring N and PPCP removal rates, as well as dissolved N_2O concentrations in effluent waters.

Table 3-1: Bioreactor treatments

	Treatment 1 (Bioreactor 1 & 4)	**Treatment 2 (Bioreactor 2 & 5)**	**Treatment 3 (Bioreactor 3 & 6)**
Stage 1A	90% WC + 10% WTR (by vol.)	90% WC + 10% WTR (by vol.)	100% WC (by vol.)
Stage 1B	90% WC + 10% WTR (by vol.)	90% WC + 10% WTR (by vol.)	100% WC (by vol.)
Stage 2A	90% WC + 10% WTR (by vol.)	20% BC + 40% ZVI + 40% Gravel (by vol.)	20% BC + 40% ZVI + 40% Gravel (by vol.)
Stage 2B	90% WC + 10% WTR (by vol.)	60% BC + 40% Gravel (by vol.)	60% BC + 40% Gravel (by vol.)

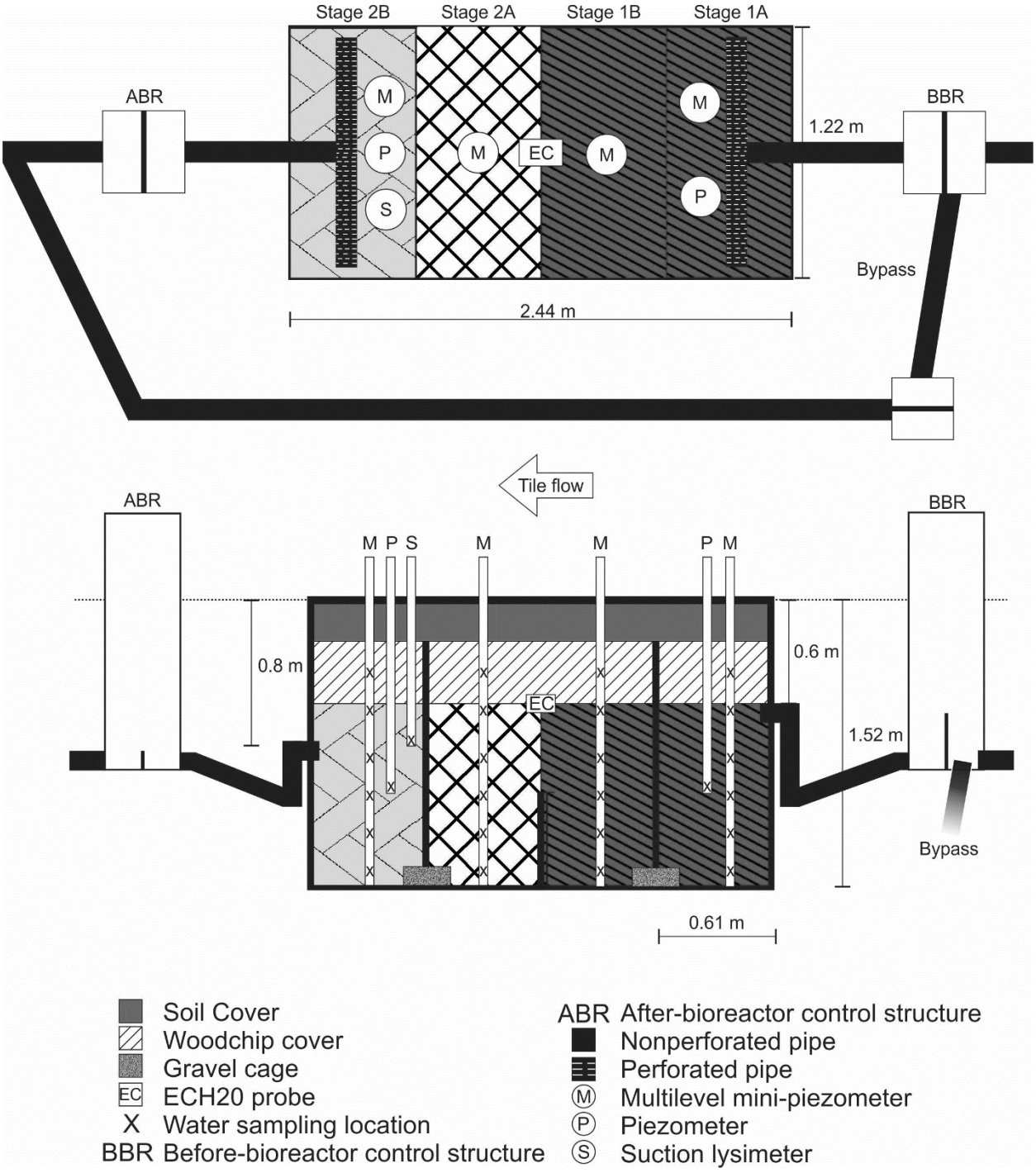

Figure 3-1: Bioreactor side and top view

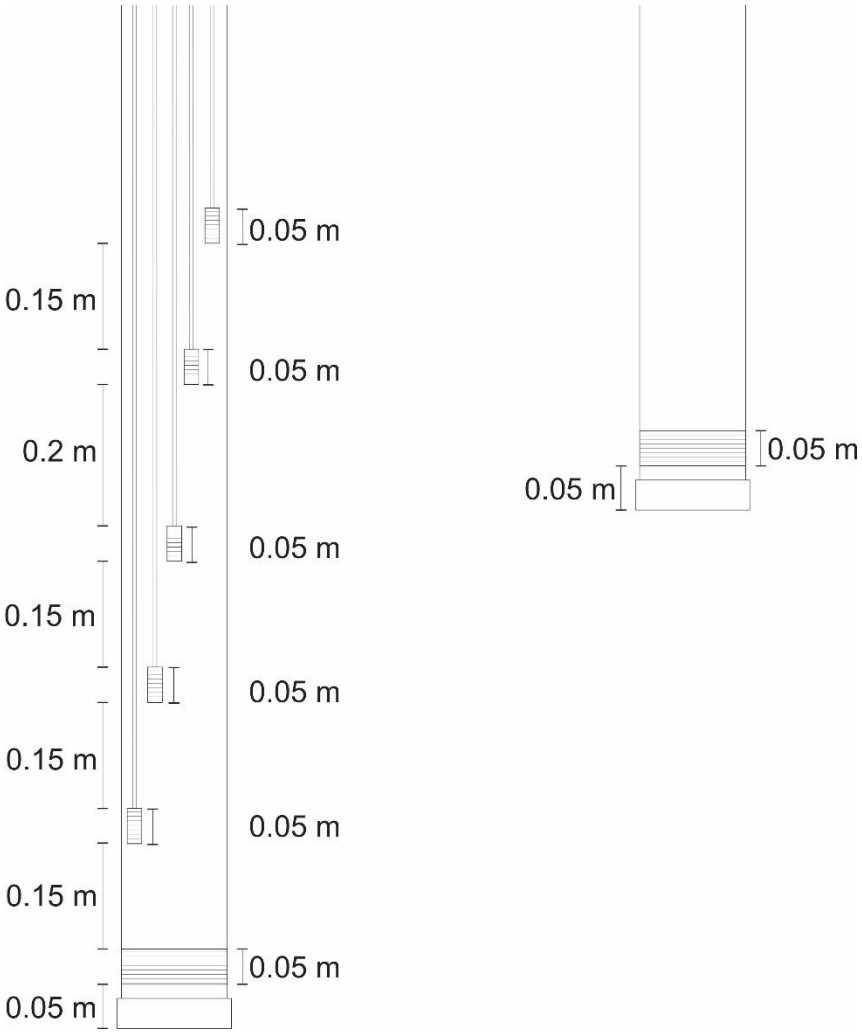

Figure 3-2: Multilevel mini-piezometer and water level piezometer

Chapter 4 - Conclusions

Agricultural practices such as the application of synthetic fertilizers, animal-manure, and biosolids have well known impacts on the natural environment. The current research, as part of the broader agriculture green house gas program, focused on mitigating the impact of such practices on air quality and water quality from the field to stream and onto large water bodies.

Applying biochar as a co-amendment with fertilizers can lower GHG emissions that are typically observed following field applications (Cayuela et al., 2014). However, the effectiveness of GHG mitigation decreases over time due to the natural weathering of biochar in soil (Spokas, 2013).

Addressing this loss of mitigation effectiveness is necessary for developing BMPs surrounding the use of biochar a co-amendment. The current study compared year-over-year applications of biochar as a co-amendment with N-rich manures and found that yearly, low-volume amounts can address this loss of effectiveness.

Contaminants associated with field amendments can be transported from agricultural fields at expedited rates due to tile-drainage networks, which are widespread in North America and around the world (Dils & Heathwaite, 1999; Kokulan, 2019; Schilling & Helmers, 2008; Skaggs et al., 1994). These contaminants have negative consequences on both aquatic ecosystems and human health, which are of growing concern around the world (Ayres, 1997; Howarth, 2008). Woodchip bioreactors can effectively remove NO_3-N (Addy et al., 2016; Bock et al., 2015; Gottschall et al., 2016), however, the potential of "pollution swapping" (Addy et al., 2016, p. 874), where the removal of NO_3-N directly increases the emission of N_2O has been identified as a drawback of these reactors (Feyereisen et al., 2016; Warneke et al., 2011a). Further, nutrients are not the only contaminants that can be transported to water bodies following

the application of amendments. Pharmaceutical and personal care products from human- and animal-waste derived fertilizers have been found in aquatic ecosystems (Burkhardt et al., 2005; Du & Liu, 2012; Kay et al., 2005). Efficient and cost-effective means to remove these contaminants from agricultural drainage are needed. The current study described the design and construction of woodchip bioreactors to mitigate N_2O emissions and filter PPCPs.

Together, the chapters within this thesis contribute to the development of BMPs that could be adopted by farmers and agricultural producers in Canada to lessen the negative impacts of agricultural practices on the natural environment.

4.1 **Future Research Recommendations**

The current research demonstrated that a yearly, lower-volume biochar amendment can counteract the deleterious effects of biochar aging that are observed with conventional one-time, larger-volume applications. In year-two of the study, it was observed that the high- and low-volume treatments performed equally in terms of N_2O mitigation, however the total cumulative N_2O emissions over two years were still lower on the HVBC plot. Future research should examine the effectiveness of these amendment schedules over a longer period to determine the cross-over point of these treatments (i.e. when the LVBC plot begins to outperform the HVBC plot).

Additionally, increasing the length of the study and the amount of microplots per treatment could help determine the additive effects of multiple yearly applications, as well as biochar weathering rates. To understand the impact of biochar weathering further research should make specific effort to examine the physical and chemical changes that occur in biochar in soil. This would best be achieved by using a larger biochar fraction that could be sampled throughout the duration of the study. This information could lead to precise recommendations to

farmers as to the frequency of application required to mitigate emissions. Future steps would also include conducting this study on a whole field scale, which would clarify the GHG mitigation potential of different amounts of biochar and allow further testing of the biochar and liquid manure slurry application method to compare dust fraction losses and general workability for farmers.

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Appendices

Appendix A: Greenhouse Gas Fluxes

Table A.1 Summary of calculated GHG fluxes from 2018.

2018 CH_4-C Flux (µg m^{-2} hr^{-1}) (R^2 >= 0.8)				
Date	MP1	MP2	MP3	MP4
08/02/18	35.54	46.14	4.99	12.32
08/08/18	45.77	62.97	--	--
08/09/18	85.97	88.33	--	--
08/10/18	30.92	50.37	--	5.59
08/13/18	42.80	67.28	7.13	4.18
08/14/18	1588.93	122.24	--	35.58
08/15/18	366.04	20.52	3.66	--
08/16/18	130.18	18.14	--	19.97
08/19/18	93.12	11.03	11.57	--
08/20/18	81.90	16.09	6.86	-2.48
08/21/18	79.28	14.57	--	--
08/22/18	71.58	11.19	--	9.34
08/27/18	19.99	14.22	--	--
08/30/18	12.73	8.08	--	7.51
09/03/18	9.67	4.42	--	--
09/06/18	10.14	4.29	--	5.28
09/10/18	--	--	--	--
09/12/18	8.01	16.69	--	--
09/24/18	--	--	--	--

Table A.1 Continued.

2018 CO_2-C Flux (kg ha^{-1} day^{-1}) (R^2 >= 0.8)				
Date	MP1	MP2	MP3	MP4
08/02/18	8.61	10.22	8.83	6.62
08/08/18	7.32	6.17	7.23	5.26
08/09/18	7.63	9.36	9.31	7.69
08/10/18	7.74	7.24	10.06	5.61
08/13/18	9.33	11.88	14.83	5.86
08/14/18	11.17	37.51	17.51	24.76
08/15/18	7.50	57.59	106.81	55.91
08/16/18	5.03	41.40	31.62	56.28
08/19/18	6.45	8.04	8.23	7.73
08/20/18	6.94	6.45	8.11	9.10
08/21/18	8.24	5.79	6.94	7.43
08/22/18	6.79	9.92	12.91	14.75
08/27/18	5.83	4.97	5.95	5.00
08/30/18	6.51	8.82	13.07	10.36
09/03/18	9.01	10.39	11.77	10.66
09/06/18	8.74	15.18	7.59	4.77
09/10/18	4.95	5.65	5.71	4.81
09/12/18	5.96	9.60	8.46	8.63
09/24/18	3.00	2.49	7.11	3.49

Table A.1 Continued.

2018 N_2O-N Flux (µg m^2 hr^{-1}) (R^2 >= 0.8)				
Date	MP1	MP2	MP3	MP4
08/02/18	31.91	162.03	91.96	59.08
08/08/18	18.80	63.87	42.83	19.70
08/09/18	18.76	82.61	39.04	12.18
08/10/18	23.38	60.21	59.75	29.26
08/13/18	19.30	114.22	86.11	32.11
08/14/18	15.32	140.94	95.16	54.74
08/15/18	42.24	366.76	259.25	112.94
08/16/18	31.28	179.63	117.70	43.47
08/19/18	39.25	226.62	106.70	37.00
08/20/18	33.96	153.56	90.87	41.60
08/21/18	35.69	153.95	96.37	41.37
08/22/18	41.03	251.37	100.31	54.54
08/27/18	42.80	185.91	92.76	53.39
08/30/18	19.83	278.83	105.47	71.45
09/03/18	65.92	443.89	134.27	78.13
09/06/18	60.89	435.77	133.32	75.55
09/10/18	31.20	170.65	66.10	58.05
09/12/18	131.18	301.84	104.35	80.89
09/24/18	51.67	220.72	71.96	68.78

Table A.2 Summary of calculated GHG fluxes from 2019.

2019 CH_4-C Flux (µg m^2 hr^{-1}) (R^2 >= 0.8)				
Date	MP1	MP2	MP3	MP4
05/19/19	--	-9.24	--	--
05/21/19	--	--	--	--
06/04/19	--	--	--	--
06/18/19	--	--	--	7.15
06/28/19	--	--	--	--
07/03/19	10.89	--	6.67	--
07/08/19	--	8.53	6.97	5.56
07/09/19	8.16	5.48	--	--
07/10/19	4.44	--	4.05	2.48
07/11/19	--	4.13	--	--
07/12/19	-3.17	--	--	--
07/16/19	--	2.09	2.88	1.73
07/17/19	--	--	4.48	--
07/18/19	--	--	--	--
07/19/19	--	--	--	--
07/23/19	5.14	2.07	-2.58	--
07/24/19	--	--	--	--
07/26/19	2.04	--	--	1.86
07/30/19	2.42	--	--	--
07/31/19	--	--	4.43	--
08/02/19	-1.85	2.82	--	--
08/06/19	--	--	--	--
08/08/19	--	--	--	--
08/21/19	-1.84	--	--	--

Table A.2 Continued.

2019 CO^2-C Flux (kg ha^{-1} day^{-1}) (R^2 >= 0.8)				
Date	MP1	MP2	MP3	MP4
05/19/19	2.34	4.99	6.46	6.25
05/21/19	3.52	4.42	5.91	7.11
06/04/19	5.19	8.38	6.98	6.17
06/18/19	8.61	14.02	9.07	9.54
06/28/19	13.39	18.46	11.25	9.81
07/03/19	9.29	15.38	9.90	9.22
07/08/19	11.57	18.35	13.71	10.88
07/09/19	13.52	29.89	24.00	20.37
07/10/19	5.44	84.27	18.82	26.23
07/11/19	2.34	25.22	9.08	10.22
07/12/19	5.77	43.56	44.78	37.43
07/16/19	2.95	8.10	5.68	3.41
07/17/19	6.17	9.80	6.13	6.76
07/18/19	2.11	6.59	4.40	3.92
07/19/19	3.70	7.35	5.01	4.18
07/23/19	4.66	10.43	7.62	5.33
07/24/19	3.07	7.85	4.67	4.94
07/26/19	3.23	3.65	3.85	1.48
07/30/19	5.42	11.83	10.10	8.18
07/31/19	5.77	11.78	9.65	8.59
08/02/19	4.29	5.76	5.73	3.83
08/06/19	3.18	7.33	4.66	3.52
08/08/19	5.33	8.91	13.40	7.42
08/21/19	4.41	7.99	--	--

Table A.2 Continued.

2019 N_2O-N Flux (µg m^2 hr^{-1}) (R^2 >= 0.8)				
Date	--	--	--	--
05/19/19	6.35	30.06	34.98	22.99
05/21/19	13.80	71.46	64.03	101.81
06/04/19	--	32.05	46.73	49.29
06/18/19	32.83	69.17	29.87	31.83
06/28/19	3.32	21.26	13.77	17.47
07/03/19	1.90	31.42	12.30	10.34
07/08/19	11.99	132.98	51.11	23.91
07/09/19	11.91	279.78	52.81	66.49
07/10/19	17.77	275.10	31.59	51.55
07/11/19	6.29	142.30	21.83	31.20
07/12/19	86.34	547.13	211.87	357.34
07/16/19	7.79	99.33	18.61	35.67
07/17/19	10.34	128.03	20.58	51.46
07/18/19	5.86	72.69	16.29	33.84
07/19/19	8.25	89.97	21.38	34.10
07/23/19	11.31	89.18	33.78	23.80
07/24/19	9.29	82.59	22.82	25.52
07/26/19	12.15	36.31	21.66	11.26
07/30/19	79.20	269.98	265.57	182.34
07/31/19	32.68	177.85	139.79	81.31
08/02/19	16.64	78.78	47.53	23.12
08/06/19	13.74	104.60	27.04	19.84
08/08/19	17.63	76.57	57.84	24.43
08/21/19	16.20	137.66	--	--

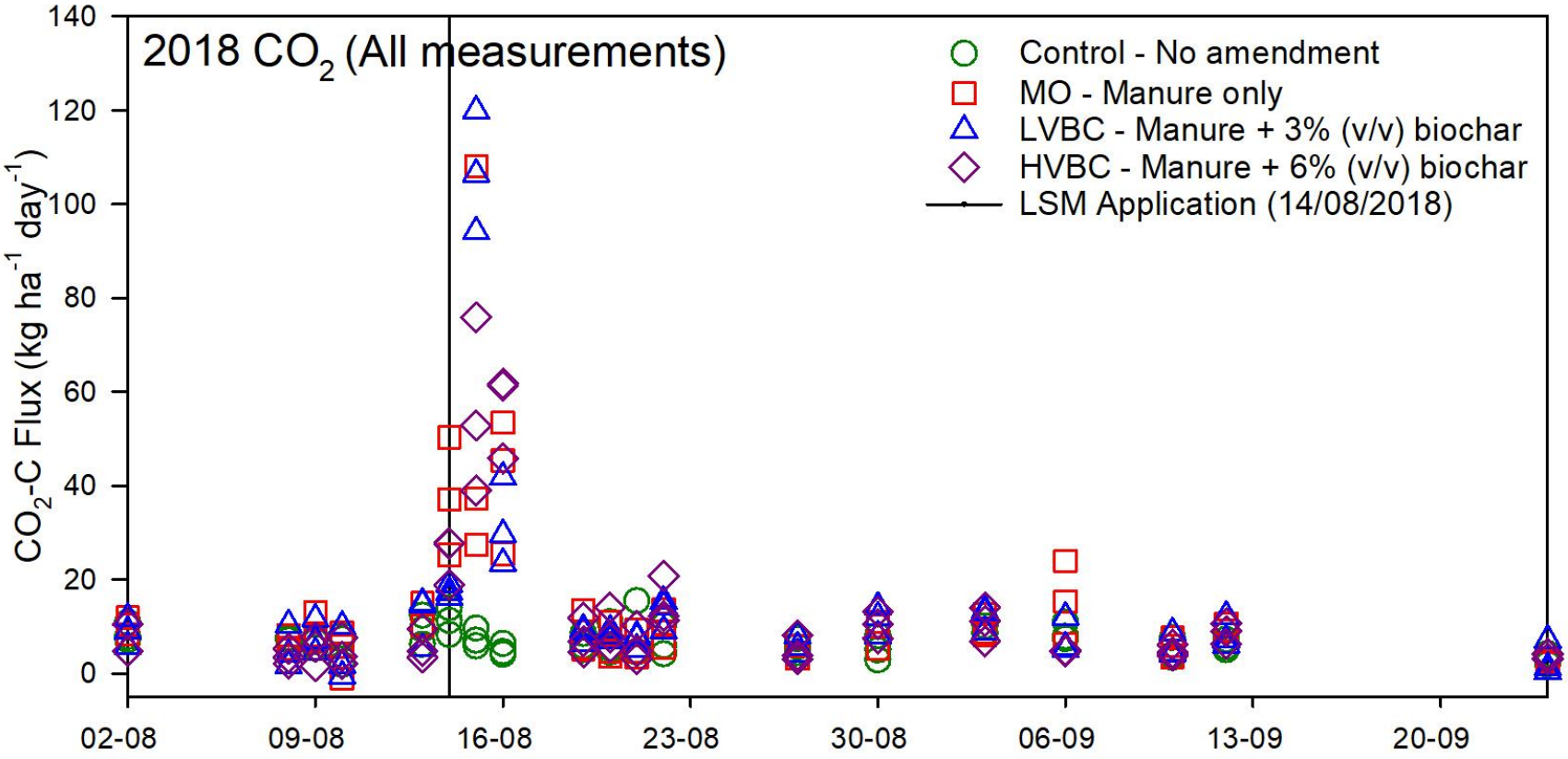

Figure A.1 All CO_2 flux measurements exceeding R^2 >= 0.8 cut-off from the Winchester microplots during the 2018 sampling season. Dates are DD-MM.

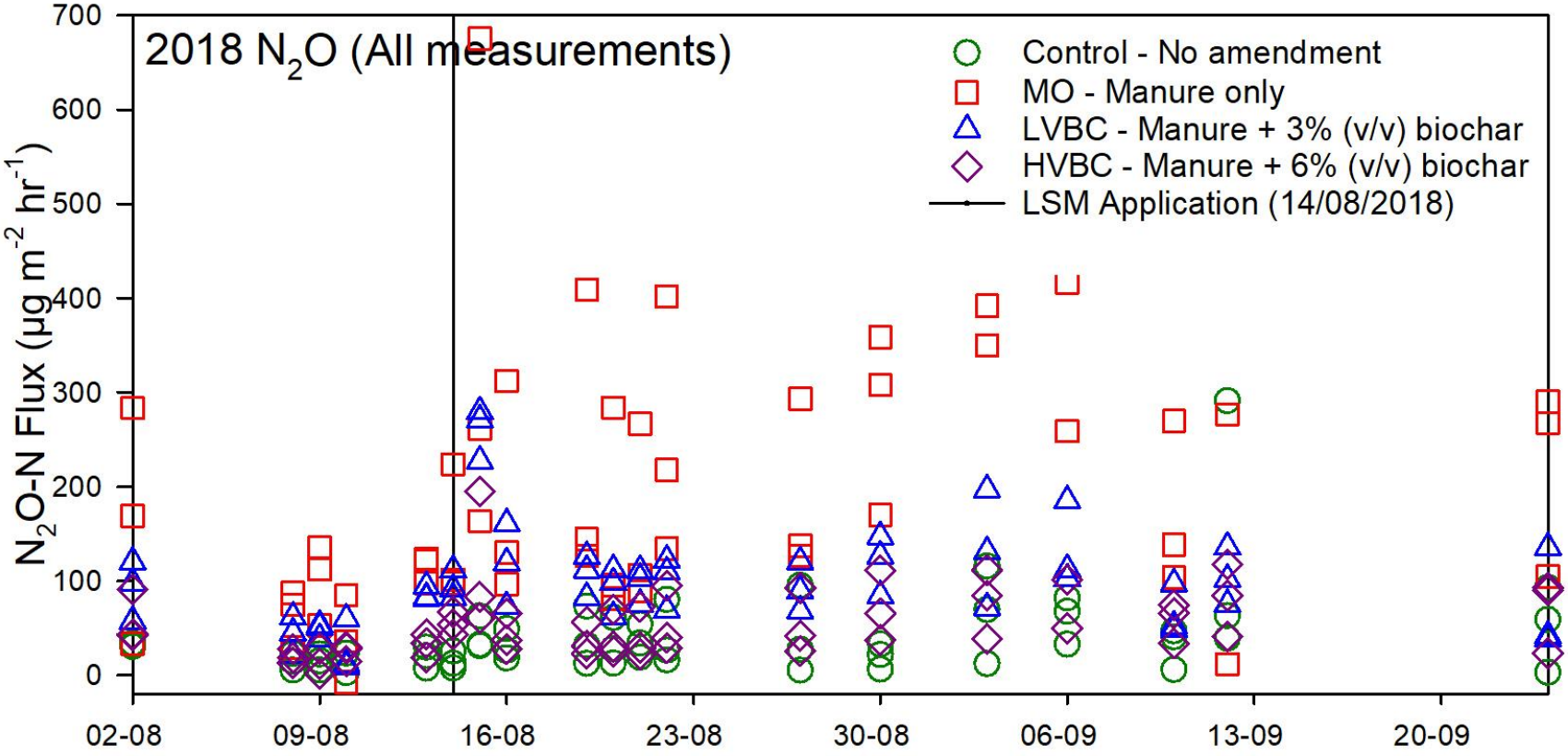

Figure A.2 All N_2O flux measurements exceeding R^2 >= 0.8 cut-off from the Winchester microplots during the 2018 sampling season. Dates are DD-MM.

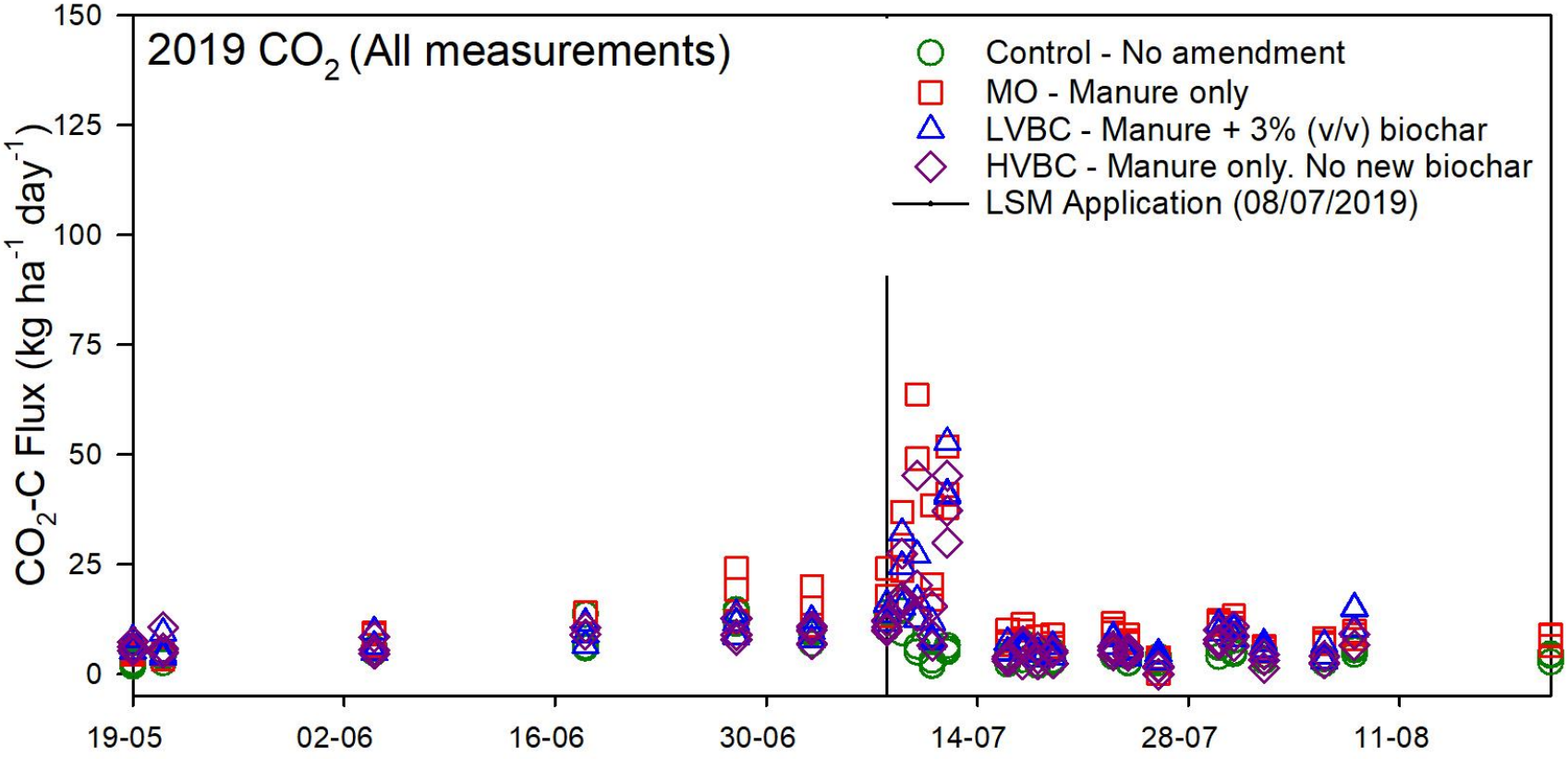

Figure A.3 All CO_2 flux measurements exceeding R^2 >= 0.8 cut-off from the Winchester microplots during the 2019 sampling season. Dates are DD-MM.

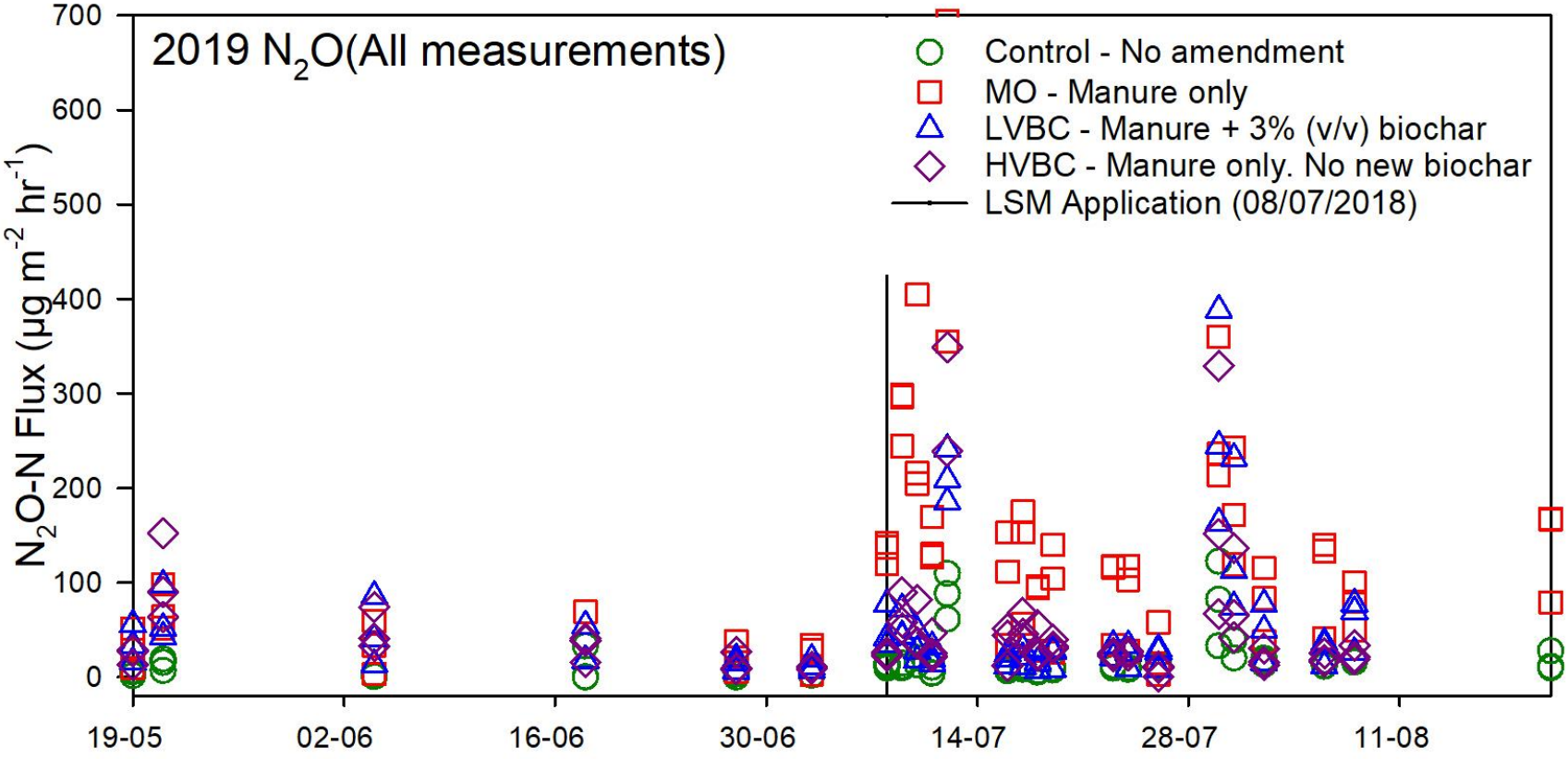

Figure A.4 All N_2O flux measurements exceeding R^2 >= 0.8 cut-off from the Winchester microplots during the 2019 sampling season. Dates are DD-MM.

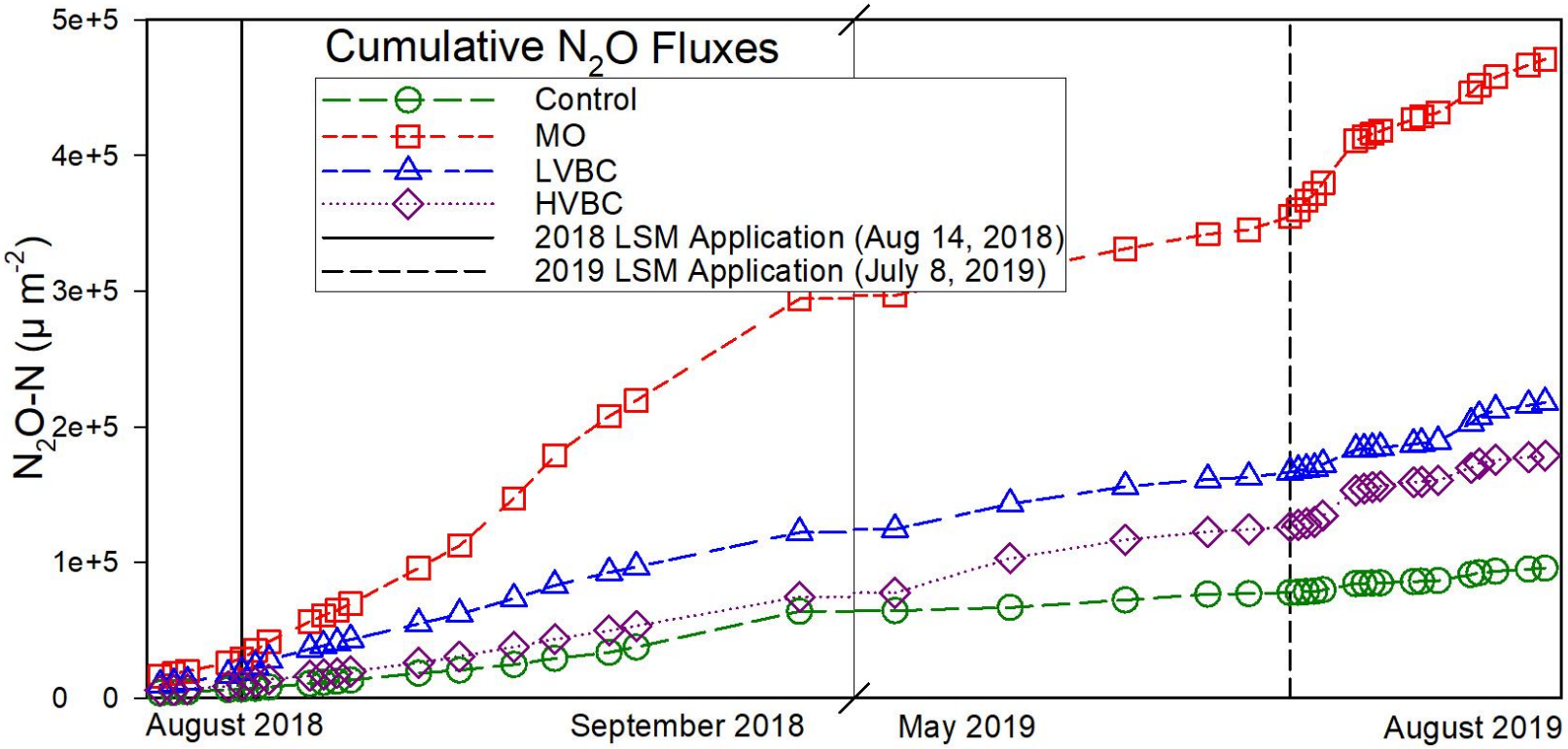

Figure A.5 Cumulative N_2O fluxes from the Winchester microplots during the 2018 - 2019 sampling seasons.

Appendix B: Solid Phase Chemistry

Table B.1 Summary of biochar analysis.

Sample	Moisture, Total	Ash		Carbon, Total Moist. Free	Hydrogen, Total Moist. Free	Nitrogen, Total Moist. Free
		As Received	Moist. Free			
	wt. %	wt. %	wt. %	wt. %	wt. %	wt. %
Biochar 2010	--	--	--	--	--	0.49
Biochar 2019 #1	4.18	5.79	6.04	69.65	3.52	0.33
Biochar 2019 #2	4.03	6.78	7.06	71.72	3.73	0.4
Biochar 2019 #3	4.11	6.55	6.83	71.63	3.84	0.31
Biochar 2019 #4	4.08	5.86	6.11	68.10	3.51	0.31
Biochar 2019 #5	4.15	6.37	6.64	71.74	3.7	0.32
Biochar 2019 #6	4.26	7.20	7.52	68.34	3.61	0.29
Biochar + LSM 2019	78.73	1.90	8.94	68.32	4.03	1.22

Table B.1 Continued.

Sample	Oxygen (calc.) Moist. Free	Sulfur, Total Moist. Free	OM	C:N	NH4-N	P	K	Ca	Mg
	wt. %	wt. %	%		%	%	%	%	%
Biochar 2010	--	--	78.90	89	0.01	0.04	0.36	0.50	0.08
Biochar 2019 #1	20.42	0.03	--	--	--	--	--	--	--
Biochar 2019 #2	17.09	<0.03	--	--	--	--	--	--	--
Biochar 2019 #3	17.38	<0.03	--	--	--	--	--	--	--
Biochar 2019 #4	21.98	<0.03	--	--	--	--	--	--	--
Biochar 2019 #5	17.59	<0.03	--	--	--	--	--	--	--
Biochar 2019 #6	20.24	<0.03	--	--	--	--	--	--	--
Biochar + LSM 2019	17.34	0.14	--	--	--	--	--	--	--

Table B.2 Summary of soil analysis from the Winchester field site in 2018.

Sample	Date Sampled	CEC	TC	IC	OC	%Soil Moisture	NH_4-N in sample	NO_3-N in sample	N	pH
		cmol+ kg^{-1}	% dry	% dry	% dry	%	mg kg^{-1} dry	mg kg^{-1} dry	% dry	
WCH-P1-0015	08/01/18	26.70	1.78	0.07	1.71	17.19	6.72	8.19	0.16	6.00
WCH-P1-1530	08/01/18	29.60	1.26	0.04	1.22	27.15	9.15	4.36	0.12	6.50
WCH-P2-0015	08/01/18	24.60	2.21	0.05	2.17	19.92	5.30	10.70	0.20	6.00
WCH-P2-1530	08/01/18	24.80	2.18	0.04	2.13	27.18	23.80	2.47	0.19	6.10
WCH-P3-0015	08/01/18	23.00	1.40	0.05	1.35	19.13	4.01	6.61	0.15	6.10
WCH-P3-1530	08/01/18	32.70	0.69	0.04	0.65	30.03	3.46	6.76	0.07	6.40
WCH-P4-0015	08/01/18	23.10	1.44	0.04	1.40	20.05	5.15	9.01	0.15	6.10
WCH-P4-1530	08/01/18	30.20	0.75	0.03	0.73	27.50	4.29	5.05	0.07	6.50
WCH-P1-0015	08/16/18	24.60	1.56	0.04	1.52	17.06	3.53	3.77	0.16	6.10
WCH-P1-1530	08/16/18	27.10	1.36	0.03	1.33	20.26	3.69	2.86	0.13	6.00
WCH-P2-0015	08/16/18	25.00	2.06	0.04	2.03	14.17	18.20	4.67	0.19	6.30
WCH-P2-1530	08/16/18	23.60	2.08	0.04	2.04	17.43	7.60	4.79	0.18	6.20
WCH-P3-0015	08/16/18	25.50	1.51	0.03	1.48	14.94	10.40	4.04	0.14	6.20
WCH-P3-1530	08/16/18	23.60	1.42	0.03	1.39	16.23	7.66	3.95	0.14	6.00
WCH-P4-0015	08/16/18	23.20	1.52	0.03	1.49	13.37	7.89	2.44	0.13	6.10
WCH-P4-1530	08/16/18	22.50	1.52	0.03	1.49	16.84	4.67	4.33	0.16	6.00
WCH-P1-0015	08/21/18	24.20	1.73	0.04	1.70	16.26	5.32	6.88	0.16	5.90
WCH-P1-1530	08/21/18	27.20	1.95	0.05	1.91	20.90	8.68	7.02	0.17	6.10
WCH-P2-0015	08/21/18	26.70	2.09	0.04	2.05	17.41	35.30	9.83	0.20	6.30
WCH-P2-1530	08/21/18	26.00	2.12	0.04	2.09	17.83	15.90	8.13	0.19	6.40
WCH-P3-0015	08/21/18	26.60	1.17	0.03	1.14	13.95	3.21	4.57	0.13	6.30
WCH-P3-1530	08/21/18	25.10	1.26	0.03	1.23	12.85	3.60	5.55	0.13	6.10
WCH-P4-0015	08/21/18	24.40	1.53	0.03	1.50	12.15	7.24	6.32	0.16	6.20
WCH-P4-1530	08/21/18	25.10	1.41	0.03	1.38	14.17	6.35	5.49	0.14	6.30

Table B.3 Summary of soil analysis from the Winchester field site in 2019.

Sample	Date Sampled	CEC	TC	IC	OC	%Soil Moisture	NH_4-N in sample	NO_3-N in sample	N	pH
		cmol+ kg^{-1}	% dry	% dry	% dry	%	mg kg^{-1} dry	mg kg^{-1} dry	% dry	
WCH-P1-0015	05/18/19	27.10	1.84	0.05	1.79	23.90	10.10	3.83	0.18	6.30
WCH-P1-1530	05/18/19	31.00	1.18	0.04	1.14	30.26	10.70	2.17	0.10	6.50
WCH-P2-0015	05/18/19	25.80	2.14	0.04	2.10	23.43	3.16	5.59	0.20	6.20
WCH-P2-1530	05/18/19	28.40	1.26	0.04	1.22	22.75	2.25	5.03	0.10	6.50
WCH-P3-0015	05/18/19	24.40	1.69	0.03	1.66	21.10	3.01	4.03	0.13	6.40
WCH-P3-1530	05/18/19	31.70	0.82	0.03	0.78	30.94	1.19	5.39	0.09	6.50
WCH-P4-0015	05/18/19	23.80	1.74	0.03	1.71	20.90	1.50	3.60	0.14	6.10
WCH-P4-1530	05/18/19	26.90	0.82	0.03	0.79	22.66	1.66	2.96	0.07	6.50
WCH-P1-0015	06/06/19	27.90	1.49	0.04	1.45	22.01	1.65	4.25	0.13	6.30
WCH-P1-1530	06/06/19	35.70	0.59	0.04	0.56	34.21	1.06	2.36	0.04	6.60
WCH-P2-0015	06/06/19	24.60	1.89	0.04	1.85	22.76	4.66	9.08	0.15	6.30
WCH-P2-1530	06/06/19	30.70	1.40	0.04	1.36	26.45	1.87	5.44	0.11	6.30
WCH-P3-0015	06/06/19	25.90	1.42	0.03	1.39	20.70	1.61	4.88	0.13	6.10
WCH-P3-1530	06/06/19	33.60	0.71	0.04	0.67	30.06	0.99	3.35	0.06	6.70
WCH-P4-0015	06/06/19	23.70	1.80	0.03	1.76	19.81	2.83	6.27	0.14	6.30
WCH-P4-1530	06/06/19	29.50	0.90	0.04	0.86	25.33	17.50	2.96	0.08	6.50
WCH-P1-0015	07/11/19	26.20	1.88	0.04	1.84	21.85	2.40	9.87	0.17	6.20
WCH-P1-1530	07/11/19	29.70	1.12	0.03	1.08	27.53	1.67	2.67	0.09	6.40
WCH-P2-0015	07/11/19	26.50	2.17	0.04	2.13	20.48	19.10	12.40	0.19	6.20
WCH-P2-1530	07/11/19	24.40	1.69	0.03	1.66	21.22	2.63	5.07	0.13	6.40
WCH-P3-0015	07/11/19	24.00	4.04	0.04	4.00	22.73	97.60	10.60	0.18	6.80
WCH-P3-1530	07/11/19	27.00	1.05	0.03	1.03	26.63	2.91	8.06	0.09	6.30
WCH-P4-0015	07/11/19	22.40	1.79	0.03	1.75	21.59	12.90	17.80	0.15	6.20
WCH-P4-1530	07/11/19	26.80	0.67	0.02	0.64	28.87	1.91	5.50	0.05	6.60

Table B.3 Continued.

Sample	Date Sampled	CEC	TC	IC	OC	%Soil Moisture	NH_4-N in sample	NO_3-N in sample	N	pH
		cmol+ kg^{-1}	% dry	% dry	% dry	%	mg kg^{-1} dry	mg kg^{-1} dry	% dry	
WCH-P1-0015	07/24/19	25.30	1.60	0.04	1.57	18.01	2.09	11.40	0.14	6.20
WCH-P1-1530	07/24/19	35.00	0.72	0.04	0.69	32.62	2.16	4.36	0.05	6.50
WCH-P2-0015	07/24/19	26.20	2.12	0.04	2.08	15.05	4.41	24.60	0.18	6.00
WCH-P2-1530	07/24/19	25.20	1.32	0.03	1.29	21.86	2.37	6.01	0.10	6.40
WCH-P3-0015	07/24/19	24.50	2.65	0.04	2.61	14.91	16.00	23.80	0.16	6.30
WCH-P3-1530	07/24/19	24.60	1.19	0.03	1.17	18.39	1.98	8.51	0.11	6.20
WCH-P4-0015	07/24/19	24.10	1.61	0.03	1.58	16.41	14.00	29.20	0.15	6.00
WCH-P4-1530	07/24/19	29.70	1.04	0.03	1.01	26.57	2.33	8.00	0.07	6.60
WCH-P1-0015	08/20/19	27.90	1.39	0.04	1.35	19.10	1.72	11.00	0.12	6.30
WCH-P1-1530	08/20/19	30.40	0.57	0.04	0.53	33.85	1.76	7.36	0.04	6.80
WCH-P2-0015	08/20/19	24.40	1.97	0.03	1.94	15.37	3.90	27.40	0.17	6.10
WCH-P2-1530	08/20/19	31.70	1.38	0.04	1.34	27.52	2.15	10.20	0.10	6.40
WCH-P3-0015	08/20/19	24.40	1.78	0.03	1.75	15.51	3.45	11.00	0.17	6.10
WCH-P3-1530	08/20/19	24.10	0.97	0.04	0.93	21.19	55.30	4.69	0.11	6.30
WCH-P4-0015	08/20/19	24.40	2.03	0.04	1.99	17.00	2.96	19.30	0.16	6.30
WCH-P4-1530	08/20/19	27.10	1.05	0.04	1.01	23.95	6.77	7.74	0.13	6.30

Table B.4 Summary of liquid swine manure analysis used at the Winchester field site in 2018 and 2019.

Sample	Dry Matter	TN	NH_4-N	TP	PO_4-P	OM	C:N	pH	Ca	Na
	%	%	ppm	%	%	%			%	%
2018 - LSM	3.20	0.50	3830.00	0.09	0.20	2.20	2:1	7.83	0.10	0.09
2018 - LSM	3.10	0.58	4438.00	0.07	0.15	2.20	2:1	7.87	0.09	0.09
2018 - LSM	3.10	0.85	7361.00	0.08	0.18	2.10	1:1	7.94	0.09	0.10
2019 - MP2	4.70	0.59	3818.00	0.11	0.26	3.60	3:1	6.79	0.13	0.08
2019 - MP3 (biochar + LSM)	21.90	0.64	3018.00	0.13	0.30	23.50	21:1	6.30	0.25	0.11
2019 - MP4	4.40	0.58	3878.00	0.11	0.26	3.30	3:1	6.81	0.14	0.08

Table B.4 Continued.

Sample	TK	Potash	S	Al	B	Cu	Fe	Mg	Mn	Zn
	%	%	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm
2018 - LSM	0.37	0.44	269.80	21.20	2.70	24.20	81.30	0.04	18.70	56.30
2018 - LSM	0.34	0.41	250.80	20.50	2.70	22.00	74.50	0.02	15.20	51.30
2018 - LSM	0.36	0.43	271.10	20.40	2.80	24.40	77.60	0.03	17.10	57.30
2019 - MP2	0.28	0.34	490.80	23.40	3.20	45.80	106.40	0.06	18.90	55.30
2019 - MP3 (biochar + LSM)	0.42	0.51	603.70	25.90	6.80	48.30	138.50	0.09	34.60	58.90
2019 - MP4	0.29	0.35	498.20	24.80	3.20	45.90	114.30	0.06	19.70	56.40

Appendix C: Pore-water Chemistry

Table C.1 Summary of pore-water general chemistry from the Winchester field site in 2018.

Sample	Date	pH	Eh	Alkalinity	NH_3-N	PO_4-P	DOC
			mV	mg L^{-1} $CaCO_3$	mg L^{-1}	mg L^{-1}	mg L^{-1} as C
Wch-P1-LY-20	08/15/18	7.50	500.54	66.00	0.02	0.01	8.29
Wch-P1-LY-20r	08/15/18	7.34	499.93	68.00	0.07	0.01	9.20
Wch-P1-LY-40	08/15/18	6.81	440.64	108.00	0.04	0.02	5.37
Wch-P1-LY-70	08/15/18	6.96	505.41	308.00	0.08	0.00	3.85
Wch-P2-LY-20	08/15/18	7.29	539.97	64.00	0.25	0.01	19.62
Wch-P2-LY-40	08/15/18	6.83	522.64	134.00	0.08	0.01	5.27
Wch-P2-LY-40r	08/15/18	6.89	524.29	106.00	0.17	0.01	5.80
Wch-P2-LY-70	08/15/18	6.90	520.38	342.00	0.23	0.01	5.69
Wch-P3-LY-20	08/15/18	7.01	525.26	50.00	0.11	0.01	8.77
Wch-P3-LY-40	08/15/18	6.61	526.11	74.00	0.03	0.02	4.79
Wch-P3-LY-70	08/15/18	7.12	514.22	210.00	0.03	0.00	5.17
Wch-P3-LY-70r	08/15/18	7.32	515.02	248.00	0.01	0.00	3.11
Wch-P4-LY-20	08/15/18	7.00	549.60	50.00	0.03	0.01	5.79
Wch-P4-LY-40	08/15/18	6.74	565.75	72.00	0.06	0.01	4.07
Wch-P4-LY-40r	08/15/18	6.55	564.88	66.00	0.02	0.01	9.72
Wch-P4-LY-70	08/15/18	7.02	526.75	126.00	0.06	0.00	3.09
Wch-P1-LY-20	08/22/18	7.40	420.71	36.00	0.03	0.01	7.42
Wch-P1-LY-20r	08/22/18	7.45	344.24	41.00	0.04	0.01	7.76
Wch-P1-LY-70	08/22/18	7.15	424.94	247.00	0.02	0.01	3.84
Wch-P2-LY-20	08/22/18	7.83	355.23	328.00	19.70	0.00	115.47
Wch-P2-LY-40	08/22/18	6.87	427.07	93.00	0.05	0.01	5.54
Wch-P2-LY-40r	08/22/18	6.94	281.00	420.00	4.50	0.00	178.22
Wch-P2-LY-70	08/22/18	6.98	391.34	280.00	0.12	0.01	5.20
Wch-P3-LY-20	08/22/18	7.19	163.62	38.00	--	0.01	7.47
Wch-P3-LY-40	08/22/18	6.80	213.95	88.00	0.03	0.01	3.49
Wch-P3-LY-70	08/22/18	7.22	155.99	248.00	0.06	0.01	4.06
Wch-P3-LY-70r	08/22/18	7.16	375.11	260.00	0.01	0.00	3.59
Wch-P4-LY-20	08/22/18	7.09	35.08	--	0.03	0.01	5.64
Wch-P4-LY-40	08/22/18	6.71	164.18	89.00	--	0.01	3.67
Wch-P4-LY-40r	08/22/18	--	258.50	--	--	0.01	7.23
Wch-P4-LY-70	08/22/18	7.33	395.94	165.00	0.01	0.00	3.56
Wch-P1-LY-20	08/29/18	7.57	221.21	67.00	0.10	--	--
Wch-P1-LY-20r	08/29/18	7.61	144.46	55.00	0.17	--	--
Wch-P1-LY-40	08/29/18	6.91	333.49	69.00	0.06	0.02	4.49
Wch-P1-LY-70	08/29/18	7.21	373.96	307.00	0.07	0.01	4.41
Wch-P2-LY-20	08/29/18	7.55	295.91	62.00	3.40	--	--
Wch-P2-LY-40	08/29/18	6.97	420.81	116.00	0.16	0.01	5.49
Wch-P2-LY-40r	08/29/18	6.97	426.29	145.00	0.76	0.00	13.97
Wch-P2-LY-70	08/29/18	6.97	455.32	352.00	0.04	0.01	5.20

Table C.1 Continued.

Sample	Date	pH	Eh	Alkalinity	NH_3-N	PO_4-P	DOC
			mV	mg L^{-1} $CaCO_3$	mg L^{-1}	mg L^{-1}	mg L^{-1} as C
Wch-P3-LY-20	08/29/18	7.28	205.51	28.00	0.26	0.01	7.73
Wch-P3-LY-40	08/29/18	6.83	136.10	73.00	0.03	0.02	3.14
Wch-P3-LY-70	08/29/18	7.04	314.64	120.00	-0.01	0.01	3.29
Wch-P3-LY-70r	08/29/18	7.23	379.68	320.00	--	0.01	3.58
Wch-P4-LY-20	08/29/18	7.44	379.98	43.00	0.29	--	--
Wch-P4-LY-40	08/29/18	7.11	388.27	88.00	0.15	0.01	4.15
Wch-P4-LY-40r	08/29/18	6.98	406.45	85.00	0.17	0.01	4.42
Wch-P4-LY-70	08/29/18	7.16	406.01	120.00	0.01	0.01	3.17
Wch-P1-LY-20	09/05/18	7.68	301.53	69.00	0.23	0.02	7.62
Wch-P1-LY-20r	09/05/18	7.73	235.62	56.00	0.35	--	--
Wch-P1-LY-40	09/05/18	7.00	355.20	94.00	0.09	0.02	5.00
Wch-P1-LY-70	09/05/18	7.16	390.80	329.00	0.08	0.01	5.22
Wch-P2-LY-20	09/05/18	7.12	400.47	38.00	1.08	0.33	20.45
Wch-P2-LY-40	09/05/18	7.01	423.10	126.00	0.21	0.01	6.50
Wch-P2-LY-40r	09/05/18	7.07	387.20	113.20	0.55	0.01	9.06
Wch-P2-LY-70	09/05/18	7.04	428.39	358.00	0.02	0.01	5.74
Wch-P3-LY-20	09/05/18	7.27	407.35	36.00	0.23	0.01	7.39
Wch-P3-LY-40	09/05/18	7.20	425.74	81.00	0.01	0.02	4.41
Wch-P3-LY-70	09/05/18	7.10	437.57	340.00	-0.01	0.01	3.69
Wch-P3-LY-70r	09/05/18	7.35	412.34	300.00	0.05	0.01	3.38
Wch-P4-LY-20	09/05/18	7.61	397.34	--	0.80	--	--
Wch-P4-LY-40r	09/05/18	7.28	420.02	82.00	0.03	0.01	4.54
Wch-P4-LY-70	09/05/18	7.20	428.12	212.00	0.28	0.01	3.42
Wch-P1-LY-40	09/12/18	7.69	375.26	84.00	0.14	0.02	3.99
Wch-P1-LY-70	09/12/18	7.29	421.13	330.00	0.09	0.01	3.90
Wch-P2-LY-40	09/12/18	7.34	415.39	137.00	0.27	0.01	5.43
Wch-P2-LY-40r	09/12/18	7.68	397.48	109.00	0.86	0.01	7.08
Wch-P2-LY-70	09/12/18	7.19	411.73	358.00	0.03	0.01	4.69
Wch-P3-LY-70	09/12/18	7.37	428.68	336.00	0.19	0.01	2.98
Wch-P3-LY-70r	09/12/18	7.43	417.77	242.00	0.26	0.01	2.58
Wch-P4-LY-40r	09/12/18	7.69	419.95	54.00	0.56	0.02	3.86
Wch-P4-LY-70	09/12/18	7.89	419.41	215.00	0.26	0.01	2.84
Wch-P1-LY-20	09/26/18	--	258.50	56.00	0.15	0.00	33.06
Wch-P1-LY-70	09/26/18	7.38	473.25	254.00	0.11	0.00	4.29
Wch-P2-LY-20	09/26/18	--	258.50	28.00	0.46	0.16	20.87
Wch-P2-LY-40	09/26/18	--	258.50	116.00	0.24	0.01	6.76
Wch-P2-LY-40r	09/26/18	--	258.50	94.00	0.32	0.01	9.65
Wch-P2-LY-70	09/26/18	7.25	465.19	302.00	0.02	0.01	6.28
Wch-P3-LY-20	09/26/18	--	258.50	32.00	0.26	0.00	25.48

Table C.1 Continued.

Sample	Date	pH	Eh	Alkalinity	NH_3-N	PO_4-P	DOC
			mV	mg L^{-1} $CaCO_3$	mg L^{-1}	mg L^{-1}	mg L^{-1} as C
Wch-P3-LY-40	09/26/18	--	258.50	70.00	0.38	0.01	4.68
Wch-P3-LY-70	09/26/18	7.42	468.27	250.00	0.06	0.01	6.96
Wch-P3-LY-70r	09/26/18	7.34	474.88	166.00	0.10	0.01	5.53
Wch-P4-LY-20	09/26/18	--	258.50	36.00	0.42	0.01	25.92
Wch-P4-LY-40	09/26/18	--	258.50	74.00	0.45	0.01	7.17
Wch-P4-LY-40r	09/26/18	--	258.50	70.00	0.35	0.01	14.28
Wch-P4-LY-70	09/26/18	7.51	478.72	168.00	0.23	0.01	4.81

Table C.2 Summary of pore-water general chemistry from the Winchester field site in 2019.

Sample	Date	pH	Eh	Alkalinity	NH_3-N	PO_4-P	DOC
			mV	mg L^{-1} $CaCO_3$	mg L^{-1}	mg L^{-1}	mg L^{-1} as C
WCH-P1-Ly-20	06/05/19	7.09	491.43	140.00	0.19	0.05	9.39
WCH-P1-Ly-40	06/05/19	7.03	485.99	200.00	0.02	0.04	5.03
WCH-P1-Ly-70	06/05/19	7.15	511.71	380.00	0.04	0.02	3.45
WCH-P1-Ly-20r	06/05/19	7.32	467.11	110.00	0.22	0.06	6.26
WCH-P2-Ly-20	06/05/19	7.39	514.26	100.00	0.11	0.06	12.31
WCH-P2-Ly-40	06/05/19	7.27	479.60	160.00	--	0.05	7.43
WCH-P2-Ly-70	06/05/19	7.05	303.08	310.00	0.01	0.04	4.57
WCH-P2-Ly-40r	06/05/19	7.27	470.69	260.00	0.34	0.06	8.48
WCH-P3-Ly-20	06/05/19	7.38	427.46	110.00	0.11	0.04	--
WCH-P3-Ly-40	06/05/19	6.77	486.90	180.00	0.05	0.02	4.02
WCH-P3-Ly-70	06/05/19	7.17	420.79	260.00	0.06	0.02	2.84
WCH-P3-Ly-70r	06/05/19	7.08	472.86	380.00	0.02	0.02	3.10
WCH-P4-Ly-20	06/05/19	7.35	485.04	110.00	0.08	0.09	9.53
WCH-P4-Ly-40	06/05/19	7.04	472.70	280.00	0.09	0.03	4.59
WCH-P4-Ly-70	06/05/19	7.17	509.53	310.00	0.04	0.02	2.90
WCH-P4-Ly-40r	06/05/19	6.95	472.03	210.00	0.06	0.03	4.33
WCH-P1-Ly-20	06/18/19	6.89	371.48	130.00	0.01	0.08	11.89
WCH-P1-Ly-40	06/18/19	7.20	407.92	220.00	--	0.04	6.48
WCH-P1-Ly-70	06/18/19	7.20	374.60	380.00	--	0.04	5.30
WCH-P1-Ly-20r	06/18/19	7.07	421.85	160.00	0.03	0.21	7.73
WCH-P2-Ly-20	06/18/19	6.80	426.25	130.00	--	0.09	15.06
WCH-P2-Ly-40	06/18/19	7.10	450.05	200.00	0.04	0.05	9.09
WCH-P2-Ly-70	06/18/19	6.88	438.20	370.00	--	0.03	5.09
WCH-P2-Ly-40r	06/18/19	7.02	462.30	220.00	0.05	0.11	8.28
WCH-P3-Ly-20	06/18/19	7.46	386.37	180.00	0.01	0.07	19.31
WCH-P3-Ly-40	06/18/19	7.02	446.38	200.00	--	0.04	3.95
WCH-P3-Ly-70	06/18/19	7.10	389.69	260.00	--	0.04	4.00
WCH-P3-Ly-70r	06/18/19	7.11	466.84	340.00	0.01	0.05	3.14
WCH-P4-Ly-20	06/18/19	6.89	413.37	110.00	0.01	0.06	12.11
WCH-P4-Ly-40	06/18/19	7.13	477.83	190.00	--	0.03	8.48
WCH-P4-Ly-70	06/18/19	7.13	436.56	320.00	--	0.05	9.23
WCH-P4-Ly-40r	06/18/19	7.07	470.38	240.00	0.02	0.02	12.23
WCH-P1-Ly-20	06/27/19	6.91	456.90	190.00	0.06	0.08	4.51
WCH-P1-Ly-40	06/27/19	6.87	--	300.00	0.07	0.03	4.88
WCH-P1-Ly-70	06/27/19	7.09	485.50	440.00	0.03	0.02	3.38
WCH-P1-Ly-20r	06/27/19	7.29	459.13	120.00	0.15	0.07	8.38
WCH-P2-Ly-20	06/27/19	7.32	465.48	60.00	0.04	--	--
WCH-P2-Ly-40	06/27/19	6.96	536.07	220.00	0.07	0.04	10.37
WCH-P2-Ly-70	06/27/19	6.96	471.96	390.00	0.03	0.03	4.84

Table C.2 Continued.

Sample	Date	pH	Eh	Alkalinity	NH_3-N	PO_4-P	DOC
			mV	mg L^{-1} $CaCO_3$	mg L^{-1}	mg L^{-1}	mg L^{-1} as C
WCH-P2-Ly-40r	06/27/19	7.07	532.13	250.00	0.05	0.08	12.23
WCH-P3-Ly-40	06/27/19	7.34	482.30	140.00	0.08	0.05	--
WCH-P3-Ly-70	06/27/19	7.04	533.09	330.00	0.07	0.02	2.72
WCH-P3-Ly-70r	06/27/19	7.10	498.03	430.00	0.04	0.03	3.19
WCH-P4-Ly-20	06/27/19	7.12	533.40	80.00	0.06	0.07	12.81
WCH-P4-Ly-40	06/27/19	6.89	505.72	220.00	0.05	0.04	5.35
WCH-P4-Ly-70	06/27/19	7.03	529.54	260.00	0.02	0.03	2.97
WCH-P4-Ly-40r	06/27/19	6.90	527.16	170.00	0.06	0.03	4.66
WCH-P1-Ly-20	07/04/19	7.13	561.69	100.00	0.25	0.12	12.82
WCH-P1-Ly-40	07/04/19	6.97	375.29	260.00	0.05	0.05	4.79
WCH-P1-Ly-70	07/04/19	7.12	284.99	400.00	0.01	0.02	3.55
WCH-P1-Ly-20r	07/04/19	7.33	495.38	100.00	0.08	0.09	9.62
WCH-P2-Ly-20	07/04/19	7.40	476.47	100.00	--	0.11	18.42
WCH-P2-Ly-40	07/04/19	6.93	396.97	260.00	0.44	0.08	11.12
WCH-P2-Ly-70	07/04/19	7.02	345.39	270.00	0.05	0.02	4.88
WCH-P2-Ly-40r	07/04/19	7.21	520.47	380.00	0.01	0.08	12.29
WCH-P3-Ly-20	07/04/19	8.05	509.81	--	--	--	--
WCH-P3-Ly-40	07/04/19	7.83	381.23	--	0.07	0.10	--
WCH-P3-Ly-70	07/04/19	7.05	310.36	240.00	0.02	0.02	2.76
WCH-P3-Ly-70r	07/04/19	7.15	353.27	290.00	--	0.09	3.21
WCH-P4-Ly-20	07/04/19	7.41	508.75	100.00	0.03	0.11	13.10
WCH-P4-Ly-40	07/04/19	6.89	407.19	250.00	0.01	0.07	5.07
WCH-P4-Ly-70	07/04/19	6.98	318.10	320.00	0.01	0.05	3.16
WCH-P4-Ly-40r	07/04/19	6.95	527.89	210.00	0.02	0.04	4.89
WCH-P1-Ly-40	07/18/19	7.04	459.65	260.00	0.03	0.11	5.18
WCH-P1-Ly-70	07/18/19	7.01	356.45	390.00	--	0.09	4.66
WCH-P2-Ly-40	07/18/19	6.78	354.33	190.00	--	0.09	12.26
WCH-P2-Ly-70	07/18/19	6.86	202.90	370.00	--	0.08	5.13
WCH-P2-Ly-40r	07/18/19	7.04	476.25	230.00	0.03	0.11	12.77
WCH-P3-Ly-40	07/18/19	6.76	478.73	160.00	0.05	0.08	4.35
WCH-P3-Ly-70	07/18/19	7.03	384.03	260.00	--	0.04	3.31
WCH-P3-Ly-70r	07/18/19	7.03	482.23	330.00	--	0.05	3.63
WCH-P4-Ly-40	07/18/19	6.82	393.54	250.00	0.01	0.06	5.48
WCH-P4-Ly-70	07/18/19	6.98	417.54	320.00	--	0.05	3.92
WCH-P4-Ly-40r	07/18/19	6.82	451.05	300.00	--	0.05	4.82
WCH-P1-Ly-40	08/01/19	7.17	460.59	270.00	0.05	0.04	4.79
WCH-P1-Ly-70	08/01/19	7.01	507.90	460.00	0.02	0.03	3.78
WCH-P1-Ly-20r	08/01/19	6.86	457.10	40.00	--	--	--
WCH-P2-Ly-20	08/01/19	6.93	489.94	40.00	--	--	--

Table C.2 Continued.

Sample	Date	pH	Eh	Alkalinity	NH_3-N	PO_4-P	DOC
			mV	mg L^{-1} $CaCO_3$	mg L^{-1}	mg L^{-1}	mg L^{-1} as C
WCH-P2-Ly-40	08/01/19	6.88	502.68	160.00	0.02	0.04	9.90
WCH-P2-Ly-70	08/01/19	7.01	456.20	580.00	0.03	0.02	5.06
WCH-P2-Ly-40r	08/01/19	7.01	475.30	220.00	--	0.16	11.85
WCH-P3-Ly-20	08/01/19	7.20	454.75	80.00	0.02	--	11.07
WCH-P3-Ly-40	08/01/19	6.79	489.28	150.00	--	0.04	3.95
WCH-P3-Ly-70	08/01/19	6.96	452.88	210.00	--	0.02	2.92
WCH-P3-Ly-70r	08/01/19	7.07	450.56	280.00	--	0.03	3.11
WCH-P4-Ly-20	08/01/19	7.08	467.46	70.00	0.03	0.08	11.15
WCH-P4-Ly-40	08/01/19	7.02	444.59	260.00	0.01	0.04	4.79
WCH-P4-Ly-70	08/01/19	7.00	518.60	180.00	0.01	0.03	3.14
WCH-P4-Ly-40r	08/01/19	6.95	467.80	220.00	0.01	0.02	4.58

Table C.3 Summary of pore-water anion concentrations from the Winchester field site in 2018.

Sample	Date	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Sulfate	Phosphate
		mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
Wch-P1-LY-20	08/15/18	0.27	11.99	< 0.1	< 0.1	13.33	54.24	< 0.1
Wch-P1-LY-20r	08/15/18	0.26	9.77	< 0.1	< 0.1	36.84	28.85	< 0.1
Wch-P1-LY-40	08/15/18	0.26	11.50	< 0.1	< 0.1	21.85	26.81	< 0.1
Wch-P1-LY-70	08/15/18	0.26	9.77	< 0.1	< 0.1	13.27	14.63	< 0.1
Wch-P2-LY-20	08/15/18	0.15	16.93	0.21	< 0.1	22.57	63.34	< 0.1
Wch-P2-LY-40	08/15/18	0.22	11.56	< 0.1	< 0.1	28.69	44.35	< 0.1
Wch-P2-LY-40r	08/15/18	0.22	11.58	< 0.1	< 0.1	40.91	36.47	< 0.1
Wch-P2-LY-70	08/15/18	0.21	8.42	0.18	< 0.1	13.58	33.01	< 0.1
Wch-P3-LY-20	08/15/18	0.22	11.09	< 0.1	< 0.1	28.17	42.15	< 0.1
Wch-P3-LY-40	08/15/18	0.20	11.08	< 0.1	< 0.1	94.33	13.36	< 0.1
Wch-P3-LY-70	08/15/18	0.19	6.98	< 0.1	< 0.1	62.72	12.94	< 0.1
Wch-P3-LY-70r	08/15/18	0.20	6.18	< 0.1	< 0.1	44.52	10.38	< 0.1
Wch-P4-LY-20	08/15/18	0.21	5.74	< 0.1	< 0.1	15.04	30.50	< 0.1
Wch-P4-LY-40	08/15/18	0.22	7.28	< 0.1	< 0.1	80.18	19.68	< 0.1
Wch-P4-LY-40r	08/15/18	0.22	14.42	< 0.1	< 0.1	49.55	86.71	< 0.1
Wch-P4-LY-70	08/15/18	0.29	6.43	< 0.1	< 0.1	64.83	18.44	< 0.1
Wch-P1-LY-20	08/22/18	0.36	10.26	0.16	< 0.1	13.48	47.29	< 0.1
Wch-P1-LY-20r	08/22/18	0.31	7.84	< 0.1	< 0.1	36.37	26.77	< 0.1
Wch-P1-LY-70	08/22/18	0.33	9.41	< 0.1	< 0.1	16.52	16.01	< 0.1
Wch-P2-LY-20	08/22/18	0.34	96.98	< 0.1	< 0.1	1.65	105.73	< 0.1
Wch-P2-LY-40	08/22/18	0.21	8.01	< 0.1	< 0.1	35.43	41.98	< 0.1
Wch-P2-LY-40r	08/22/18	--	60.59	< 0.1	< 0.1	2.13	43.69	< 0.1
Wch-P2-LY-70	08/22/18	0.24	5.89	< 0.1	< 0.1	19.01	40.18	< 0.1
Wch-P3-LY-20	08/22/18	0.27	7.64	< 0.1	< 0.1	33.94	35.55	< 0.1
Wch-P3-LY-40	08/22/18	0.22	8.94	< 0.1	< 0.1	98.17	11.82	< 0.1
Wch-P3-LY-70	08/22/18	0.31	5.38	< 0.1	< 0.1	74.32	11.82	< 0.1
Wch-P3-LY-70r	08/22/18	0.25	5.85	< 0.1	< 0.1	47.47	10.23	< 0.1
Wch-P4-LY-20	08/22/18	0.27	3.84	< 0.1	< 0.1	19.18	33.17	< 0.1
Wch-P4-LY-40	08/22/18	0.22	3.75	< 0.1	< 0.1	66.55	15.88	< 0.1
Wch-P4-LY-40r	08/22/18	0.23	10.59	< 0.1	< 0.1	57.82	74.63	< 0.1
Wch-P4-LY-70	08/22/18	0.29	4.20	< 0.1	< 0.1	67.29	16.45	< 0.1
Wch-P1-LY-40	08/29/18	0.21	9.01	< 0.1	< 0.1	27.43	28.04	< 0.1
Wch-P1-LY-70	08/29/18	0.33	9.24	< 0.1	< 0.1	15.88	17.45	< 0.1
Wch-P2-LY-20	08/29/18	< 0.1	32.25	< 0.1	< 0.1	171.45	89.25	< 0.1
Wch-P2-LY-40	08/29/18	0.23	6.65	< 0.1	< 0.1	34.96	43.62	< 0.1
Wch-P2-LY-40r	08/29/18	0.23	24.25	2.33	< 0.1	87.00	45.82	< 0.1
Wch-P2-LY-70	08/29/18	0.23	5.16	< 0.1	< 0.1	18.09	42.33	< 0.1
Wch-P3-LY-20	08/29/18	0.23	5.69	< 0.1	< 0.1	28.70	38.89	< 0.1
Wch-P3-LY-40	08/29/18	0.25	6.69	< 0.1	< 0.1	91.83	12.15	< 0.1
Wch-P3-LY-70	08/29/18	0.25	4.27	< 0.1	< 0.1	73.42	10.92	< 0.1

Table C.3 Continued.

Sample	Date	Fluoride mg L^{-1}	Chloride mg L^{-1}	Nitrite mg L^{-1}	Bromide mg L^{-1}	Nitrate mg L^{-1}	Sulfate mg L^{-1}	Phosphate mg L^{-1}
Wch-P3-LY-70r	08/29/18	0.28	5.51	< 0.1	< 0.1	49.77	10.90	< 0.1
Wch-P4-LY-20	08/29/18	0.28	2.56	< 0.1	< 0.1	20.24	32.37	< 0.1
Wch-P4-LY-40	08/29/18	0.25	3.78	< 0.1	< 0.1	82.00	18.68	< 0.1
Wch-P4-LY-40r	08/29/18	0.25	7.01	< 0.1	< 0.1	63.10	45.06	< 0.1
Wch-P4-LY-70	08/29/18	0.33	3.43	< 0.1	< 0.1	65.74	16.94	< 0.1
Wch-P1-LY-20	09/05/18	0.26	3.92	< 0.1	< 0.1	9.03	42.38	< 0.1
Wch-P1-LY-40	09/05/18	0.25	8.14	< 0.1	< 0.1	26.74	26.80	< 0.1
Wch-P1-LY-70	09/05/18	0.30	7.40	< 0.1	< 0.1	11.56	14.84	< 0.1
Wch-P2-LY-20	09/05/18	0.10	21.31	< 0.1	< 0.1	150.06	89.71	1.20
Wch-P2-LY-40	09/05/18	0.25	5.53	< 0.1	< 0.1	30.00	43.22	< 0.1
Wch-P2-LY-40r	09/05/18	0.23	17.44	0.13	< 0.1	101.58	47.77	< 0.1
Wch-P2-LY-70	09/05/18	0.23	3.71	< 0.1	< 0.1	11.27	35.42	< 0.1
Wch-P3-LY-40	09/05/18	0.32	5.79	< 0.1	< 0.1	79.92	11.56	< 0.1
Wch-P3-LY-70	09/05/18	0.29	3.15	< 0.1	< 0.1	62.67	9.44	< 0.1
Wch-P3-LY-70r	09/05/18	0.27	5.57	< 0.1	< 0.1	52.11	10.57	< 0.1
Wch-P4-LY-40r	09/05/18	0.26	6.02	< 0.1	< 0.1	65.07	37.39	< 0.1
Wch-P4-LY-70	09/05/18	0.32	2.71	< 0.1	< 0.1	49.48	14.00	< 0.1
Wch-P1-LY-40	09/12/18	0.30	7.78	< 0.1	< 0.1	26.41	23.92	< 0.1
Wch-P1-LY-70	09/12/18	0.33	4.69	< 0.1	< 0.1	3.11	13.23	< 0.1
Wch-P2-LY-40	09/12/18	0.27	4.72	< 0.1	< 0.1	26.66	38.75	< 0.1
Wch-P2-LY-40r	09/12/18	0.29	8.07	< 0.1	< 0.1	47.23	34.58	< 0.1
Wch-P2-LY-70	09/12/18	0.26	2.35	0.44	< 0.1	5.08	31.45	< 0.1
Wch-P3-LY-70	09/12/18	0.32	1.91	< 0.1	< 0.1	31.18	9.06	< 0.1
Wch-P3-LY-70r	09/12/18	0.33	5.76	< 0.1	< 0.1	50.07	11.51	< 0.1
Wch-P4-LY-40r	09/12/18	0.26	5.86	< 0.1	< 0.1	63.93	33.55	< 0.1
Wch-P4-LY-70	09/12/18	0.35	1.34	< 0.1	< 0.1	21.93	10.01	< 0.1
Wch-P1-LY-20	09/26/18	0.21	22.05	< 0.1	< 0.1	43.30	599.67	< 0.1
Wch-P1-LY-70	09/26/18	0.34	5.34	< 0.1	< 0.1	3.94	18.61	< 0.1
Wch-P2-LY-20	09/26/18	0.11	48.19	< 0.1	< 0.1	167.26	227.18	0.41
Wch-P2-LY-40	09/26/18	0.20	12.92	< 0.1	< 0.1	32.23	54.75	< 0.1
Wch-P2-LY-40r	09/26/18	0.19	26.12	< 0.1	< 0.1	49.88	67.80	< 0.1
Wch-P2-LY-70	09/26/18	0.26	6.19	0.23	< 0.1	2.27	35.14	< 0.1
Wch-P3-LY-20	09/26/18	0.13	37.36	< 0.1	< 0.1	90.52	359.17	< 0.1
Wch-P3-LY-40	09/26/18	0.23	7.30	< 0.1	< 0.1	23.38	14.69	< 0.1
Wch-P3-LY-70	09/26/18	0.33	14.94	< 0.1	< 0.1	32.04	32.89	< 0.1
Wch-P3-LY-70r	09/26/18	0.30	18.41	< 0.1	< 0.1	86.40	67.32	< 0.1
Wch-P4-LY-20	09/26/18	0.09	67.39	< 0.1	< 0.1	126.41	411.28	< 0.1
Wch-P4-LY-40	09/26/18	0.20	10.91	< 0.1	< 0.1	41.18	57.03	< 0.1
Wch-P4-LY-40r	09/26/18	0.17	41.88	< 0.1	< 0.1	134.53	290.17	< 0.1
Wch-P4-LY-70	09/26/18	0.30	9.88	< 0.1	< 0.1	23.82	17.30	< 0.1

Table C.4 Summary of pore-water anions from the Winchester field site in 2019.

Sample	Date	Fluoride mg L^{-1}	Chloride mg L^{-1}	Nitrite mg L^{-1}	Bromide mg L^{-1}	Nitrate mg L^{-1}	Sulfate mg L^{-1}	Phosphate mg L^{-1}
WCH-P1-Ly-20	06/05/19	< 0.1	6.90	< 0.1	< 0.1	3.82	215.69	< 0.1
WCH-P1-Ly-40	06/05/19	< 0.1	5.81	< 0.1	< 0.1	8.49	71.99	< 0.1
WCH-P1-Ly-70	06/05/19	< 0.1	5.32	< 0.1	< 0.1	< 0.1	38.15	< 0.1
WCH-P1-Ly-20r	06/05/19	< 0.1	7.24	< 0.1	< 0.1	22.51	95.76	< 0.1
WCH-P2-Ly-20	06/05/19	< 0.1	8.41	< 0.1	< 0.1	11.42	77.77	< 0.1
WCH-P2-Ly-40	06/05/19	< 0.1	8.15	< 0.1	< 0.1	11.03	66.44	< 0.1
WCH-P2-Ly-70	06/05/19	< 0.1	24.89	< 0.1	< 0.1	35.75	47.04	< 0.1
WCH-P2-Ly-40r	06/05/19	< 0.1	23.57	< 0.1	< 0.1	29.30	267.60	< 0.1
WCH-P3-Ly-20	06/05/19	< 0.1	7.41	< 0.1	< 0.1	25.19	77.63	< 0.1
WCH-P3-Ly-40	06/05/19	< 0.1	16.41	< 0.1	< 0.1	42.96	162.20	< 0.1
WCH-P3-Ly-70	06/05/19	< 0.1	16.93	< 0.1	< 0.1	37.79	94.33	< 0.1
WCH-P3-Ly-70r	06/05/19	< 0.1	16.74	< 0.1	< 0.1	30.45	50.13	< 0.1
WCH-P4-Ly-20	06/05/19	< 0.1	17.32	< 0.1	< 0.1	10.99	97.15	< 0.1
WCH-P4-Ly-40	06/05/19	< 0.1	24.70	< 0.1	< 0.1	26.70	143.13	< 0.1
WCH-P4-Ly-70	06/05/19	< 0.1	14.44	< 0.1	< 0.1	26.78	47.20	< 0.1
WCH-P4-Ly-40r	06/05/19	< 0.1	23.35	< 0.1	< 0.1	36.46	149.00	< 0.1
WCH-P1-Ly-20	06/18/19	< 0.1	4.71	< 0.1	< 0.1	3.85	284.87	< 0.1
WCH-P1-Ly-40	06/18/19	< 0.1	4.38	< 0.1	< 0.1	6.55	47.12	< 0.1
WCH-P1-Ly-70	06/18/19	< 0.1	5.16	< 0.1	< 0.1	< 0.1	37.50	< 0.1
WCH-P1-Ly-20r	06/18/19	< 0.1	4.20	< 0.1	< 0.1	16.88	199.76	< 0.1
WCH-P2-Ly-20	06/18/19	< 0.1	4.57	< 0.1	< 0.1	1.43	196.99	< 0.1
WCH-P2-Ly-40	06/18/19	< 0.1	22.20	< 0.1	< 0.1	21.80	98.55	< 0.1
WCH-P2-Ly-70	06/18/19	< 0.1	12.02	< 0.1	< 0.1	9.90	49.82	< 0.1
WCH-P2-Ly-40r	06/18/19	< 0.1	22.78	< 0.1	< 0.1	51.57	166.33	< 0.1
WCH-P3-Ly-20	06/18/19	< 0.1	4.95	< 0.1	< 0.1	10.48	115.21	< 0.1
WCH-P3-Ly-40	06/18/19	< 0.1	14.99	< 0.1	< 0.1	52.95	137.23	< 0.1
WCH-P3-Ly-70	06/18/19	< 0.1	17.51	< 0.1	< 0.1	42.36	77.25	< 0.1
WCH-P3-Ly-70r	06/18/19	< 0.1	16.55	< 0.1	< 0.1	34.68	47.00	< 0.1
WCH-P4-Ly-20	06/18/19	< 0.1	15.93	< 0.1	< 0.1	11.02	134.60	< 0.1
WCH-P4-Ly-40	06/18/19	< 0.1	19.06	< 0.1	< 0.1	27.55	78.36	< 0.1
WCH-P4-Ly-70	06/18/19	< 0.1	14.04	< 0.1	< 0.1	29.07	47.07	< 0.1
WCH-P4-Ly-40r	06/18/19	< 0.1	20.77	< 0.1	< 0.1	42.69	122.87	< 0.1
WCH-P1-Ly-20	06/27/19	< 0.1	18.83	< 0.1	< 0.1	44.70	134.89	< 0.1
WCH-P1-Ly-40	06/27/19	< 0.1	4.32	< 0.1	< 0.1	8.09	58.72	< 0.1
WCH-P1-Ly-70	06/27/19	< 0.1	5.17	< 0.1	< 0.1	< 0.1	34.10	< 0.1
WCH-P1-Ly-20r	06/27/19	< 0.1	2.41	< 0.1	< 0.1	18.59	175.68	< 0.1
WCH-P2-Ly-40	06/27/19	< 0.1	21.51	< 0.1	< 0.1	22.05	104.30	< 0.1
WCH-P2-Ly-70	06/27/19	< 0.1	11.45	< 0.1	< 0.1	8.49	46.30	< 0.1
WCH-P2-Ly-40r	06/27/19	< 0.1	23.35	< 0.1	< 0.1	41.67	250.52	< 0.1
WCH-P3-Ly-70	06/27/19	< 0.1	16.85	< 0.1	< 0.1	41.91	74.05	< 0.1

Table C.4 Continued.

Sample	Date	Fluoride mg L^{-1}	Chloride mg L^{-1}	Nitrite mg L^{-1}	Bromide mg L^{-1}	Nitrate mg L^{-1}	Sulfate mg L^{-1}	Phosphate mg L^{-1}
WCH-P3-Ly-70r	06/27/19	< 0.1	15.05	< 0.1	< 0.1	32.09	44.76	< 0.1
WCH-P4-Ly-20	06/27/19	< 0.1	15.77	< 0.1	< 0.1	21.32	122.76	< 0.1
WCH-P4-Ly-40	06/27/19	< 0.1	--	< 0.1	< 0.1	< 0.1	99.38	< 0.1
WCH-P4-Ly-70	06/27/19	< 0.1	12.92	< 0.1	< 0.1	27.24	39.47	< 0.1
WCH-P4-Ly-40r	06/27/19	< 0.1	18.84	< 0.1	< 0.1	44.61	129.02	< 0.1
WCH-P1-Ly-20	07/04/19	< 0.1	2.75	< 0.1	< 0.1	20.51	223.78	< 0.1
WCH-P1-Ly-40	07/04/19	< 0.1	4.12	< 0.1	< 0.1	10.72	69.13	< 0.1
WCH-P1-Ly-70	07/04/19	< 0.1	5.08	< 0.1	< 0.1	< 0.1	29.31	< 0.1
WCH-P1-Ly-20r	07/04/19	< 0.1	2.21	< 0.1	< 0.1	40.75	187.26	< 0.1
WCH-P2-Ly-20	07/04/19	< 0.1	3.93	< 0.1	< 0.1	19.11	299.49	< 0.1
WCH-P2-Ly-40	07/04/19	< 0.1	20.12	< 0.1	< 0.1	27.65	109.26	< 0.1
WCH-P2-Ly-70	07/04/19	< 0.1	10.98	< 0.1	< 0.1	7.22	40.40	< 0.1
WCH-P2-Ly-40r	07/04/19	< 0.1	22.66	< 0.1	< 0.1	48.35	236.92	< 0.1
WCH-P3-Ly-70	07/04/19	< 0.1	16.76	< 0.1	< 0.1	43.85	73.09	< 0.1
WCH-P3-Ly-70r	07/04/19	< 0.1	16.04	< 0.1	< 0.1	36.61	58.62	< 0.1
WCH-P4-Ly-20	07/04/19	< 0.1	13.76	< 0.1	< 0.1	28.55	115.94	< 0.1
WCH-P4-Ly-40	07/04/19	< 0.1	20.04	< 0.1	< 0.1	40.77	94.17	< 0.1
WCH-P4-Ly-70	07/04/19	< 0.1	13.84	< 0.1	< 0.1	29.19	44.51	< 0.1
WCH-P4-Ly-40r	07/04/19	< 0.1	17.81	< 0.1	< 0.1	48.29	117.26	< 0.1
WCH-P1-Ly-40	07/18/19	< 0.1	4.06	< 0.1	< 0.1	16.20	78.02	< 0.1
WCH-P1-Ly-70	07/18/19	< 0.1	4.75	< 0.1	< 0.1	2.92	43.50	< 0.1
WCH-P2-Ly-40	07/18/19	< 0.1	19.10	< 0.1	< 0.1	35.31	116.03	< 0.1
WCH-P2-Ly-70	07/18/19	< 0.1	11.44	< 0.1	< 0.1	13.92	45.40	< 0.1
WCH-P2-Ly-40r	07/18/19	< 0.1	22.30	< 0.1	< 0.1	57.46	248.63	< 0.1
WCH-P3-Ly-40	07/18/19	< 0.1	13.51	< 0.1	< 0.1	69.77	160.77	< 0.1
WCH-P3-Ly-70	07/18/19	< 0.1	16.55	< 0.1	< 0.1	50.26	84.07	< 0.1
WCH-P3-Ly-70r	07/18/19	< 0.1	16.44	< 0.1	< 0.1	46.12	72.14	< 0.1
WCH-P4-Ly-40	07/18/19	< 0.1	20.70	< 0.1	< 0.1	51.10	117.69	< 0.1
WCH-P4-Ly-70	07/18/19	< 0.1	14.30	< 0.1	< 0.1	34.80	60.52	< 0.1
WCH-P4-Ly-40r	07/18/19	< 0.1	16.26	< 0.1	< 0.1	54.76	147.94	< 0.1
WCH-P1-Ly-40	08/01/19	< 0.1	2.34	< 0.1	< 0.1	10.85	84.78	< 0.1
WCH-P1-Ly-70	08/01/19	< 0.1	4.46	< 0.1	< 0.1	12.15	73.24	< 0.1
WCH-P2-Ly-40	08/01/19	< 0.1	17.08	< 0.1	< 0.1	42.96	110.41	< 0.1
WCH-P2-Ly-70	08/01/19	< 0.1	11.46	< 0.1	< 0.1	21.84	57.09	< 0.1
WCH-P2-Ly-40r	08/01/19	< 0.1	21.51	< 0.1	< 0.1	68.10	230.60	< 0.1
WCH-P3-Ly-20	08/01/19	< 0.1	2.51	< 0.1	< 0.1	135.56	63.69	< 0.1
WCH-P3-Ly-40	08/01/19	< 0.1	12.57	< 0.1	< 0.1	73.88	131.78	< 0.1
WCH-P3-Ly-70	08/01/19	< 0.1	15.68	< 0.1	< 0.1	52.29	90.28	< 0.1
WCH-P3-Ly-70r	08/01/19	< 0.1	15.77	< 0.1	< 0.1	50.44	71.64	< 0.1
WCH-P4-Ly-20	08/01/19	< 0.1	10.34	< 0.1	< 0.1	70.27	90.95	< 0.1

Table C.4 Continued.

Sample	Date	Fluoride mg L^{-1}	Chloride mg L^{-1}	Nitrite mg L^{-1}	Bromide mg L^{-1}	Nitrate mg L^{-1}	Sulfate mg L^{-1}	Phosphate mg L^{-1}
WCH-P4-Ly-40	08/01/19	< 0.1	19.49	< 0.1	< 0.1	55.85	99.29	< 0.1
WCH-P4-Ly-70	08/01/19	< 0.1	13.60	< 0.1	< 0.1	39.19	63.10	< 0.1
WCH-P4-Ly-40r	08/01/19	< 0.1	14.85	< 0.1	< 0.1	57.09	160.97	< 0.1

Table C.5 Summary of pore-water cations from the Winchester field site in 2018.

Sample	Date	Al	As	B	Ca	Cd	Co	Cr	Cu	Fe
		µg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Wch-P1-LY-20	08/15/18	7.09	1.23	56.27	34.57	0.30	0.97	< 0.3	3.73	2.50
Wch-P1-LY-20r	08/15/18	6.72	1.61	53.90	36.47	0.50	0.99	< 0.3	7.36	< 2
Wch-P1-LY-40	08/15/18	19.03	0.73	53.19	44.93	0.25	0.59	< 0.3	3.11	< 2
Wch-P1-LY-70	08/15/18	4.69	< 0.3	44.05	91.42	0.28	0.31	< 0.07	4.40	< 0.7
Wch-P2-LY-20	08/15/18	10.84	2.71	94.39	44.55	0.52	2.16	0.62	16.73	15.88
Wch-P2-LY-40	08/15/18	4.34	1.09	59.82	58.38	0.44	1.09	< 0.07	2.89	< 0.7
Wch-P2-LY-40r	08/15/18	5.87	1.42	59.49	53.90	0.58	1.61	< 0.3	4.09	6.55
Wch-P2-LY-70	08/15/18	4.91	0.92	56.05	110.00	0.53	0.61	< 0.07	5.13	2.17
Wch-P3-LY-20	08/15/18	6.89	1.08	56.67	33.01	0.71	2.35	< 0.3	6.74	9.68
Wch-P3-LY-40	08/15/18	6.93	0.61	43.68	53.84	0.15	0.36	< 0.07	2.24	< 0.7
Wch-P3-LY-70	08/15/18	12.74	< 0.3	33.10	99.90	0.33	0.29	0.38	2.95	7.01
Wch-P3-LY-70r	08/15/18	5.73	< 0.3	32.71	101.60	0.24	0.24	0.34	1.89	< 0.7
Wch-P4-LY-20	08/15/18	6.62	0.79	40.69	32.41	0.48	1.24	< 0.3	5.11	2.12
Wch-P4-LY-40	08/15/18	4.00	0.37	36.10	51.16	0.44	0.39	< 0.3	2.68	< 0.7
Wch-P4-LY-40r	08/15/18	6.81	0.49	36.75	64.05	0.41	0.51	< 0.07	2.48	< 0.7
Wch-P4-LY-70	08/15/18	4.38	< 0.3	23.06	66.77	0.32	0.24	< 0.07	2.29	< 0.7
Wch-P1-LY-20	08/22/18	8.09	1.22	53.00	30.84	0.21	0.74	< 0.3	4.54	3.81
Wch-P1-LY-20r	08/22/18	7.47	1.26	51.56	32.48	0.35	0.81	< 0.3	8.83	6.24
Wch-P1-LY-70	08/22/18	6.23	0.35	41.95	87.81	0.22	0.27	< 0.3	5.17	2.02
Wch-P2-LY-20	08/22/18	7.86	5.72	139.20	125.10	0.19	4.29	0.99	11.06	39.81
Wch-P2-LY-40	08/22/18	5.13	0.85	56.30	58.93	0.47	0.61	< 0.3	3.77	< 0.7
Wch-P2-LY-40r	08/22/18	6.87	3.00	75.50	173.50	0.65	2.30	0.26	10.56	57.27
Wch-P2-LY-70	08/22/18	5.61	0.77	52.93	109.10	0.39	0.50	< 0.07	5.93	< 0.7
Wch-P3-LY-20	08/22/18	8.77	0.88	54.55	29.71	0.56	1.24	< 0.3	7.21	2.34
Wch-P3-LY-40	08/22/18	6.16	0.41	40.51	49.14	0.11	0.27	< 0.07	1.66	< 0.7
Wch-P3-LY-70	08/22/18	8.59	< 0.3	32.62	101.40	0.17	< 0.2	0.41	2.47	< 0.7
Wch-P3-LY-70r	08/22/18	6.78	0.30	32.41	99.36	0.15	0.20	0.45	1.84	< 0.7

Table C.5 Continued.

Sample	Date	Al	As	B	Ca	Cd	Co	Cr	Cu	Fe
		µg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Wch-P4-LY-20	08/22/18	7.95	0.72	37.92	25.40	0.39	0.93	< 0.07	4.87	< 2
Wch-P4-LY-40	08/22/18	5.85	0.35	34.49	48.37	0.28	0.37	< 0.07	1.74	< 0.7
Wch-P4-LY-40r	08/22/18	6.12	0.42	34.00	56.22	0.26	0.34	< 0.07	2.17	< 0.7
Wch-P4-LY-70	08/22/18	4.94	< 0.3	20.57	67.82	0.20	0.21	< 0.3	3.05	8.82
Wch-P1-LY-40	08/29/18	5.61	0.80	49.29	42.73	0.20	0.35	< 0.3	2.84	< 2
Wch-P1-LY-70	08/29/18	5.74	0.47	43.21	85.58	0.14	0.31	< 0.3	5.20	< 0.7
Wch-P2-LY-20	08/29/18	8.75	3.34	124.70	77.50	0.86	1.54	0.58	57.11	7.00
Wch-P2-LY-40	08/29/18	5.87	0.77	53.09	56.87	0.36	0.44	< 0.07	4.17	< 0.7
Wch-P2-LY-40r	08/29/18	6.60	1.75	61.47	77.42	0.79	0.73	< 0.3	27.95	3.98
Wch-P2-LY-70	08/29/18	5.30	0.74	52.67	103.30	0.36	0.34	< 0.3	7.13	< 0.7
Wch-P3-LY-20	08/29/18	11.23	0.84	52.97	26.40	0.40	0.95	0.34	12.44	< 2
Wch-P3-LY-40	08/29/18	5.79	0.43	36.17	44.78	0.12	0.24	< 0.07	1.75	< 0.7
Wch-P3-LY-70	08/29/18	5.71	< 0.3	31.25	103.30	0.12	< 0.2	0.58	1.78	< 0.7
Wch-P3-LY-70r	08/29/18	5.43	< 0.3	31.61	96.80	0.07	< 0.2	0.45	1.77	< 0.7
Wch-P4-LY-40	08/29/18	5.84	0.39	32.58	46.22	0.15	0.37	< 0.3	3.27	< 0.7
Wch-P4-LY-40r	08/29/18	4.78	0.46	32.50	46.43	0.16	0.30	< 0.3	2.93	< 0.7
Wch-P4-LY-70	08/29/18	6.14	< 0.3	21.49	67.23	0.12	< 0.2	< 0.3	2.21	< 0.7
Wch-P1-LY-20	09/05/18	10.90	1.31	52.27	31.90	0.14	0.60	< 0.3	5.09	< 0.7
Wch-P1-LY-40	09/05/18	6.82	0.70	48.64	45.27	0.16	0.28	< 0.07	2.82	< 0.7
Wch-P1-LY-70	09/05/18	6.68	0.52	44.63	86.82	0.12	0.25	< 0.07	4.01	< 0.7
Wch-P2-LY-20	09/05/18	14.28	2.91	111.90	65.12	0.80	1.02	0.61	42.01	39.26
Wch-P2-LY-40	09/05/18	5.75	0.69	54.85	54.00	0.24	0.35	< 0.07	4.06	< 2
Wch-P2-LY-40r	09/05/18	7.22	0.84	64.63	68.22	0.43	0.55	< 0.3	15.49	2.40
Wch-P2-LY-70	09/05/18	5.36	0.63	52.51	100.80	0.30	0.29	< 0.07	7.24	< 0.7
Wch-P3-LY-40	09/05/18	6.86	0.50	36.34	41.86	0.07	0.22	< 0.07	2.47	< 0.7
Wch-P3-LY-70	09/05/18	5.73	< 0.3	29.56	101.30	0.08	< 0.2	0.45	1.40	< 0.7
Wch-P3-LY-70r	09/05/18	6.12	0.34	30.52	90.66	0.09	< 0.2	0.40	1.73	< 0.7

Table C.5 Continued.

Sample	Date	Al	As	B	Ca	Cd	Co	Cr	Cu	Fe
		µg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Wch-P4-LY-40r	09/05/18	6.01	0.48	31.56	43.03	0.12	0.28	< 0.07	2.25	< 0.7
Wch-P4-LY-70	09/05/18	6.04	< 0.3	23.96	63.92	0.08	< 0.2	< 0.07	3.12	< 0.7
Wch-P1-LY-40	09/12/18	6.79	0.60	43.80	38.90	0.09	0.21	< 0.3	2.89	< 0.7
Wch-P1-LY-70	09/12/18	6.21	0.45	42.98	82.78	0.11	0.25	< 0.07	3.84	< 0.7
Wch-P2-LY-40	09/12/18	7.52	0.77	49.73	54.68	0.20	0.32	< 0.07	5.10	< 0.7
Wch-P2-LY-40r	09/12/18	7.99	0.87	55.23	47.13	0.28	0.46	0.25	12.30	< 2
Wch-P2-LY-70	09/12/18	6.17	0.72	51.74	98.86	0.29	0.23	< 0.07	7.13	< 0.7
Wch-P3-LY-70	09/12/18	5.89	0.32	27.65	99.48	0.06	< 0.2	0.34	1.92	< 0.7
Wch-P3-LY-70r	09/12/18	7.61	0.34	31.05	86.36	0.06	0.20	0.31	1.65	< 0.7
Wch-P4-LY-40r	09/12/18	6.65	0.55	29.09	39.15	0.09	0.21	< 0.3	3.17	8.36
Wch-P4-LY-70	09/12/18	7.49	0.36	18.75	61.25	0.06	< 0.2	< 0.3	1.93	< 0.7
Wch-P1-LY-20	09/26/18	10.90	0.58	81.93	117.20	0.57	0.49	0.25	20.86	5.00
Wch-P1-LY-70	09/26/18	6.60	0.50	38.96	82.44	0.12	0.25	0.30	5.92	< 2
Wch-P2-LY-20	09/26/18	15.11	1.74	72.46	84.65	0.89	0.67	0.64	26.71	12.17
Wch-P2-LY-40	09/26/18	5.52	0.49	42.56	52.81	0.27	0.28	< 0.3	5.24	< 0.7
Wch-P2-LY-40r	09/26/18	5.22	0.60	51.53	55.97	0.43	0.47	< 0.3	13.66	2.44
Wch-P2-LY-70	09/26/18	6.44	0.67	41.58	85.73	0.18	0.19	< 0.3	6.99	< 2
Wch-P3-LY-20	09/26/18	24.49	0.58	49.15	100.00	0.85	0.55	< 0.3	16.61	6.23
Wch-P3-LY-40	09/26/18	5.19	0.53	27.43	26.89	0.05	0.19	< 0.3	2.50	< 0.7
Wch-P3-LY-70	09/26/18	5.59	0.35	19.59	83.32	0.08	0.20	0.33	4.14	6.48
Wch-P3-LY-70r	09/26/18	4.97	0.36	26.65	83.44	0.10	0.24	0.40	4.49	< 0.7
Wch-P4-LY-20	09/26/18	15.10	0.46	47.05	133.00	1.01	0.89	< 0.3	21.42	9.77
Wch-P4-LY-40	09/26/18	4.72	0.39	25.40	43.57	0.23	0.45	< 0.3	4.28	< 0.7
Wch-P4-LY-40r	09/26/18	4.95	0.45	31.07	122.50	0.32	0.37	< 0.3	4.02	< 0.7
Wch-P4-LY-70	09/26/18	6.35	0.37	17.18	57.47	0.08	0.27	< 0.3	4.16	< 0.7

Table C.5 Continued.

Sample	Date	K	Li	Mg	Mn	Na	Ni	Pb	S	Sb
		mg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}
Wch-P1-LY-20	08/15/18	1.96	16.63	8.33	77.62	10.79	10.80	< 0.01	18.25	0.74
Wch-P1-LY-20r	08/15/18	1.54	10.38	9.04	49.35	9.00	14.14	< 0.04	10.49	0.60
Wch-P1-LY-40	08/15/18	1.30	15.08	11.64	27.10	10.71	8.73	< 0.01	9.92	0.57
Wch-P1-LY-70	08/15/18	1.30	14.45	28.39	6.76	10.66	3.21	< 0.01	6.78	0.17
Wch-P2-LY-20	08/15/18	2.52	16.28	9.97	323.00	8.58	19.61	< 0.04	21.71	1.02
Wch-P2-LY-40	08/15/18	1.34	13.63	15.03	50.96	11.05	13.53	< 0.01	15.64	0.49
Wch-P2-LY-40r	08/15/18	1.81	13.30	13.77	93.98	10.66	19.53	< 0.01	13.71	0.52
Wch-P2-LY-70	08/15/18	1.77	12.26	31.95	37.38	14.27	9.30	0.07	13.25	2.14
Wch-P3-LY-20	08/15/18	1.26	12.89	7.68	257.10	7.74	17.22	< 0.01	13.93	0.58
Wch-P3-LY-40	08/15/18	1.33	16.48	13.46	6.76	9.72	2.21	< 0.04	5.65	0.54
Wch-P3-LY-70	08/15/18	1.38	13.33	24.73	9.66	8.26	2.58	0.06	6.28	0.20
Wch-P3-LY-70r	08/15/18	2.01	14.84	27.71	3.02	8.29	1.15	0.18	5.48	0.13
Wch-P4-LY-20	08/15/18	1.54	10.59	7.77	56.55	9.52	17.18	< 0.04	11.30	0.50
Wch-P4-LY-40	08/15/18	1.42	13.77	12.96	4.19	11.25	3.34	0.28	7.78	0.39
Wch-P4-LY-40r	08/15/18	1.28	13.53	15.23	5.01	16.02	3.15	< 0.04	29.57	0.38
Wch-P4-LY-70	08/15/18	1.31	13.05	17.97	8.10	11.31	2.30	< 0.01	7.36	0.18
Wch-P1-LY-20	08/22/18	1.58	12.60	7.23	30.38	10.19	9.76	< 0.01	16.42	0.70
Wch-P1-LY-20r	08/22/18	1.63	8.90	7.85	19.67	8.19	11.43	< 0.01	9.77	0.60
Wch-P1-LY-70	08/22/18	1.11	12.38	27.14	2.12	10.56	3.11	< 0.04	6.84	0.20
Wch-P2-LY-20	08/22/18	32.04	12.43	29.89	127.20	50.85	26.03	< 0.04	36.63	0.98
Wch-P2-LY-40	08/22/18	2.19	11.77	15.43	6.71	11.48	9.15	< 0.01	15.51	0.41
Wch-P2-LY-40r	08/22/18	5.80	16.98	42.53	269.70	32.70	23.18	0.07	18.15	0.92
Wch-P2-LY-70	08/22/18	1.90	13.51	31.72	3.60	13.38	7.22	< 0.01	14.93	0.47
Wch-P3-LY-20	08/22/18	1.81	11.65	7.02	59.63	7.49	11.27	< 0.01	11.99	1.11
Wch-P3-LY-40	08/22/18	1.24	13.47	12.25	2.26	8.88	1.66	< 0.01	4.83	0.55
Wch-P3-LY-70	08/22/18	1.85	12.60	25.25	1.90	7.78	1.35	< 0.04	5.56	0.24
Wch-P3-LY-70r	08/22/18	1.77	14.32	27.11	0.99	8.00	1.17	< 0.01	5.18	0.17

Table C.5 Continued.

Sample	Date	K	Li	Mg	Mn	Na	Ni	Pb	S	Sb
		mg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}
Wch-P4-LY-20	08/22/18	1.11	8.98	6.03	21.79	8.15	10.98	< 0.01	11.40	0.75
Wch-P4-LY-40	08/22/18	1.38	12.70	12.41	2.09	10.77	2.49	< 0.01	7.03	0.54
Wch-P4-LY-40r	08/22/18	1.26	12.66	13.26	2.37	16.27	2.41	< 0.01	24.38	0.47
Wch-P4-LY-70	08/22/18	0.92	12.12	18.48	1.01	11.38	2.19	< 0.01	8.19	0.25
Wch-P1-LY-40	08/29/18	1.24	15.60	11.20	5.15	9.93	5.78	< 0.01	10.14	0.63
Wch-P1-LY-70	08/29/18	1.56	13.75	26.57	1.42	10.19	2.88	< 0.04	7.07	0.23
Wch-P2-LY-20	08/29/18	11.71	10.11	17.53	33.45	19.75	22.75	< 0.01	29.65	0.85
Wch-P2-LY-40	08/29/18	1.36	11.63	14.85	2.58	10.44	6.73	< 0.01	15.46	0.34
Wch-P2-LY-40r	08/29/18	1.96	13.26	19.69	26.51	14.20	11.08	0.10	16.04	0.29
Wch-P2-LY-70	08/29/18	1.53	12.49	30.38	1.53	12.28	5.74	< 0.01	15.32	0.20
Wch-P3-LY-20	08/29/18	1.89	14.27	6.18	20.30	7.47	11.59	< 0.01	13.09	0.56
Wch-P3-LY-40	08/29/18	1.15	13.71	11.05	1.41	8.01	1.65	< 0.04	4.81	0.48
Wch-P3-LY-70	08/29/18	0.76	12.14	25.72	0.95	7.52	0.86	< 0.01	5.26	0.09
Wch-P3-LY-70r	08/29/18	1.39	14.29	26.10	0.80	7.70	0.79	< 0.01	5.13	0.11
Wch-P4-LY-40	08/29/18	1.60	17.24	11.67	2.18	10.44	3.50	< 0.01	7.11	0.55
Wch-P4-LY-40r	08/29/18	1.59	15.31	11.26	1.64	12.58	2.45	< 0.01	15.02	0.46
Wch-P4-LY-70	08/29/18	1.14	12.71	18.13	0.73	10.64	1.41	< 0.01	6.46	0.17
Wch-P1-LY-20	09/05/18	1.86	13.71	7.46	11.71	10.48	7.46	< 0.01	14.37	0.55
Wch-P1-LY-40	09/05/18	1.41	14.45	11.61	3.38	10.45	4.19	< 0.01	10.24	0.52
Wch-P1-LY-70	09/05/18	1.69	14.42	26.89	1.24	10.00	2.47	< 0.01	6.69	0.18
Wch-P2-LY-20	09/05/18	7.64	10.58	14.13	18.03	18.60	18.49	< 0.01	29.60	0.69
Wch-P2-LY-40	09/05/18	1.64	11.75	13.82	1.75	9.85	5.66	< 0.01	14.94	0.82
Wch-P2-LY-40r	09/05/18	1.53	14.20	17.21	11.92	13.21	8.78	< 0.01	16.86	0.43
Wch-P2-LY-70	09/05/18	1.41	12.64	29.43	1.21	11.79	5.30	< 0.01	14.43	0.27
Wch-P3-LY-40	09/05/18	1.68	14.66	10.50	1.37	8.08	1.93	< 0.01	5.08	0.61
Wch-P3-LY-70	09/05/18	0.80	12.36	25.14	0.74	7.17	0.80	< 0.01	5.07	0.11
Wch-P3-LY-70r	09/05/18	1.35	14.47	24.67	0.79	7.31	0.83	< 0.01	6.20	0.13

Table C.5 Continued.

Sample	Date	K	Li	Mg	Mn	Na	Ni	Pb	S	Sb
		mg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}
Wch-P4-LY-40r	09/05/18	1.86	14.92	10.43	1.25	11.51	2.15	< 0.01	12.93	0.45
Wch-P4-LY-70	09/05/18	1.14	13.51	17.27	0.74	9.81	1.19	< 0.01	5.86	0.22
Wch-P1-LY-40	09/12/18	1.10	13.73	10.12	1.79	9.26	2.98	< 0.01	8.78	0.57
Wch-P1-LY-70	09/12/18	1.58	14.11	25.52	1.08	9.61	2.35	< 0.01	5.95	0.19
Wch-P2-LY-40	09/12/18	1.22	11.50	14.39	1.45	10.06	5.14	< 0.01	14.03	0.31
Wch-P2-LY-40r	09/12/18	1.92	13.79	12.08	4.04	9.84	6.60	0.10	12.17	2.37
Wch-P2-LY-70	09/12/18	1.52	12.81	28.89	1.03	11.48	4.61	< 0.01	11.75	0.72
Wch-P3-LY-70	09/12/18	1.30	12.84	24.31	1.06	7.22	1.09	< 0.01	4.77	0.41
Wch-P3-LY-70r	09/12/18	1.99	15.01	23.22	1.05	7.26	0.84	< 0.01	5.23	0.33
Wch-P4-LY-40r	09/12/18	1.66	15.56	9.48	0.96	10.84	2.23	< 0.01	11.44	0.62
Wch-P4-LY-70	09/12/18	0.89	13.76	16.60	0.63	9.17	1.38	< 0.01	4.42	0.40
Wch-P1-LY-20	09/26/18	1.72	5.84	25.82	3.97	162.70	7.86	0.07	191.80	0.25
Wch-P1-LY-70	09/26/18	1.39	12.79	25.30	1.22	9.98	2.84	< 0.04	7.38	0.26
Wch-P2-LY-20	09/26/18	5.72	5.84	17.74	12.88	76.28	13.55	< 0.01	73.17	0.40
Wch-P2-LY-40	09/26/18	0.96	8.13	13.46	0.97	9.94	4.80	< 0.01	17.94	0.19
Wch-P2-LY-40r	09/26/18	1.62	10.35	14.02	3.85	14.11	6.34	< 0.01	22.13	0.24
Wch-P2-LY-70	09/26/18	0.82	10.26	25.07	0.79	11.16	3.75	< 0.04	12.37	0.75
Wch-P3-LY-20	09/26/18	2.37	7.55	21.96	10.57	74.86	10.49	< 0.01	113.60	0.37
Wch-P3-LY-40	09/26/18	1.47	10.12	6.65	0.87	6.40	1.96	< 0.01	5.46	0.46
Wch-P3-LY-70	09/26/18	1.01	9.52	20.81	0.85	8.79	1.20	< 0.01	11.91	0.16
Wch-P3-LY-70r	09/26/18	1.21	10.90	22.28	0.90	8.46	1.74	< 0.01	22.03	0.17
Wch-P4-LY-20	09/26/18	1.96	8.45	29.08	10.91	84.51	12.31	< 0.01	131.10	0.27
Wch-P4-LY-40	09/26/18	1.62	11.12	10.78	2.00	10.23	3.74	< 0.01	18.42	0.32
Wch-P4-LY-40r	09/26/18	1.91	12.20	28.04	1.72	39.51	3.56	< 0.01	93.92	0.24
Wch-P4-LY-70	09/26/18	1.32	11.80	15.37	0.90	10.23	2.30	< 0.01	7.29	0.28

Table C.5 Continued.

Sample	Date	Se	Si	Sr	Ti	Tl	V	Zn
		µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Wch-P1-LY-20	08/15/18	< 2	16.20	283.10	< 2	< 0.007	168.00	12.23
Wch-P1-LY-20r	08/15/18	< 2	19.33	283.20	< 2	< 0.007	93.73	38.02
Wch-P1-LY-40	08/15/18	< 2	17.55	354.80	< 2	< 0.007	137.20	7.03
Wch-P1-LY-70	08/15/18	< 2	14.33	711.70	2.04	< 0.007	24.83	22.45
Wch-P2-LY-20	08/15/18	< 2	19.13	338.80	< 2	< 0.007	135.90	15.19
Wch-P2-LY-40	08/15/18	< 2	16.30	410.50	< 2	< 0.03	82.58	20.32
Wch-P2-LY-40r	08/15/18	< 2	17.86	366.60	< 0.5	< 0.007	83.33	78.59
Wch-P2-LY-70	08/15/18	< 2	15.96	699.90	1.57	0.04	23.10	37.75
Wch-P3-LY-20	08/15/18	< 2	17.91	265.90	< 2	< 0.007	102.40	61.63
Wch-P3-LY-40	08/15/18	< 2	15.06	372.80	< 2	< 0.007	126.70	4.17
Wch-P3-LY-70	08/15/18	< 2	14.27	621.80	2.31	< 0.007	40.83	38.48
Wch-P3-LY-70r	08/15/18	< 2	14.11	654.60	< 2	< 0.03	28.06	28.75
Wch-P4-LY-20	08/15/18	< 2	16.12	231.80	< 2	< 0.007	79.32	52.65
Wch-P4-LY-40	08/15/18	< 2	16.08	359.80	< 2	< 0.007	68.99	45.36
Wch-P4-LY-40r	08/15/18	< 2	15.71	457.20	< 2	< 0.007	91.99	39.72
Wch-P4-LY-70	08/15/18	< 2	14.34	472.10	< 2	< 0.03	31.81	41.80
Wch-P1-LY-20	08/22/18	< 2	16.79	244.90	< 2	< 0.007	124.30	9.13
Wch-P1-LY-20r	08/22/18	< 2	19.04	255.10	< 2	< 0.007	77.87	20.55
Wch-P1-LY-70	08/22/18	< 2	14.88	670.10	1.80	< 0.007	19.60	16.79
Wch-P2-LY-20	08/22/18	< 2	18.71	1006.00	2.61	0.07	118.00	10.03
Wch-P2-LY-40	08/22/18	< 2	17.18	395.90	< 2	< 0.03	52.49	22.20
Wch-P2-LY-40r	08/22/18	< 2	17.93	1336.00	2.02	0.06	62.66	65.58
Wch-P2-LY-70	08/22/18	< 2	17.48	696.80	2.09	< 0.03	20.71	24.93
Wch-P3-LY-20	08/22/18	< 2	18.61	225.10	< 2	< 0.007	67.31	46.44
Wch-P3-LY-40	08/22/18	< 2	14.70	347.30	< 2	< 0.007	88.30	3.93
Wch-P3-LY-70	08/22/18	< 2	14.13	626.60	< 2	< 0.007	20.72	20.92
Wch-P3-LY-70r	08/22/18	< 2	14.35	656.20	< 2	< 0.03	20.62	17.33

Table C.5 Continued.

Sample	Date	Se	Si	Sr	Ti	Tl	V	Zn
		µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Wch-P4-LY-20	08/22/18	< 2	16.40	183.60	< 2	< 0.007	62.96	35.63
Wch-P4-LY-40	08/22/18	< 2	16.31	341.30	< 2	< 0.007	55.80	25.12
Wch-P4-LY-40r	08/22/18	< 2	15.55	398.90	< 2	< 0.007	73.49	21.33
Wch-P4-LY-70	08/22/18	< 2	14.37	463.30	< 2	< 0.007	22.16	24.44
Wch-P1-LY-40	08/29/18	< 2	16.84	331.40	< 2	< 0.007	127.70	4.78
Wch-P1-LY-70	08/29/18	< 2	16.92	666.90	< 2	< 0.007	25.20	10.21
Wch-P2-LY-20	08/29/18	< 2	23.40	601.80	1.53	0.05	76.78	10.53
Wch-P2-LY-40	08/29/18	< 2	17.08	372.80	< 2	< 0.007	44.16	18.25
Wch-P2-LY-40r	08/29/18	< 2	17.87	559.30	< 2	< 0.03	63.97	23.29
Wch-P2-LY-70	08/29/18	< 2	17.87	677.40	1.81	< 0.03	16.18	22.98
Wch-P3-LY-20	08/29/18	< 2	19.40	203.50	< 2	< 0.007	37.63	38.96
Wch-P3-LY-40	08/29/18	< 2	14.58	318.20	< 2	< 0.007	83.84	3.58
Wch-P3-LY-70	08/29/18	< 2	14.30	620.80	< 2	< 0.007	10.86	143.60
Wch-P3-LY-70r	08/29/18	< 2	15.00	605.80	< 2	< 0.007	21.67	8.64
Wch-P4-LY-40	08/29/18	< 2	16.90	317.50	< 2	< 0.007	80.53	12.55
Wch-P4-LY-40r	08/29/18	< 2	15.90	314.40	< 2	< 0.007	87.21	12.35
Wch-P4-LY-70	08/29/18	< 2	14.98	459.70	< 2	< 0.007	23.96	13.08
Wch-P1-LY-20	09/05/18	< 2	17.82	245.60	< 2	< 0.007	77.73	5.12
Wch-P1-LY-40	09/05/18	< 2	17.77	330.10	< 2	< 0.007	101.40	4.05
Wch-P1-LY-70	09/05/18	< 2	17.06	674.30	1.68	< 0.007	25.04	8.06
Wch-P2-LY-20	09/05/18	< 2	23.17	505.30	1.77	< 0.03	55.37	24.42
Wch-P2-LY-40	09/05/18	< 2	16.21	364.40	< 2	< 0.03	43.20	14.92
Wch-P2-LY-40r	09/05/18	< 2	17.02	495.10	< 2	< 0.03	54.06	24.82
Wch-P2-LY-70	09/05/18	< 2	18.29	662.30	< 2	< 0.03	17.18	20.12
Wch-P3-LY-40	09/05/18	< 2	14.75	290.80	< 0.5	< 0.007	82.45	6.16
Wch-P3-LY-70	09/05/18	< 2	14.32	615.10	2.00	< 0.007	9.45	11.85
Wch-P3-LY-70r	09/05/18	< 2	16.07	577.00	< 2	< 0.007	21.68	7.70

Table C.5 Continued.

Sample	Date	Se	Si	Sr	Ti	Tl	V	Zn
		µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Wch-P4-LY-40r	09/05/18	< 2	16.11	300.00	< 2	< 0.007	83.43	7.35
Wch-P4-LY-70	09/05/18	< 2	15.70	452.30	< 2	< 0.03	25.01	9.21
Wch-P1-LY-40	09/12/18	< 2	15.83	300.20	< 2	< 0.007	82.63	1.31
Wch-P1-LY-70	09/12/18	< 2	17.51	653.40	< 2	< 0.007	22.86	6.71
Wch-P2-LY-40	09/12/18	< 2	17.40	352.50	< 2	< 0.03	40.78	9.69
Wch-P2-LY-40r	09/12/18	< 2	15.81	337.90	< 2	0.10	46.74	11.06
Wch-P2-LY-70	09/12/18	< 2	19.32	654.40	1.63	0.03	18.47	16.02
Wch-P3-LY-70	09/12/18	< 2	16.93	604.00	1.72	< 0.03	17.79	8.16
Wch-P3-LY-70r	09/12/18	< 2	17.50	559.50	< 2	< 0.03	28.55	6.06
Wch-P4-LY-40r	09/12/18	< 2	15.83	274.10	< 2	< 0.007	72.73	4.80
Wch-P4-LY-70	09/12/18	< 2	16.78	433.10	< 2	< 0.03	31.48	4.11
Wch-P1-LY-20	09/26/18	< 2	8.80	997.90	< 2	< 0.007	19.32	38.04
Wch-P1-LY-70	09/26/18	< 2	15.98	651.90	< 2	< 0.007	18.42	8.63
Wch-P2-LY-20	09/26/18	< 2	13.87	654.50	1.57	< 0.03	29.66	58.91
Wch-P2-LY-40	09/26/18	< 2	12.89	367.00	< 2	< 0.03	21.71	16.39
Wch-P2-LY-40r	09/26/18	< 2	13.75	397.70	< 2	< 0.007	33.21	29.91
Wch-P2-LY-70	09/26/18	< 2	15.75	548.40	< 2	0.03	11.84	15.39
Wch-P3-LY-20	09/26/18	< 2	11.63	760.00	< 2	< 0.03	18.75	91.02
Wch-P3-LY-40	09/26/18	< 2	11.72	190.90	< 2	< 0.007	68.05	3.91
Wch-P3-LY-70	09/26/18	< 2	12.66	508.80	< 2	< 0.007	9.53	8.73
Wch-P3-LY-70r	09/26/18	< 2	13.59	545.30	< 2	< 0.03	12.48	12.17
Wch-P4-LY-20	09/26/18	< 2	11.58	992.70	< 2	< 0.03	28.88	92.84
Wch-P4-LY-40	09/26/18	< 2	13.77	299.80	< 2	< 0.007	48.97	28.89
Wch-P4-LY-40r	09/26/18	< 2	12.44	892.90	< 2	< 0.007	40.65	35.49
Wch-P4-LY-70	09/26/18	< 2	17.38	374.40	< 2	< 0.03	30.49	6.68

Table C.6 Summary of pore-water cation concentrations from the Winchester field site in 2019.

Sample	Date	Al	As	B	Ca	Cd	Co	Cr	Cu	Fe
		µg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
WCH-P1-Ly-20	06/05/19	14.69	1.39	45.58	42.66	0.37	0.65	0.38	21.34	9.58
WCH-P1-Ly-40	06/05/19	5.72	0.79	41.23	48.25	0.33	0.21	< 0.3	13.57	7.27
WCH-P1-Ly-70	06/05/19	3.37	0.67	25.10	73.06	0.18	< 0.2	< 0.3	10.75	25.66
WCH-P1-Ly-20r	06/05/19	6.68	0.79	34.87	32.81	0.39	0.26	0.27	18.38	7.94
WCH-P2-Ly-20	06/05/19	17.75	0.79	37.76	31.74	0.32	0.48	0.44	27.61	18.88
WCH-P2-Ly-40	06/05/19	5.65	1.32	39.81	58.06	0.64	0.99	< 0.3	15.12	5.41
WCH-P2-Ly-70	06/05/19	3.28	0.39	22.68	79.99	0.43	0.37	< 0.3	12.34	164.40
WCH-P2-Ly-40r	06/05/19	4.27	1.19	49.62	68.62	0.42	0.57	< 0.3	19.09	7.17
WCH-P3-Ly-20	06/05/19	10.19	0.72	29.04	30.99	0.27	0.57	0.25	22.97	13.61
WCH-P3-Ly-40	06/05/19	5.66	0.91	36.00	47.48	0.47	0.65	< 0.3	12.21	4.60
WCH-P3-Ly-70	06/05/19	14.36	1.99	25.43	41.95	0.24	< 0.2	< 0.3	10.71	17.42
WCH-P3-Ly-70r	06/05/19	4.41	0.77	15.18	83.14	0.14	< 0.2	< 0.3	11.47	4.06
WCH-P4-Ly-20	06/05/19	7.94	0.88	35.60	36.28	0.23	0.65	0.44	20.33	7.72
WCH-P4-Ly-40	06/05/19	3.14	1.74	27.93	35.80	0.17	0.20	< 0.3	12.12	3.08
WCH-P4-Ly-70	06/05/19	3.43	0.83	13.98	57.25	0.18	< 0.2	< 0.3	11.10	2.51
WCH-P4-Ly-40r	06/05/19	4.18	2.03	34.12	33.96	0.23	0.21	< 0.3	12.13	4.01
WCH-P1-Ly-20	06/18/19	12.60	1.21	55.49	50.29	0.43	0.53	0.49	25.17	15.51
WCH-P1-Ly-40	06/18/19	5.69	0.52	39.15	49.08	0.22	< 0.2	< 0.3	13.16	6.94
WCH-P1-Ly-70	06/18/19	4.24	0.68	25.62	78.69	0.11	< 0.2	< 0.07	10.28	53.11
WCH-P1-Ly-20r	06/18/19	7.16	0.72	43.01	48.77	0.41	0.20	0.26	20.43	8.77
WCH-P2-Ly-20	06/18/19	20.29	0.94	51.28	44.58	0.40	0.45	0.54	33.98	16.92
WCH-P2-Ly-40	06/18/19	5.65	1.18	45.22	62.31	0.62	0.46	< 0.3	18.07	5.32
WCH-P2-Ly-70	06/18/19	4.51	0.35	25.73	83.67	0.18	0.19	< 0.3	14.11	16.39
WCH-P2-Ly-40r	06/18/19	4.70	0.89	41.89	78.14	0.35	0.25	< 0.3	17.40	6.89
WCH-P3-Ly-20	06/18/19	15.38	1.12	38.31	31.66	0.43	0.51	0.36	29.01	17.36
WCH-P3-Ly-40	06/18/19	4.39	0.76	36.27	44.65	0.29	0.29	< 0.3	12.15	4.92
WCH-P3-Ly-70	06/18/19	14.46	1.14	23.55	48.72	0.13	< 0.2	0.23	10.77	19.90
WCH-P3-Ly-70r	06/18/19	8.68	0.59	15.31	86.77	0.10	< 0.2	0.30	11.29	3.82

Table C.6 Continued.

Sample	Date	Al	As	B	Ca	Cd	Co	Cr	Cu	Fe
		µg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
WCH-P4-Ly-20	06/18/19	11.87	1.05	45.66	37.86	0.26	0.47	0.26	24.44	10.30
WCH-P4-Ly-40	06/18/19	3.25	1.36	25.18	41.20	0.15	0.18	< 0.3	11.28	3.55
WCH-P4-Ly-70	06/18/19	4.94	0.57	15.20	56.58	0.10	< 0.2	< 0.3	11.08	7.08
WCH-P4-Ly-40r	06/18/19	3.23	1.36	30.08	35.59	0.18	< 0.2	< 0.3	11.68	2.54
WCH-P1-Ly-20	06/27/19	3.16	1.85	41.99	35.67	0.21	0.20	< 0.3	13.23	3.38
WCH-P1-Ly-40	06/27/19	1.65	0.53	52.60	49.29	0.23	< 0.2	< 0.3	12.15	3.45
WCH-P1-Ly-70	06/27/19	1.97	0.67	27.47	77.99	0.08	< 0.2	< 0.07	10.66	12.78
WCH-P1-Ly-20r	06/27/19	6.58	0.86	51.05	45.51	0.37	0.17	0.23	22.04	6.15
WCH-P2-Ly-40	06/27/19	3.38	1.29	54.92	63.69	0.53	0.38	< 0.3	17.82	16.45
WCH-P2-Ly-70	06/27/19	3.43	0.34	29.74	87.67	0.15	< 0.2	< 0.3	13.07	6.80
WCH-P2-Ly-40r	06/27/19	5.64	1.62	66.36	74.97	0.41	0.24	< 0.3	20.81	6.51
WCH-P3-Ly-70	06/27/19	3.60	1.10	26.74	45.44	0.10	< 0.2	0.26	10.30	7.14
WCH-P3-Ly-70r	06/27/19	3.58	0.56	16.97	84.88	0.06	< 0.2	0.31	10.31	2.76
WCH-P4-Ly-20	06/27/19	11.19	1.29	56.53	36.04	0.23	0.45	0.29	25.58	12.23
WCH-P4-Ly-40	06/27/19	3.92	1.80	36.53	35.70	0.15	0.17	< 0.07	12.20	2.59
WCH-P4-Ly-70	06/27/19	4.31	0.81	19.89	55.97	0.28	0.27	0.33	10.11	3.12
WCH-P4-Ly-40r	06/27/19	4.29	1.97	42.78	33.95	0.20	0.18	< 0.3	12.03	2.97
WCH-P1-Ly-20	07/04/19	12.92	1.29	83.16	42.58	0.29	0.46	0.35	27.91	11.00
WCH-P1-Ly-40	07/04/19	3.54	0.71	60.75	48.07	0.20	0.17	< 0.3	13.24	3.67
WCH-P1-Ly-70	07/04/19	3.57	0.51	29.66	77.40	0.06	< 0.2	< 0.07	11.57	4.07
WCH-P1-Ly-20r	07/04/19	15.81	1.05	65.69	49.69	0.34	0.24	0.30	25.81	12.39
WCH-P2-Ly-20	07/04/19	15.49	1.06	87.63	63.43	0.44	0.46	0.48	35.89	13.47
WCH-P2-Ly-40	07/04/19	4.66	1.25	61.53	64.81	0.39	0.40	< 0.3	21.14	4.94
WCH-P2-Ly-70	07/04/19	2.22	0.40	32.10	81.98	0.12	< 0.2	< 0.3	14.40	3.39
WCH-P2-Ly-40r	07/04/19	3.92	1.75	76.91	71.41	0.30	0.27	< 0.3	22.91	4.52
WCH-P3-Ly-70	07/04/19	6.92	1.03	30.68	50.22	0.09	< 0.2	0.25	11.31	2.72
WCH-P3-Ly-70r	07/04/19	13.69	9.19	22.56	77.83	10.19	9.25	8.26	21.21	10.15
WCH-P4-Ly-20	07/04/19	10.94	1.23	69.18	35.12	0.22	0.44	0.29	28.98	9.84

Table C.6 Continued.

Sample	Date	Al	As	B	Ca	Cd	Co	Cr	Cu	Fe
		µg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
WCH-P4-Ly-40	07/04/19	3.74	1.95	42.76	34.40	0.17	0.20	< 0.3	13.87	2.80
WCH-P4-Ly-70	07/04/19	5.51	0.58	19.69	49.75	0.14	< 0.2	< 0.3	11.69	37.14
WCH-P4-Ly-40r	07/04/19	4.41	1.93	43.80	37.16	0.23	0.19	< 0.3	13.27	2.85
WCH-P1-Ly-40	07/18/19	28.47	0.91	61.19	47.20	2.07	1.95	1.26	14.51	4.15
WCH-P1-Ly-70	07/18/19	4.13	0.57	42.54	75.80	0.08	< 0.2	< 0.3	11.48	2.77
WCH-P2-Ly-40	07/18/19	6.20	1.06	67.71	61.68	0.33	0.40	< 0.3	20.44	3.95
WCH-P2-Ly-70	07/18/19	3.81	0.37	41.37	87.82	0.16	0.17	< 0.3	13.31	2.97
WCH-P2-Ly-40r	07/18/19	5.22	1.55	84.56	75.67	0.34	0.29	< 0.3	21.87	3.97
WCH-P3-Ly-40	07/18/19	5.92	0.76	51.26	47.23	0.27	0.36	< 0.3	12.14	2.34
WCH-P3-Ly-70	07/18/19	3.46	0.85	35.62	57.58	0.13	< 0.2	0.27	11.20	2.66
WCH-P3-Ly-70r	07/18/19	5.07	0.78	31.36	83.68	0.07	< 0.2	0.43	10.97	4.95
WCH-P4-Ly-40	07/18/19	11.42	1.64	50.76	37.69	0.13	0.20	< 0.3	18.16	3.83
WCH-P4-Ly-70	07/18/19	4.09	0.66	31.45	57.17	0.09	< 0.2	< 0.3	11.05	3.27
WCH-P4-Ly-40r	07/18/19	4.05	1.66	50.70	40.24	0.17	0.20	< 0.07	12.50	2.42
WCH-P1-Ly-40	08/01/19	< 0.5	0.52	53.81	37.73	0.10	0.18	< 0.3	12.52	< 2
WCH-P1-Ly-70	08/01/19	< 0.5	0.63	47.80	61.69	0.07	< 0.2	< 0.3	11.79	< 2
WCH-P2-Ly-40	08/01/19	< 0.5	0.81	58.44	54.67	0.25	0.37	< 0.3	18.89	2.36
WCH-P2-Ly-70	08/01/19	< 0.5	0.42	43.78	66.49	0.11	0.22	< 0.3	13.84	2.28
WCH-P2-Ly-40r	08/01/19	< 0.5	1.22	78.60	64.07	0.28	0.37	< 0.3	21.01	3.42
WCH-P3-Ly-20	08/01/19	< 0.5	1.19	50.97	32.01	0.23	0.41	< 0.3	25.44	3.89
WCH-P3-Ly-40	08/01/19	< 0.5	0.69	40.71	39.56	0.18	0.26	< 0.3	11.73	4.08
WCH-P3-Ly-70	08/01/19	< 0.5	0.65	31.73	44.95	0.09	< 0.2	< 0.3	10.49	2.81
WCH-P3-Ly-70r	08/01/19	< 0.5	0.69	28.09	64.26	0.06	< 0.2	0.25	10.98	2.42
WCH-P4-Ly-20	08/01/19	< 0.5	0.94	58.91	32.89	0.17	0.38	< 0.3	21.79	3.75
WCH-P4-Ly-40	08/01/19	< 0.5	1.32	43.21	34.48	0.47	0.48	0.30	14.55	3.61
WCH-P4-Ly-70	08/01/19	< 0.5	0.59	29.77	51.64	0.33	0.32	0.27	10.74	3.77
WCH-P4-Ly-40r	08/01/19	< 0.5	1.09	39.04	39.87	0.19	0.21	< 0.3	12.35	2.62

Table C.6 Continued.

Sample	Date	K	Li	Mg	Mn	Na	Ni	Pb	S	Sb
		µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}
WCH-P1-Ly-20	06/05/19	3063.00	9.79	9.82	40.14	93.83	7.94	0.12	71.88	1.98
WCH-P1-Ly-40	06/05/19	1140.00	9.49	12.21	2.38	63.91	2.23	0.06	23.79	1.43
WCH-P1-Ly-70	06/05/19	682.80	10.41	23.20	14.61	34.11	1.67	0.04	14.04	0.35
WCH-P1-Ly-20r	06/05/19	1776.00	6.26	7.89	6.78	51.44	5.78	0.05	31.44	1.79
WCH-P2-Ly-20	06/05/19	2039.00	6.63	6.83	10.86	32.56	6.16	0.07	25.79	0.75
WCH-P2-Ly-40	06/05/19	1299.00	8.90	14.06	13.39	37.98	5.01	0.03	21.55	1.48
WCH-P2-Ly-70	06/05/19	860.10	6.28	23.52	15.05	20.70	5.90	< 0.04	16.41	0.15
WCH-P2-Ly-40r	06/05/19	2386.00	14.16	15.65	16.84	137.40	5.13	0.07	89.59	1.48
WCH-P3-Ly-20	06/05/19	1827.00	6.35	7.06	11.97	42.43	6.58	0.07	26.38	0.90
WCH-P3-Ly-40	06/05/19	1534.00	15.07	11.49	7.32	96.77	3.35	0.04	54.89	1.34
WCH-P3-Ly-70	06/05/19	893.90	13.78	11.30	5.49	104.70	1.76	0.03	31.82	1.49
WCH-P3-Ly-70r	06/05/19	785.30	9.86	20.81	2.04	49.27	1.26	< 0.04	18.34	0.39
WCH-P4-Ly-20	06/05/19	1891.00	7.42	8.03	9.86	52.22	5.35	0.05	36.18	1.55
WCH-P4-Ly-40	06/05/19	1083.00	12.45	8.89	4.87	133.50	1.96	0.03	48.64	1.57
WCH-P4-Ly-70	06/05/19	729.50	10.12	15.99	1.87	77.94	1.28	< 0.04	16.97	0.79
WCH-P4-Ly-40r	06/05/19	1097.00	17.37	8.94	2.07	138.90	2.05	0.03	49.28	2.05
WCH-P1-Ly-20	06/18/19	3480.00	8.88	11.56	20.60	116.50	7.62	0.05	94.36	1.64
WCH-P1-Ly-40	06/18/19	817.00	8.38	12.42	1.03	60.87	1.60	0.03	16.48	0.78
WCH-P1-Ly-70	06/18/19	686.30	11.20	24.77	20.02	41.03	1.57	< 0.04	14.12	0.19
WCH-P1-Ly-20r	06/18/19	2698.00	8.64	11.28	2.97	97.60	5.53	0.05	66.04	1.93
WCH-P2-Ly-20	06/18/19	2702.00	8.20	9.43	11.65	75.49	6.46	0.06	65.03	1.09
WCH-P2-Ly-40	06/18/19	1415.00	9.22	14.79	5.01	63.81	3.58	0.04	34.44	1.27
WCH-P2-Ly-70	06/18/19	762.80	7.13	24.79	13.50	32.41	2.61	< 0.04	18.18	0.22
WCH-P2-Ly-40r	06/18/19	1507.00	8.72	18.24	8.46	85.44	3.40	< 0.04	55.61	0.73
WCH-P3-Ly-20	06/18/19	1612.00	7.92	6.77	7.67	68.60	6.78	0.09	39.56	1.31
WCH-P3-Ly-40	06/18/19	891.00	39.96	10.82	2.32	91.83	1.67	0.04	45.76	1.10
WCH-P3-Ly-70	06/18/19	698.40	13.41	12.88	6.65	85.94	0.88	0.03	78.69	1.14
WCH-P3-Ly-70r	06/18/19	641.10	10.26	21.46	1.33	48.28	0.91	< 0.04	16.88	0.41

Table C.6 Continued.

Sample	Date	K	Li	Mg	Mn	Na	Ni	Pb	S	Sb
		µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}
WCH-P4-Ly-20	06/18/19	1557.00	6.47	8.34	4.40	66.86	4.37	0.04	44.89	1.54
WCH-P4-Ly-40	06/18/19	591.40	9.43	9.95	14.90	100.50	1.44	< 0.04	32.92	1.24
WCH-P4-Ly-70	06/18/19	441.70	10.66	15.63	1.23	79.23	1.05	< 0.04	16.47	0.87
WCH-P4-Ly-40r	06/18/19	542.70	14.17	9.37	2.18	113.30	1.36	< 0.04	40.80	1.52
WCH-P1-Ly-20	06/27/19	623.90	15.39	9.15	3.80	126.10	1.82	0.07	44.93	2.32
WCH-P1-Ly-40	06/27/19	782.90	10.37	12.49	1.03	74.61	1.61	< 0.04	20.28	1.22
WCH-P1-Ly-70	06/27/19	524.70	11.63	24.19	17.38	39.82	1.09	< 0.04	12.93	0.18
WCH-P1-Ly-20r	06/27/19	1951.00	7.11	10.65	2.09	78.70	4.81	< 0.04	58.64	1.49
WCH-P2-Ly-40	06/27/19	1107.00	9.52	14.92	4.16	58.90	3.43	< 0.04	34.77	1.12
WCH-P2-Ly-70	06/27/19	567.90	7.60	25.79	10.83	35.12	1.83	< 0.04	16.78	0.25
WCH-P2-Ly-40r	06/27/19	1841.00	13.27	16.81	6.11	155.90	3.56	0.04	84.09	1.65
WCH-P3-Ly-70	06/27/19	560.30	14.51	11.91	10.57	93.99	0.81	< 0.04	24.82	1.32
WCH-P3-Ly-70r	06/27/19	465.80	10.91	20.75	1.58	48.57	0.84	< 0.04	16.65	0.38
WCH-P4-Ly-20	06/27/19	1711.00	5.35	8.07	2.22	59.86	4.10	< 0.04	40.72	1.56
WCH-P4-Ly-40	06/27/19	520.60	9.92	8.49	13.81	114.80	1.54	< 0.04	32.91	1.73
WCH-P4-Ly-70	06/27/19	374.20	10.99	15.66	1.22	70.92	1.19	0.28	13.91	2.07
WCH-P4-Ly-40r	06/27/19	567.10	15.45	8.73	3.80	120.10	1.49	0.05	42.71	2.31
WCH-P1-Ly-20	07/04/19	2934.00	8.10	9.45	6.94	92.43	5.14	0.05	73.15	1.52
WCH-P1-Ly-40	07/04/19	879.00	11.84	12.14	1.50	80.98	1.55	< 0.04	23.08	1.32
WCH-P1-Ly-70	07/04/19	507.90	11.88	24.07	9.62	32.17	1.27	< 0.04	11.10	0.20
WCH-P1-Ly-20r	07/04/19	2062.00	8.02	11.36	2.83	77.57	5.03	0.04	62.12	1.56
WCH-P2-Ly-20	07/04/19	3414.00	9.19	13.10	6.88	98.41	5.96	0.03	96.85	1.07
WCH-P2-Ly-40	07/04/19	1306.00	10.28	15.00	4.42	62.33	3.55	< 0.04	36.31	1.07
WCH-P2-Ly-70	07/04/19	573.50	7.66	24.38	8.12	26.76	1.78	< 0.04	14.84	0.19
WCH-P2-Ly-40r	07/04/19	1797.00	14.50	15.97	4.75	149.60	3.43	0.04	77.84	1.63
WCH-P3-Ly-70	07/04/19	654.30	15.56	13.20	14.51	86.03	0.98	< 0.04	24.32	1.33
WCH-P3-Ly-70r	07/04/19	557.10	13.07	19.13	10.88	67.18	9.95	3.90	19.94	8.46
WCH-P4-Ly-20	07/04/19	1645.00	5.76	7.77	2.67	53.44	4.14	0.04	37.73	1.40

Table C.6 Continued.

Sample	Date	K	Li	Mg	Mn	Na	Ni	Pb	S	Sb
		µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	mg L^{-1}	µg L^{-1}
WCH-P4-Ly-40	07/04/19	513.80	10.54	8.17	18.87	115.10	1.51	< 0.04	31.36	1.99
WCH-P4-Ly-70	07/04/19	443.50	12.54	13.71	3.64	83.78	1.13	0.08	14.96	1.05
WCH-P4-Ly-40r	07/04/19	646.00	15.75	9.50	5.01	113.00	1.55	0.04	39.38	1.83
WCH-P1-Ly-40	07/18/19	997.00	12.77	11.89	3.49	78.22	3.83	0.16	26.26	1.16
WCH-P1-Ly-70	07/18/19	658.70	15.22	23.39	2.46	60.33	1.84	< 0.04	14.97	0.74
WCH-P2-Ly-40	07/18/19	1072.00	11.35	14.51	3.48	63.91	3.54	< 0.04	38.47	0.93
WCH-P2-Ly-70	07/18/19	654.30	9.57	26.01	1.16	39.31	1.87	< 0.01	15.67	0.28
WCH-P2-Ly-40r	07/18/19	1805.00	15.99	17.04	5.60	148.90	3.69	< 0.04	81.82	1.40
WCH-P3-Ly-40	07/18/19	1128.00	16.74	11.35	2.69	98.61	1.96	< 0.04	52.65	1.06
WCH-P3-Ly-70	07/18/19	724.30	16.79	14.87	15.23	85.95	1.05	< 0.04	27.99	1.17
WCH-P3-Ly-70r	07/18/19	579.40	15.25	20.75	0.86	79.15	0.91	< 0.01	24.55	0.89
WCH-P4-Ly-40	07/18/19	614.60	11.76	9.03	23.87	119.00	3.90	< 0.04	35.53	2.03
WCH-P4-Ly-70	07/18/19	542.80	14.59	15.74	1.11	92.67	1.07	< 0.04	19.76	1.37
WCH-P4-Ly-40r	07/18/19	772.00	17.80	10.43	6.32	118.80	1.70	< 0.04	49.09	1.80
WCH-P1-Ly-40	08/01/19	908.00	12.02	10.18	1.14	60.23	1.58	< 0.01	27.71	0.64
WCH-P1-Ly-70	08/01/19	834.00	17.09	20.19	3.87	76.13	1.95	< 0.01	24.48	0.77
WCH-P2-Ly-40	08/01/19	976.00	10.83	12.84	3.33	54.28	3.33	< 0.04	36.01	0.55
WCH-P2-Ly-70	08/01/19	890.00	10.97	21.42	0.98	47.85	2.40	< 0.01	19.33	0.33
WCH-P2-Ly-40r	08/01/19	1617.00	14.76	15.34	5.08	131.20	3.77	< 0.04	76.00	1.03
WCH-P3-Ly-20	08/01/19	1719.00	8.92	6.93	15.80	43.13	4.67	< 0.04	20.79	0.47
WCH-P3-Ly-40	08/01/19	993.00	15.45	9.70	2.27	77.64	1.81	< 0.01	43.65	0.48
WCH-P3-Ly-70	08/01/19	726.30	16.32	13.61	11.61	73.55	1.00	< 0.04	29.44	0.75
WCH-P3-Ly-70r	08/01/19	541.90	14.80	16.97	0.73	69.26	1.07	< 0.04	23.91	0.67
WCH-P4-Ly-20	08/01/19	1540.00	5.85	7.52	2.19	41.04	3.29	< 0.04	29.77	0.33
WCH-P4-Ly-40	08/01/19	611.60	11.13	8.31	28.73	102.60	1.94	0.22	32.71	1.07
WCH-P4-Ly-70	08/01/19	555.90	14.22	14.76	1.13	82.04	1.54	0.07	21.18	0.93
WCH-P4-Ly-40r	08/01/19	805.00	15.89	10.38	5.54	107.90	1.72	< 0.04	51.17	0.95

Table C.6 Continued.

Sample	Date	Se	Si	Sr	Ti	Tl	V	Zn
		µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
WCH-P1-Ly-20	06/05/19	< 2	10.18	396.20	< 2	0.03	13.60	42.73
WCH-P1-Ly-40	06/05/19	< 2	8.59	418.20	2.22	0.04	17.80	29.54
WCH-P1-Ly-70	06/05/19	< 2	7.63	608.60	< 2	< 0.03	2.00	13.44
WCH-P1-Ly-20r	06/05/19	< 2	10.83	288.10	< 2	0.02	10.37	35.97
WCH-P2-Ly-20	06/05/19	< 2	10.84	279.70	< 2	< 0.03	10.68	34.82
WCH-P2-Ly-40	06/05/19	< 2	10.59	438.60	< 2	0.04	14.08	97.80
WCH-P2-Ly-70	06/05/19	< 2	6.91	583.90	< 2	0.04	3.19	50.35
WCH-P2-Ly-40r	06/05/19	< 2	10.05	584.70	< 2	0.04	19.11	40.94
WCH-P3-Ly-20	06/05/19	< 2	11.52	255.80	< 2	< 0.03	10.35	33.44
WCH-P3-Ly-40	06/05/19	< 7	12.49	390.60	< 2	< 0.03	19.77	90.33
WCH-P3-Ly-70	06/05/19	< 2	10.41	309.90	1.57	0.03	3.57	28.78
WCH-P3-Ly-70r	06/05/19	< 2	9.13	546.80	< 2	0.04	2.58	14.76
WCH-P4-Ly-20	06/05/19	< 2	10.39	310.30	< 2	0.03	16.66	37.75
WCH-P4-Ly-40	06/05/19	< 7	9.39	299.70	< 2	0.03	12.52	13.18
WCH-P4-Ly-70	06/05/19	< 7	8.68	444.80	< 2	0.03	3.53	12.54
WCH-P4-Ly-40r	06/05/19	< 7	11.84	288.20	< 2	0.04	10.90	29.14
WCH-P1-Ly-20	06/18/19	< 2	11.91	435.70	< 2	< 0.03	20.02	56.35
WCH-P1-Ly-40	06/18/19	< 2	8.97	392.40	< 2	< 0.03	11.36	16.01
WCH-P1-Ly-70	06/18/19	< 2	8.79	613.60	< 2	< 0.03	1.61	9.18
WCH-P1-Ly-20r	06/18/19	< 2	13.03	399.50	< 2	< 0.03	15.38	37.36
WCH-P2-Ly-20	06/18/19	< 2	12.40	376.20	< 2	< 0.03	18.05	46.76
WCH-P2-Ly-40	06/18/19	< 2	11.15	459.60	< 2	0.03	12.65	73.82
WCH-P2-Ly-70	06/18/19	< 2	7.56	600.30	< 2	0.03	2.95	16.56
WCH-P2-Ly-40r	06/18/19	< 2	8.90	625.20	< 2	0.03	14.19	41.31
WCH-P3-Ly-20	06/18/19	< 2	13.91	262.00	< 2	< 0.03	18.28	37.97
WCH-P3-Ly-40	06/18/19	< 2	12.51	365.10	< 2	< 0.03	12.14	32.51
WCH-P3-Ly-70	06/18/19	< 2	11.46	368.00	< 2	0.03	2.60	14.56
WCH-P3-Ly-70r	06/18/19	< 2	9.71	557.40	< 2	0.04	2.54	9.24

Table C.6 Continued.

Sample	Date	Se	Si	Sr	Ti	Tl	V	Zn
		µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
WCH-P4-Ly-20	06/18/19	< 2	11.59	305.60	< 2	0.02	16.93	35.04
WCH-P4-Ly-40	06/18/19	< 2	10.05	338.10	< 2	0.03	9.53	15.62
WCH-P4-Ly-70	06/18/19	< 7	9.30	439.80	< 2	< 0.03	2.71	6.90
WCH-P4-Ly-40r	06/18/19	< 2	11.46	302.00	< 2	0.02	7.07	17.04
WCH-P1-Ly-20	06/27/19	< 2	13.47	317.10	< 0.5	0.05	6.89	14.59
WCH-P1-Ly-40	06/27/19	< 2	10.73	413.80	< 2	< 0.03	15.48	14.65
WCH-P1-Ly-70	06/27/19	< 2	9.19	629.40	< 2	< 0.03	1.96	4.67
WCH-P1-Ly-20r	06/27/19	< 2	13.41	387.80	< 0.5	< 0.03	14.41	20.28
WCH-P2-Ly-40	06/27/19	< 2	12.58	487.20	< 2	0.03	14.09	46.53
WCH-P2-Ly-70	06/27/19	< 2	8.00	602.50	< 2	0.03	3.22	11.93
WCH-P2-Ly-40r	06/27/19	< 2	11.80	621.80	< 2	0.04	19.11	30.42
WCH-P3-Ly-70	06/27/19	< 2	11.97	344.50	< 2	0.04	2.58	10.33
WCH-P3-Ly-70r	06/27/19	< 2	10.45	551.30	< 2	0.03	2.31	6.51
WCH-P4-Ly-20	06/27/19	< 2	12.36	294.00	< 2	< 0.03	17.33	18.91
WCH-P4-Ly-40	06/27/19	< 2	10.79	306.50	< 2	0.02	7.42	9.73
WCH-P4-Ly-70	06/27/19	< 7	9.42	444.10	< 2	0.24	2.82	5.34
WCH-P4-Ly-40r	06/27/19	< 2	12.89	313.90	< 2	0.05	6.88	14.41
WCH-P1-Ly-20	07/04/19	< 2	12.68	383.50	< 2	0.02	21.89	56.73
WCH-P1-Ly-40	07/04/19	< 2	11.37	410.00	< 2	< 0.03	17.28	16.08
WCH-P1-Ly-70	07/04/19	< 2	8.83	636.80	< 2	< 0.03	2.27	6.19
WCH-P1-Ly-20r	07/04/19	< 2	15.36	432.80	< 2	0.03	16.83	20.03
WCH-P2-Ly-20	07/04/19	< 2	14.50	513.20	< 2	< 0.03	19.58	36.14
WCH-P2-Ly-40	07/04/19	< 2	12.87	507.70	< 2	0.03	13.59	35.60
WCH-P2-Ly-70	07/04/19	< 2	8.63	611.40	< 2	0.04	4.18	10.59
WCH-P2-Ly-40r	07/04/19	< 2	12.42	617.30	< 2	0.03	19.54	22.99
WCH-P3-Ly-70	07/04/19	< 2	12.58	396.80	< 2	0.03	3.32	11.14
WCH-P3-Ly-70r	07/04/19	8.67	10.86	533.10	6.25	8.06	12.13	16.73
WCH-P4-Ly-20	07/04/19	< 2	12.82	302.10	< 2	0.03	16.76	19.93

Table C.6 Continued.

Sample	Date	Se	Si	Sr	Ti	Tl	V	Zn
		µg L^{-1}	mg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
WCH-P4-Ly-40	07/04/19	< 2	11.50	301.80	< 2	0.02	7.07	12.12
WCH-P4-Ly-70	07/04/19	< 2	10.07	425.00	< 2	0.10	3.06	7.49
WCH-P4-Ly-40r	07/04/19	< 2	13.63	338.30	< 0.5	0.02	8.38	44.51
WCH-P1-Ly-40	07/18/19	< 2	11.27	418.50	< 2	0.97	23.35	18.63
WCH-P1-Ly-70	07/18/19	< 2	10.68	653.20	< 2	< 0.03	3.67	5.96
WCH-P2-Ly-40	07/18/19	< 2	12.67	508.40	< 2	< 0.03	15.66	33.01
WCH-P2-Ly-70	07/18/19	< 2	9.66	656.30	< 2	0.03	4.72	11.77
WCH-P2-Ly-40r	07/18/19	< 2	12.50	664.20	< 2	0.02	21.27	24.20
WCH-P3-Ly-40	07/18/19	< 2	14.70	411.30	< 2	< 0.03	19.75	26.01
WCH-P3-Ly-70	07/18/19	< 2	13.25	457.00	< 2	0.03	4.09	12.32
WCH-P3-Ly-70r	07/18/19	< 2	12.40	571.60	< 2	0.04	3.54	7.70
WCH-P4-Ly-40	07/18/19	< 2	11.97	328.70	< 2	< 0.03	7.95	11.13
WCH-P4-Ly-70	07/18/19	< 2	11.21	505.10	< 2	0.02	4.38	6.57
WCH-P4-Ly-40r	07/18/19	< 2	13.88	377.90	< 2	< 0.03	9.70	13.81
WCH-P1-Ly-40	08/01/19	< 2	4.40	352.50	< 0.5	< 0.03	21.13	33.43
WCH-P1-Ly-70	08/01/19	< 2	5.50	592.00	< 0.5	< 0.03	4.71	5.61
WCH-P2-Ly-40	08/01/19	< 2	3.44	458.80	< 0.5	< 0.03	13.77	29.69
WCH-P2-Ly-70	08/01/19	< 2	4.74	568.40	< 0.5	0.04	7.01	9.55
WCH-P2-Ly-40r	08/01/19	< 2	6.43	585.50	< 0.5	0.03	19.10	13.81
WCH-P3-Ly-20	08/01/19	< 2	7.91	280.30	< 0.5	< 0.03	21.51	17.41
WCH-P3-Ly-40	08/01/19	< 2	3.78	355.30	< 0.5	< 0.03	15.19	17.71
WCH-P3-Ly-70	08/01/19	< 2	4.64	402.20	< 0.5	0.02	4.17	9.28
WCH-P3-Ly-70r	08/01/19	< 2	5.52	488.70	< 0.5	0.03	3.46	5.22
WCH-P4-Ly-20	08/01/19	< 2	3.79	294.10	< 0.5	< 0.03	14.76	17.79
WCH-P4-Ly-40	08/01/19	< 2	4.06	307.30	< 0.5	0.28	7.67	10.15
WCH-P4-Ly-70	08/01/19	< 2	3.95	472.40	< 0.5	0.19	4.66	7.85
WCH-P4-Ly-40r	08/01/19	< 2	3.66	364.60	< 0.5	0.06	8.26	12.47

Table C.7 Summary of pore-water saturation indices from the Winchester field site in 2018.

		Saturation indices calculated with PHREEQC				
Sample	Date	Calcite	Dolomite	Rhodochrosite	Ferrihydrite	Goethite
Wch-P1-LY-20	08/15/18	-0.62	-1.55	-1.30	1.31	4.03
Wch-P1-LY-20r	08/15/18	-0.74	-1.77	-1.64	-0.75	1.97
Wch-P1-LY-40	08/15/18	-0.98	-2.24	-2.24	-1.24	1.48
Wch-P1-LY-70	08/15/18	-0.14	-0.46	-2.32	-1.11	1.62
Wch-P2-LY-20	08/15/18	-0.75	-1.84	-0.92	1.93	4.65
Wch-P2-LY-40	08/15/18	-0.79	-1.85	-1.89	-1.22	1.50
Wch-P2-LY-40r	08/15/18	-0.86	-1.99	-1.65	1.17	3.90
Wch-P2-LY-70	08/15/18	-0.09	-0.41	-1.62	0.69	3.42
Wch-P3-LY-20	08/15/18	-1.24	-2.81	-1.38	1.46	4.18
Wch-P3-LY-40	08/15/18	-1.30	-2.88	-3.24	-1.44	1.28
Wch-P3-LY-70	08/15/18	-0.11	-0.51	-2.17	1.41	4.13
Wch-P3-LY-70r	08/15/18	0.17	0.09	-2.41	-0.78	1.94
Wch-P4-LY-20	08/15/18	-1.24	-2.80	-2.03	0.80	3.52
Wch-P4-LY-40	08/15/18	-1.20	-2.68	-3.32	-1.31	1.41
Wch-P4-LY-40r	08/15/18	-1.36	-3.02	-3.50	-1.50	1.23
Wch-P4-LY-70	08/15/18	-0.57	-1.40	-2.53	-1.05	1.68
Wch-P1-LY-20	08/22/18	-1.02	-2.35	-2.06	1.41	4.13
Wch-P1-LY-20r	08/22/18	-0.89	-2.09	-2.14	1.66	4.39
Wch-P1-LY-70	08/22/18	-0.05	-0.30	-2.72	0.90	3.62
Wch-P2-LY-20	08/22/18	0.81	1.32	-0.24	2.74	5.46
Wch-P2-LY-40	08/22/18	-0.90	-2.06	-2.88	-1.19	1.54
Wch-P2-LY-40r	08/22/18	0.18	0.07	-0.69	2.08	4.80
Wch-P2-LY-70	08/22/18	-0.10	-0.42	-2.63	-1.09	1.63
Wch-P3-LY-20	08/22/18	-1.22	-2.76	-1.95	0.30	3.02
Wch-P3-LY-40	08/22/18	-1.07	-2.43	-3.45	-1.94	0.78
Wch-P3-LY-70	08/22/18	0.06	-0.17	-2.72	-1.69	1.03
Wch-P3-LY-70r	08/22/18	0.02	-0.21	-3.03	-0.92	1.80
Wch-P4-LY-40	08/22/18	-1.15	-2.58	-3.56	-2.96	-0.24
Wch-P4-LY-70	08/22/18	-0.15	-0.54	-3.02	1.70	4.42
Wch-P1-LY-40	08/29/18	-1.10	-2.46	-3.05	-1.15	1.57
Wch-P1-LY-70	08/29/18	0.09	-0.02	-2.74	-0.87	1.85
Wch-P2-LY-20	08/29/18	-0.37	-1.06	-1.78	1.78	4.50
Wch-P2-LY-40	08/29/18	-0.72	-1.71	-3.10	-1.09	1.63
Wch-P2-LY-40r	08/29/18	-0.53	-1.34	-2.05	1.02	3.75
Wch-P2-LY-70	08/29/18	-0.04	-0.29	-2.92	-1.10	1.62
Wch-P3-LY-20	08/29/18	-1.31	-2.94	-2.45	-0.98	1.74

Table C.7 Continued.

		Saturation indices calculated with PHREEQC				
Sample	Date	Calcite	Dolomite	Rhodochrosite	Ferrihydrite	Goethite
Wch-P3-LY-40	08/29/18	-1.15	-2.60	-3.69	-3.08	-0.36
Wch-P3-LY-70	08/29/18	-0.41	-1.11	-3.50	-1.04	1.68
Wch-P3-LY-70r	08/29/18	0.16	0.07	-2.98	-0.86	1.86
Wch-P4-LY-40	08/29/18	-0.78	-1.85	-3.15	-0.96	1.76
Wch-P4-LY-40r	08/29/18	-0.93	-2.16	-3.42	-1.08	1.64
Wch-P4-LY-70	08/29/18	-0.45	-1.16	-3.46	-0.92	1.81
Wch-P1-LY-20	09/05/18	-0.44	-1.21	-1.91	-0.47	2.25
Wch-P1-LY-40	09/05/18	-0.85	-1.98	-3.02	-1.06	1.66
Wch-P1-LY-70	09/05/18	0.07	-0.05	-2.83	-0.92	1.80
Wch-P2-LY-20	09/05/18	-1.08	-2.49	-2.68	2.16	4.88
Wch-P2-LY-40	09/05/18	-0.66	-1.60	-3.19	-1.05	1.67
Wch-P2-LY-40r	09/05/18	-0.59	-1.46	-2.39	0.90	3.62
Wch-P2-LY-70	09/05/18	0.03	-0.15	-2.94	-1.03	1.69
Wch-P3-LY-40	09/05/18	-0.76	-1.81	-3.29	-0.88	1.85
Wch-P3-LY-70	09/05/18	0.07	-0.14	-3.12	-0.98	1.74
Wch-P3-LY-70r	09/05/18	0.23	0.21	-2.88	-0.75	1.97
Wch-P4-LY-40r	09/05/18	-0.67	-1.65	-3.25	-0.81	1.92
Wch-P4-LY-70	09/05/18	-0.19	-0.63	-3.17	-0.88	1.84
Wch-P1-LY-40	09/12/18	-0.27	-0.81	-2.64	-0.47	2.25
Wch-P1-LY-70	09/12/18	0.19	0.18	-2.74	-0.80	1.92
Wch-P2-LY-40	09/12/18	-0.29	-0.85	-2.91	-0.75	1.97
Wch-P2-LY-40r	09/12/18	-0.11	-0.51	-2.22	-0.48	2.24
Wch-P2-LY-70	09/12/18	0.18	0.14	-2.85	-0.89	1.83
Wch-P3-LY-70	09/12/18	0.34	0.38	-2.69	-0.73	1.99
Wch-P3-LY-70r	09/12/18	0.21	0.16	-2.76	-0.68	2.04
Wch-P4-LY-40r	09/12/18	-0.48	-1.26	-3.13	1.97	4.70
Wch-P4-LY-70	09/12/18	0.49	0.74	-2.54	-0.34	2.38
Wch-P1-LY-20	09/26/18	-0.39	-1.10	-2.90	1.60	4.33
Wch-P1-LY-70	09/26/18	0.17	0.14	-2.71	-0.72	2.00
Wch-P2-LY-20	09/26/18	-0.58	-1.52	-2.45	2.13	4.86
Wch-P2-LY-40	09/26/18	-0.74	-1.76	-3.52	-1.19	1.53
Wch-P2-LY-40r	09/26/18	-0.92	-2.12	-3.12	0.58	3.30
Wch-P2-LY-70	09/26/18	0.12	0.02	-2.97	-0.84	1.89
Wch-P3-LY-20	09/26/18	-0.76	-1.85	-2.78	1.59	4.31
Wch-P3-LY-40	09/26/18	-1.32	-2.93	-3.84	-1.37	1.36
Wch-P3-LY-70	09/26/18	0.19	0.10	-2.84	1.64	4.37

Table C.7 Continued.

		Saturation indices calculated with PHREEQC				
Sample	Date	Calcite	Dolomite	Rhodochrosite	Ferrihydrite	Goethite
Wch-P3-LY-70r	09/26/18	-0.09	-0.43	-3.10	-0.76	1.96
Wch-P4-LY-20	09/26/18	-1.09	-2.52	-3.23	1.17	3.90
Wch-P4-LY-40	09/26/18	-1.16	-2.62	-3.54	-1.42	1.30
Wch-P4-LY-40r	09/26/18	-0.31	-0.92	-3.21	-0.71	2.01
Wch-P4-LY-70	09/26/18	-0.01	-0.27	-2.85	-0.61	2.11

Table C.8 Summary of pore-water saturation indices from the Winchester field site in 2019.

		Saturation indices calculated with PHREEQC				
Sample	Date	Calcite	Dolomite	Rhodochrosite	Ferrihydrite	Goethite
WCH-P1-Ly-20	06/05/19	-0.73	-1.77	-1.79	1.52	4.24
WCH-P1-Ly-20r	06/05/19	-0.65	-1.59	-2.36	1.65	4.37
WCH-P1-Ly-40	06/05/19	-0.52	-1.31	-2.86	1.35	4.07
WCH-P1-Ly-70	06/05/19	0.04	-0.10	-1.71	2.00	4.73
WCH-P2-Ly-20	06/05/19	-0.61	-1.57	-2.11	2.09	4.81
WCH-P2-Ly-40	06/05/19	-0.29	-0.87	-1.96	1.44	4.16
WCH-P2-Ly-40r	06/05/19	-0.13	-0.57	-1.78	1.55	4.27
WCH-P2-Ly-70	06/05/19	-0.12	-0.45	-1.89	2.70	5.42
WCH-P3-Ly-20	06/05/19	-0.60	-1.52	-2.04	1.94	4.66
WCH-P3-Ly-40	06/05/19	-0.89	-2.07	-2.74	0.90	3.62
WCH-P3-Ly-70	06/05/19	-0.36	-0.97	-2.29	1.85	4.58
WCH-P3-Ly-70r	06/05/19	0.01	-0.27	-2.66	1.13	3.86
WCH-P4-Ly-20	06/05/19	-0.57	-1.48	-2.17	1.67	4.39
WCH-P4-Ly-40	06/05/19	-0.55	-1.38	-2.46	0.98	3.70
WCH-P4-Ly-40r	06/05/19	-0.78	-1.83	-3.04	1.01	3.73
WCH-P4-Ly-70	06/05/19	-0.13	-0.50	-2.67	1.01	3.74
WCH-P1-Ly-20	06/18/19	-0.92	-2.15	-2.34	1.54	4.26
WCH-P1-Ly-20r	06/18/19	-0.63	-1.58	-2.88	1.46	4.18
WCH-P1-Ly-40	06/18/19	-0.29	-0.85	-3.01	1.49	4.21
WCH-P1-Ly-70	06/18/19	0.12	0.05	-1.52	2.36	5.09
WCH-P2-Ly-20	06/18/19	-1.02	-2.38	-2.63	1.49	4.22
WCH-P2-Ly-40	06/18/19	-0.36	-1.03	-2.50	1.27	4.00
WCH-P2-Ly-40r	06/18/19	-0.35	-1.02	-2.36	1.31	4.03
WCH-P2-Ly-70	06/18/19	-0.19	-0.60	-2.04	1.55	4.28
WCH-P3-Ly-20	06/18/19	-0.33	-1.01	-1.98	2.11	4.83
WCH-P3-Ly-40	06/18/19	-0.61	-1.51	-2.94	1.16	3.89
WCH-P3-Ly-70	06/18/19	-0.36	-0.97	-2.27	1.85	4.57
WCH-P3-Ly-70r	06/18/19	0.01	-0.27	-2.86	1.14	3.86
WCH-P4-Ly-20	06/18/19	-1.04	-2.41	-3.00	1.37	4.09
WCH-P4-Ly-40	06/18/19	-0.52	-1.34	-2.00	1.13	3.85
WCH-P4-Ly-40r	06/18/19	-0.58	-1.41	-2.83	0.92	3.65
WCH-P4-Ly-70	06/18/19	-0.17	-0.57	-2.88	1.43	4.15
WCH-P1-Ly-20	06/27/19	-0.84	-1.94	-2.85	0.90	3.62
WCH-P1-Ly-20r	06/27/19	-0.55	-1.41	-2.92	1.51	4.23
WCH-P1-Ly-40	06/27/19	-0.50	-1.28	-3.23	0.57	3.29
WCH-P1-Ly-70	06/27/19	0.06	-0.06	-1.64	1.64	4.37

Table C.8 Continued.

		Saturation indices calculated with PHREEQC				
Sample	Date	Calcite	Dolomite	Rhodochrosite	Ferrihydrite	Goethite
WCH-P2-Ly-40	06/27/19	-0.46	-1.23	-2.69	1.63	4.36
WCH-P2-Ly-40r	06/27/19	-0.31	-0.93	-2.44	1.33	4.05
WCH-P2-Ly-70	06/27/19	-0.07	-0.36	-2.03	1.25	3.97
WCH-P3-Ly-70	06/27/19	-0.35	-0.96	-2.03	1.34	4.07
WCH-P3-Ly-70r	06/27/19	0.08	-0.12	-2.70	0.99	3.71
WCH-P4-Ly-20	06/27/19	-0.96	-2.25	-3.20	1.66	4.38
WCH-P4-Ly-40	06/27/19	-0.76	-1.82	-2.21	0.77	3.49
WCH-P4-Ly-40r	06/27/19	-0.91	-2.09	-2.90	0.83	3.56
WCH-P4-Ly-70	06/27/19	-0.35	-0.93	-3.05	0.98	3.70
WCH-P1-Ly-20	07/04/19	-0.84	-2.00	-2.66	1.62	4.34
WCH-P1-Ly-20r	07/04/19	-0.56	-1.44	-2.84	1.85	4.57
WCH-P1-Ly-40	07/04/19	-0.48	-1.23	-3.02	0.99	3.72
WCH-P1-Ly-70	07/04/19	0.06	-0.07	-1.90	1.15	3.88
WCH-P2-Ly-20	07/04/19	-0.43	-1.22	-2.43	1.94	4.66
WCH-P2-Ly-40	07/04/19	-0.42	-1.15	-2.63	1.08	3.80
WCH-P2-Ly-40r	07/04/19	-0.01	-0.35	-2.24	1.29	4.02
WCH-P2-Ly-70	07/04/19	-0.18	-0.57	-2.23	1.00	3.72
WCH-P3-Ly-70	07/04/19	-0.43	-1.11	-2.01	0.92	3.64
WCH-P3-Ly-70r	07/04/19	-0.07	-0.42	-1.97	1.60	4.32
WCH-P4-Ly-20	07/04/19	-0.58	-1.50	-2.73	1.82	4.54
WCH-P4-Ly-40	07/04/19	-0.74	-1.78	-2.04	0.80	3.52
WCH-P4-Ly-40r	07/04/19	-0.73	-1.73	-2.64	0.86	3.58
WCH-P4-Ly-70	07/04/19	-0.37	-0.97	-2.55	1.99	4.72
WCH-P1-Ly-40	07/18/19	-0.42	-1.12	-2.59	1.11	3.84
WCH-P1-Ly-70	07/18/19	-0.08	-0.35	-2.62	0.90	3.63
WCH-P2-Ly-40	07/18/19	-0.72	-1.75	-3.01	0.83	3.56
WCH-P2-Ly-40r	07/18/19	-0.37	-1.06	-2.54	1.08	3.81
WCH-P2-Ly-70	07/18/19	-0.20	-0.60	-3.13	0.01	2.73
WCH-P3-Ly-40	07/18/19	-0.96	-2.21	-3.24	0.59	3.31
WCH-P3-Ly-70	07/18/19	-0.37	-1.00	-1.99	0.91	3.63
WCH-P3-Ly-70r	07/18/19	-0.12	-0.51	-3.16	1.17	3.90
WCH-P4-Ly-40	07/18/19	-0.79	-1.87	-2.03	0.86	3.59
WCH-P4-Ly-40r	07/18/19	-0.70	-1.66	-2.55	0.66	3.39
WCH-P4-Ly-70	07/18/19	-0.32	-0.88	-3.08	0.95	3.67
WCH-P1-Ly-40	08/01/19	-0.36	-0.97	-2.92	-0.91	1.82
WCH-P1-Ly-70	08/01/19	-0.12	-0.40	-2.37	-1.06	1.66

Table C.8 Continued.

		Saturation indices calculated with PHREEQC				
Sample	Date	Calcite	Dolomite	Rhodochrosite	Ferrihydrite	Goethite
WCH-P2-Ly-40	08/01/19	-0.74	-1.78	-2.99	0.72	3.44
WCH-P2-Ly-40r	08/01/19	-0.48	-1.25	-2.62	0.99	3.71
WCH-P2-Ly-70	08/01/19	0.00	-0.16	-2.88	0.82	3.54
WCH-P3-Ly-20	08/01/19	-0.93	-2.21	-2.28	1.23	3.95
WCH-P3-Ly-40	08/01/19	-1.01	-2.31	-3.29	0.86	3.59
WCH-P3-Ly-70	08/01/19	-0.63	-1.45	-2.25	0.87	3.59
WCH-P3-Ly-70r	08/01/19	-0.24	-0.75	-3.24	0.90	3.62
WCH-P4-Ly-20	08/01/19	-1.09	-2.50	-3.30	1.11	3.83
WCH-P4-Ly-40	08/01/19	-0.60	-1.49	-1.72	1.03	3.75
WCH-P4-Ly-40r	08/01/19	-0.70	-1.67	-2.60	0.82	3.55
WCH-P4-Ly-70	08/01/19	-0.58	-1.38	-3.28	1.03	3.75

Appendix D: Microplot Experiment and Bioreactor Construction Photos

Figure D.1 Winchester microplot post application and incorporation of amendment.

Figure D.2 Winchester microplot GHG flux chamber during deployment.

Figure D.3 Winchester bioreactor frame being lowered into pit during installation.

Figure D.4 Winchester bioreactor fill material during installation.

Figure D.5 Backfilling soil around Winchester bioreactor during installation.