

**Development of a Comprehensive Nitrogen Budget to Increase
Nitrogen Use Efficiency and Reduce Nitrogen Losses in Semi-Arid
Southern Alberta**

by

Kiah Leicht

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Soil Science

Department of Renewable Resources
University of Alberta

© Kiah Leicht, 2024

Abstract

Synthetic nitrogen (N) fertilizer has increased crop yields, but crop nitrogen use efficiency (NUE) is low. The N fertilizer not taken up by the crop is subject to nitrate leaching, ammonia volatilization, and denitrification losses, contributing to declining air and water quality, ozone layer depletion, and N₂O emissions. Nitrogen budgets, which account for N inputs, N outputs, and changes in soil N stocks, can be used to assess the fate of N in the agroecosystem and to develop effective N management practices that increase NUE and reduce N losses. Process-based ecosystem models such as *ecosys*, which simulate biogeochemical cycling and feedback processes, may be used to generate low-cost and time-efficient estimates of the fate of N in the agroecosystem at variable spatial and temporal resolutions. To identify effective N fertilizer management practices, a comprehensive N budget was developed using the process-based model *ecosys* to assess the effects of N rate (0 – 120 kg N ha⁻¹), N source (Urea vs ESN), irrigation vs dryland, and interannual climatic variability (2008 – 2011) on modelled crop yields, grain N, NUE, N losses, and soil N stocks at a cool, semi-arid site in Southern Alberta. Cool soil temperatures early in the growing season slowed modelled N release from ESN such that N availability from ESN did not better match early season crop N demand compared to conventional urea fertilizer, and ESN did not increase yields, or NUE, or reduce N losses. Nitrogen rate had a greater impact on the N budget than the N source, indicating the importance of optimal N rate applications in effective N fertilizer management. As modelled yield gains diminished (<3%) at N rates >90 kg N ha⁻¹, and modelled N₂O emissions increased linearly with N rate, reducing N fertilizer rate applications from the maximum N rate (120 kg N ha⁻¹) in this study to economically optimum N rates (71 – 79 kg N ha⁻¹) would result in N₂O emission reductions of 18 – 22%, with only minimal yield reductions of 2.7 – 3.6%. Nitrogen fertilizer rate applications > 90 kg N ha⁻¹ greatly increased modelled residual nitrate-N (15 – 51 kg N ha⁻¹) compared to lower N rates, which was subject to downward nitrate-N movement beyond the crop rooting depth and

N leaching. Irrigation and interannual climatic variability affected the magnitude of modelled NH_3 and subsurface N losses, with dry years (e.g., 2009) and dryland sites having greater modelled volatilization losses and wet years (e.g., 2010) and irrigated sites having greater modelled subsurface N losses. When indirect N_2O emissions from modelled volatilization, subsurface and surface N losses were included in N_2O emissions accounting, on average, area-based emission factors increased by 0.06% (+24%), indicating the opportunity for N_2O mitigation by reducing indirect N_2O losses. The results from this thesis could provide a methodology for developing effective N management strategies that balance agronomic benefits with environmental impacts for policymakers and producers.

Preface

This dissertation is an original work by Kiah Leicht. Kiah Leicht conducted the modelling experiments and data analyses, and wrote the thesis under the supervision of Dr. Robert Grant and Dr. Symon Mezbahuddin.

Dr. Robert Grant and Dr. Symon Mezbahuddin assisted with model setup and performance and provided suggestions for the research and writing. Ray Dowbenko, a retired senior agronomist with Nutrien, provided the laboratory dataset in chapter 2 for model testing. Len Kryzanowski, a retired director with Alberta Agriculture, provided the field dataset for model comparison and testing in chapters 2 and 3.

Acknowledgements

I would like to express my deepest gratitude to my supervisors, Dr. Robert Grant and Dr. Symon Mezbahuddin, for providing their time, support, and invaluable advice and guidance. I would like to extend a special thank you to my thesis examiner and chair, Dr. Miles Dyck, for the time he spent reviewing my thesis and chairing my defence. I am also grateful to Ray Dowbenko, and Len Kryzanowski for providing the laboratory and field datasets used for model testing. Thank you to the Land Reclamation International Graduate School (LRIGS) staff for the opportunity to participate in the LRIGS program and for creating a valuable support system among the graduate students. I would also like to thank the Digital Research Alliance of Canada for providing the computational resources for the modelling research.

I would also like to acknowledge the financial support from the Western Grains Research Foundation, as well as the financial support provided by the Alberta Graduate Excellence Scholarship and the Helen & Fred Bentley Forage Crops Graduate Scholarship.

Finally, I would also like to express my gratitude to my friends and family for their love and support, and to my husband, Gleb, for always being there for me and supporting me.

Table of Contents

Abstract	ii
Preface	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	xi
1.0 Introduction	1
2.0 Variation in NUE due to Irrigation and Interannual Climatic Variability Highlights Need for Optimal N Rates, not N Source, to Increase NUE in Semi-Arid Southern Alberta	3
2.1 Introduction.....	3
2.1.1 Right Time.....	4
2.1.2 Right Place.....	4
2.1.3 Right Source.....	5
2.1.4 Right Rate.....	6
2.1.5 Computer Modelling to Inform N Management Practices.....	7
2.1.6 Objectives and Hypotheses.....	8
2.2 Methods.....	9
2.2.1 Model Validation of N Release under Laboratory Conditions.....	9
2.2.1.1 Laboratory Dataset.....	9
2.2.1.2 Modelling N Release under an Increasing Temperature Regime.....	10
2.2.1.3 Modelling Temperature and Moisture Effects on N Release.....	11
2.2.2 Modelling N Source and N Rate Effects on Barley Yields, NUE, and Soil N.....	12
2.2.2.1 Field Dataset.....	12
2.2.2.2 Model Set Up and Simulations.....	13
2.2.2.3 Data Processing and Analyses.....	15
2.3 Results.....	17
2.3.1 Model Validation of N Release under Laboratory Conditions.....	17
2.3.1.1 Modelled vs Measured N Release.....	17
2.3.1.2 Effects of Temperature and Moisture on Modelled N Release.....	18
2.3.2 Modelling N Source and N Rate Effects on Barley Yields, NUE, and Soil N.....	18
2.3.2.1 Soil Moisture and Temperature.....	18
2.3.2.2 Inorganic and Organic Soil N.....	19

2.3.2.3 Synchronization of Modelled N Release from Urea and ESN with Barley N Uptake	20
2.3.2.4 Barley Grain Yields and Grain N	20
2.3.2.5 EONR	21
2.3.2.6 NUE	22
2.4 Discussion.....	23
2.4.1 Sensitivity of N Release to Temperature and Moisture	23
2.4.2 Lag in N Release from ESN	24
2.4.3 Effectiveness of ESN in Increasing Barley Grain Yields, Grain N, and NUE	25
2.4.4 Modelled Barley Grain Yield Response to Increasing N Rates and Factors Affecting the EONR	28
2.4.5 Effects of N Fertilization on NUE	29
2.4.6 Variation in NUE with Irrigation and Interannual Climatic Variability	31
2.4.7 Economic and Environmental Sustainability: NUE at the EONR	33
2.5 Conclusion.....	34
2.6 References.....	35
2.7 Tables	41
2.8 Figures.....	46
2.9 Appendix.....	55
3.0 Development of a Comprehensive Nitrogen Budget Indicates Need for Optimal N Rate, not N source, to Reduce Direct and Indirect N₂O Emissions at Dryland and Irrigated Sites in Semi-Arid Southern Alberta	68
3.1 Introduction	68
3.2 Methods.....	72
3.2.1 Field Dataset	72
3.2.2 Model Set Up and Simulations.....	73
3.2.3 Data Processing and Analyses	75
3.3 Results.....	77
3.3.1 Modelled Soil Temperature, Soil Moisture and Discharge.....	77
3.3.2 Nitrogen Budget.....	77
3.3.2.1 Modelled Inorganic and Organic Soil N.....	77
3.3.2.2 Modelled Nitrogen Losses: N ₂ O, N ₂ , NH ₃ , N Runoff, and Subsurface N Losses.....	79
3.3.3 Area-Based Emission Factors and Yield-Scaled Emissions	82
3.4 Discussion.....	84
3.4.1 Effectiveness of ESN in Reducing Nitrogen Losses	84
3.4.1.1 Inorganic N Accumulation	84

3.4.1.2 N ₂ O-N, NH ₃ -N and Subsurface N Losses.....	85
3.4.1.3 Factors Influencing ESN Effectiveness: Climatic Conditions, Soil Properties, and Management Practices	87
3.4.2 Nitrogen Losses and Nitrogen Rate.....	89
3.4.2.1 N ₂ O-N Emissions	89
3.4.2.2 NH ₃ -N Losses	91
3.4.2.3 Deep Soil Nitrate-N and Subsurface N Losses.....	92
3.4.3 Nitrogen Losses at Dryland vs Irrigated Sites.....	94
3.4.4 Area-Based Emission Factors and Yield-Scaled Emissions for Direct and Indirect N ₂ O-N Emissions.....	96
3.4.5 Soil N Stocks: SON and Residual Nitrate-N.....	98
3.5 Conclusion.....	99
3.6 References.....	101
3.7 Tables	107
3.8 Figures.....	113
3.9 Appendix.....	118
4.0 Conclusion	127
References.....	130

List of Tables

Table 2-1. Monthly mean air temperature (°C) for the growing season (May – September), mean annual temperature (°C)(MAT) for 2008 – 2011, monthly total precipitation (mm) for the growing season (May – September) and total annual precipitation (mm) for 2008 – 2011 at Lethbridge, Alberta compared to the 30-year climate normal (1971 – 2000) (ACIS 2021). Monthly irrigation amounts (mm) for the growing season (May – September), and total growing season irrigation + precipitation for 2008 – 2011 at the irrigated site in Lethbridge, Alberta (Kryzanowski et al. 2009).	41
Table 2-2. Model inputs for the soil properties at Lethbridge, Alberta obtained from field and laboratory measurements (Kryzanowski et al. 2009). *Estimated from Saxton and Rawls (2006).	42
Table 2-3. Average change in modelled soil organic and inorganic N stocks (kg N ha ⁻¹ year ⁻¹) over a 4-year period (2008 – 2011) for N rates (0, 30, 60, 90, and 120 kg N ha ⁻¹), and N sources (Control (0 kg N ha ⁻¹), Urea, ESN), at dryland and irrigated sites in Lethbridge, Alberta. The change in N stocks is the gain (positive) or loss (negative) at the year's end compared to the year's beginning. *Change in soil organic nitrogen is the sum of the average change in residue and humus N. **Change in soil inorganic nitrogen is the sum of the average change in nitrate-N and ammonium-N.	43
Table 2-4. Modelled vs measured barley grain yields (kg C ha ⁻¹) and modelled vs measured barley grain N (kg N ha ⁻¹) coefficient of determination (R ²), p-value, linear regression intercept, linear regression slope, root mean square error (RMSE); and standard deviation (SD) of measured results for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta. Measured barley grain yields and barley grain N obtained from a field experiment by Kryzanowski et al. (2009).	44
Table 2-5. Nitrogen rate (kg N ha ⁻¹) to obtain the economic optimum N rate (EONR) (kg N ha ⁻¹), barley grain yield at EONR (kg C ha ⁻¹), and the nitrogen use efficiency (NUE) (% kg Grain N kg ⁻¹ N Fertilizer) at the EONR for modelled and measured results for N sources of urea and ESN for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta. EONR was estimated by setting the first derivative of the regression equations of N fertilizer with barley grain yield equal to the fertilizer-to-grain price ratios for urea and ESN (7.4 for urea, 9.0 for ESN) (McKenzie et al. 2004; Calvo et al. 2022). Barley grain yield at EONR was determined by the regression equations of N fertilizer with barley grain yield (Supplementary Table 3). NUE at EONR was determined by inserting the EONR as x into the regression equation of N fertilizer with the NUE (% kg Grain N kg ⁻¹ Fertilizer N) (Supplementary Table 5). Measured 2010 Dryland results were not listed as there was no N fertilizer required due to a highly linearized relationship between the N rate and measured barley grain yields.	45
Table 3-1. Monthly mean air temperature (°C) for the growing season (May – September), mean annual temperature (°C)(MAT) for 2008 – 2011, monthly total precipitation (mm) for the growing season (May – September) and total annual precipitation (mm) for 2008 – 2011 at Lethbridge, Alberta compared to the 30-year climate normal (1971 – 2000) (ACIS 2021). Monthly irrigation amounts (mm) for the growing season (May – September), and total growing season irrigation + precipitation for 2008 – 2011 at the irrigated site in Lethbridge, Alberta (Kryzanowski et al. 2009).	107
Table 3-2. Model inputs for the soil properties at Lethbridge, Alberta obtained from field and laboratory measurements (Kryzanowski et al. 2009). *Estimated from Saxton and Rawls (2006).	108
Table 3-3. Average N budgets (kg N ha ⁻¹ year ⁻¹) from modelled outputs over a 4-year period (2008 – 2011) for N rates (0, 30, 60, 90, and 120 kg N ha ⁻¹), and N sources (Control (0 kg N ha ⁻¹), Urea, ESN), at dryland and irrigated sites in Lethbridge, Alberta. The change in N stocks is the gain (positive) or loss (negative) at the year's end compared to the year's beginning. Modelled gaseous and aqueous N ₂ O and	

N₂ gases within the soil profile were not included in the stock changes, likely resulting in negative N budget balances. 109

Table 3-4. Measured annual N₂O emissions based on linear interpolation (Kryzanowski et al. 2009) (standard deviations presented in brackets), and modelled annual N₂O-N emissions (kg N ha⁻¹), measured and modelled area-based emission factors (% kg N₂O-N kg⁻¹ N Fertilizer), and measured and modelled yield-based emission intensities (g N₂O-N kg⁻¹ Grain Yield Dry Matter (DM)) for N rates (0, 60, and 120 kg N ha⁻¹), and N sources (Control (0 kg N ha⁻¹), Urea, ESN), at the irrigated site in Lethbridge, Alberta for 2008 – 2011. 110

Table 3-5. Annual modelled subsurface N, surface N, N₂O-N, NH₃-N, and N₂ losses (kg N ha⁻¹ year⁻¹) for N rates (0, 30, 60, 90, and 120 kg N ha⁻¹), and N sources (Control (0 kg N ha⁻¹), Urea, ESN), at dryland and irrigated sites for 2008 – 2011 in Lethbridge, Alberta. 111

Table 3-6. Modelled N₂O emissions, Area-based emission factors, and yield scaled emissions for direct and direct + indirect N₂O emissions for urea at N rates of 0, 30, 60, 90 and 120 kg N ha⁻¹ at dryland and irrigated sites for 2008 – 2011 at Lethbridge, Alberta. (Results for ESN presented in Supplementary Table 3-3). 112

List of Figures

Figure 2-1. A) Modelled (lines) and measured (points) volumetric soil water content ($\text{m}^3 \text{m}^{-3}$) (SWC) for dryland (red) and irrigated (blue) sites at N fertilizer application rates of 0 kg N ha^{-1} (two dashed line, circle symbol) and 120 kg N ha^{-1} (solid line, star symbol) for 2008 – 2011 in Lethbridge, AB. Measured SWC was only available for the irrigated site. The field capacity ($0.293 \text{ m}^3 \text{m}^{-3}$) and wilting point ($0.157 \text{ m}^3 \text{m}^{-3}$) are represented by long dashed and short dashed horizontal lines, respectively. **B)** Modelled (lines) and measured (points) soil temperature ($^{\circ}\text{C}$) at 0.05 (orange) and 0.1 (green) meters for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. **C)** Daily average air temperature ($^{\circ}\text{C}$) (red line), daily total precipitation (mm) (blue bars), or total daily irrigation (mm) (green bars) for 2008 – 2011 in Lethbridge, Alberta. For all panels, vertical dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). The solid vertical line is the seeding/fertilizer application date for the irrigated site in 2008. Daily average air temperature and total precipitation data were obtained from ACIS (2021) and measured soil moisture, soil temperature, and irrigation data from Kryzanowski et al. (2009).

..... 46

Figure 2-2. Cumulative nitrogen release (% nitrogen applied) for Environmentally Smart Nitrogen (ESN) (orange) and Urea (green) nitrogen sources for measured (points) and modelled (lines) results at 50% and 70% field capacity, with an increase of 5°C every 7 days of the experiment..... 47

Figure 2-3. Cumulative nitrogen release (% nitrogen applied) for modelled Environmentally Smart Nitrogen (ESN) (dashed) and Urea (solid) nitrogen sources at 70% and 100% field capacity at temperatures of 10°C (orange), 20°C (green) and 30°C (blue) over a period of 92 days. 48

Figure 2-4. Modelled (lines) and measured (points) soil nitrate + nitrite N (kg N ha^{-1}) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at the dryland site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). Measured soil nitrate is obtained from a field experiment by Kryzanowski et al. (2009). 49

Figure 2-5. Modelled (lines) and measured (points) soil nitrate + nitrite N (kg N ha^{-1}) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). Measured soil nitrate is obtained from a field experiment by Kryzanowski et al. (2009). 50

Figure 2-6. A) Modelled vs measured barley grain yields (kg C ha^{-1}) and **B)** Modelled vs measured barley grain nitrogen (kg N ha^{-1}) for all sites (Dryland and Irrigated) and years (2008 – 2011) in Lethbridge, Alberta. The solid blue line represents the linear regression between modelled vs measured results. The dashed line is a 1:1 line representing a perfect relationship between modelled and measured results. Error bars represent the standard deviation of mean barley grain yields or grain nitrogen due to variability among replicates in the field experiment. Measured barley grain yields and grain N obtained from a field experiment by Kryzanowski et al. (2009). 51

Figure 2-7. Modelled (triangles) and mean measured (circles) barley grain yield (kg C ha^{-1}) response to increasing nitrogen rates of 30, 60, 90 and 120 kg N ha^{-1} for urea (green) and Environmentally Smart Nitrogen (ESN) (orange) at dryland and irrigated sites for 2008 – 2011 in Lethbridge, Alberta. Error bars represent the standard deviation of mean barley grain yields due to variability among replicates in the

field experiment. Measured barley grain yields obtained from a field experiment by Kryzanowski et al. (2009). Quadratic regression lines for measured (solid) and modelled (dashed) barley grain yield (kg C ha^{-1}) response to increasing nitrogen rates (kg N ha^{-1}) for urea (green) and ESN (orange) are shown above. Quadratic regression results are presented in Supplementary Table 2-3..... 52

Figure 2-8. Modelled (triangles) and mean measured (circles) barley grain nitrogen (kg N ha^{-1}) response to increasing nitrogen rates of 30, 60, 90 and 120 kg N ha^{-1} for urea (green) and Environmentally Smart Nitrogen (ESN) (orange) at dryland and irrigated sites for 2008 – 2011 in Lethbridge, Alberta. Error bars represent the standard deviation of mean grain nitrogen due to variability among replicates in the field experiment. Measured barley grain nitrogen obtained from a field experiment by Kryzanowski et al. (2009). Quadratic regression lines for measured (solid) and modelled (dashed) barley grain nitrogen (kg N ha^{-1}) response to increasing nitrogen rates (kg N ha^{-1}) for urea (green) and ESN (orange) are shown above. Quadratic regression results are presented in Supplementary Table 2-4. 53

Figure 2-9. Modelled (triangles) and mean measured (circles) barley nitrogen use efficiency (% $\text{kg Grain N kg}^{-1}$ N Fertilizer) (NUE) response to increasing N rates of 30, 60, 90 and 120 kg N ha^{-1} for urea (green) and Environmentally Smart Nitrogen (ESN) (orange) at dryland and irrigated sites for 2008 – 2011 in Lethbridge, Alberta. Error bars represent the standard deviation of the mean measured NUE due to variability among replicates in the field experiment. Measured NUE values obtained from a field experiment by Kryzanowski et al. (2009). Quadratic regression lines for measured (solid) and modelled (dashed) NUE (% $\text{kg Grain N kg}^{-1}$ N Fertilizer) response to increasing nitrogen rates (kg N ha^{-1}) for urea (green) and ESN (orange) are shown above. Quadratic regression results are presented in Supplementary Table 2-5. 54

Figure 3-1. A) Modelled (lines) and measured (points) volumetric soil water content ($\text{m}^3 \text{ m}^{-3}$) (SWC) for dryland (red) and irrigated (blue) sites at N fertilizer application rates of 0 kg N ha^{-1} (two dashed line, circle symbol) and 120 kg N ha^{-1} (solid line, star symbol) for 2008 – 2011 in Lethbridge, AB. Measured SWC was only available for the irrigated site. The field capacity ($0.293 \text{ m}^3 \text{ m}^{-3}$) and wilting point ($0.157 \text{ m}^3 \text{ m}^{-3}$) are represented by long dashed and short dashed horizontal lines, respectively. **B)** Modelled daily discharge (mm) for dryland (red) and irrigated (blue) sites at N fertilizer application rates of 0 kg N ha^{-1} (two dashed line) and 120 kg N ha^{-1} (solid line) for 2008 – 2011 in Lethbridge, AB. **C)** Modelled (lines) and measured (points) soil temperature ($^{\circ}\text{C}$) at 0.05 (orange) and 0.1 (green) meters for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. **D)** Daily average air temperature ($^{\circ}\text{C}$) (red line), daily total precipitation (mm) (blue bars), or total daily irrigation (mm) (green bars) for 2008 – 2011 in Lethbridge, Alberta. For all panels, vertical dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). The solid vertical line is the seeding/fertilizer application date for the irrigated site in 2008. Daily average air temperature and total precipitation data were obtained from ACIS (2021) and measured soil moisture, soil temperature, and irrigation data from Kryzanowski et al. (2009). 113

Figure 3-2. Modelled (lines) and measured (points) soil nitrate + nitrite N (kg N ha^{-1}) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at the dryland site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). Measured soil nitrate is obtained from a field experiment by Kryzanowski et al. (2009). 114

Figure 3-3. Modelled (lines) and measured (points) soil nitrate + nitrite N (kg N ha^{-1}) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed

line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha⁻¹ for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). Measured soil nitrate is obtained from a field experiment by Kryzanowski et al. (2009). 115

Figure 3-4. Daily modelled **A**) nitrous oxide-N (N₂O-N) flux, **B**) nitrogen gas (N₂) flux, **C**) ammonium-N (NH₃-N) flux, **D**) Surface N flux, and **E**) Subsurface N flux (kg N ha⁻¹ d⁻¹) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha⁻¹ for 2008 – 2011 at the dryland site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). 116

Figure 3-5. Daily modelled **A**) nitrous oxide-N (N₂O-N) flux, **B**) nitrogen gas (N₂) flux, **C**) ammonium-N (NH₃-N) flux, **D**) Surface N flux, and **E**) Subsurface N flux (kg N ha⁻¹ d⁻¹) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha⁻¹ for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). 117

Figure 4-1. A) Mean modelled barley grain yields (kg C ha⁻¹ yr⁻¹) and **B)** Mean modelled N₂O-N emissions (kg N ha⁻¹ yr⁻¹) response to increasing N rates (0 – 120 kg N ha⁻¹) for urea fertilizer at dryland (red) and irrigated (blue) sites in Lethbridge, Alberta for 2008 – 2011. Error bars represent the standard deviation of mean-modelled barley grain yields or mean-modelled N₂O-N emissions due to yearly variability (2008 – 2011). Vertical dashed lines indicate the economic optimum N rate (EONR) based on a 7.4 fertilizer-to-grain price ratio for dryland (red; 71 kg N ha⁻¹) and irrigated (blue; 79 kg N ha⁻¹) sites for 2008 – 2011. Quadratic regression results for modelled grain yields: Dryland: $y = -0.11x^2 + 23x + 1636$; $R^2 = 0.74$; $p < 0.001$. Irrigated: $y = -0.13x^2 + 29x + 1437$; $R^2 = 0.69$; $p < 0.001$. Linear regression results for modelled N₂O-N emissions: Dryland: $y = 0.002x + 0.23$; $R^2 = 0.44$; $p = 0.002$. Irrigated: $y = 0.002x + 0.19$; $R^2 = 0.64$; $p < 0.001$ 129

1.0 Introduction

Nitrogen is the most common limiting nutrient in agricultural crop production, and synthetic N fertilizers have allowed for an increase in crop yields of 40 – 60% (Stewart et al. 2005; Zebarth et al. 2009). However, due to the temporal and spatial asynchronization of N supply with crop N demand, nitrogen use efficiency (NUE), which is the proportion of N fertilizer taken up by the crop, is as low as 30 to 50% (Cassman et al. 2002; Zebarth et al. 2009; Setiyono et al. 2011; Udvardi et al. 2021). The remaining N (50 – 70%) may be lost via volatilization, leaching, or denitrification, retained as residual inorganic N, or immobilized to soil organic N (SON). Nitrogen lost from the agroecosystem increases N loading to the environment and contributes to declining air and water quality, eutrophication, acidification, atmospheric ozone depletion, and N₂O emissions, which negatively impacts human and environmental health (Cassman et al. 2002; Cameron et al. 2013; United Nations Environment Programme 2014; Steffen et al. 2015). To maintain crop productivity and reduce N losses, NUE must be increased, which may be accomplished through effective N fertilizer management (Cassman et al. 2002; Udvardi et al. 2021). Nitrogen budgets, which account for N inputs, N outputs, and changes in soil N stocks, can be used to assess the fate of N in the agroecosystem and to develop effective N management practices that increase NUE and reduce N losses (Mezbahuddin et al. 2020; Karimi et al. 2020; Yang et al. 2023). Process-based ecosystem models such as *ecosys*, which simulate biogeochemical cycling and feedback processes, may be used to generate low-cost and time-efficient estimates of the fate of N in the agroecosystem as affected by different N management options (Grant et al. 2020; Mezbahuddin et al. 2020).

Accordingly, the objective of this thesis was to use the model *ecosys* to develop a comprehensive N budget to determine the fate of N at a field site in the cool, semi-arid Canadian prairies as influenced by N source (urea vs ESN; a polymer-coated urea fertilizer), N rate (0 – 120 kg N ha⁻¹), irrigation vs

dryland, and interannual climatic variability (2008 – 2011). In chapter 1, N release will be simulated under field conditions to determine how differing modelled N release patterns from urea and ESN affect the synchronization between modelled N availability and crop N uptake. The effect of N source, N rate, irrigation vs dryland, and interannual climatic variability on modelled crop yields, grain N, and NUE will be assessed, and estimates of economic optimum nitrogen rates (EONRs) will be made from modelled yield response curves. In chapter 2, the effect of N source, N rate, irrigation vs dryland and interannual climatic variability on the type and magnitude of modelled N losses (NH_3 , N_2O , N_2 , subsurface and surface N losses), and organic and inorganic N stocks will be assessed by constructing a comprehensive N budget. Direct and indirect N_2O emission factors and yield-scaled emissions will be quantified from model results and IPCC emission factors. This thesis will test the following hypotheses: (1) A simulated lag in modelled N release from ESN will improve synchronization between modelled N availability and crop N demand and allow for increased modelled crop N uptake, yields, and NUE, thereby reducing inorganic N accumulation and N losses. (2) Increasing N rates will reduce the depletion of modelled SON, and increase modelled yields but at diminishing rates of return as crop N demand is met, and therefore, increasing N rates will also increase modelled N losses and residual inorganic N. (3) The irrigated site will reduce modelled N losses if the increased water availability enhances modelled crop N uptake, otherwise the higher SWC will increase modelled N leaching and denitrification losses. Results from this modelling experiment will improve our understanding of the controls on NUE and the magnitude of different N loss pathways as influenced by different N management options, irrigation vs dryland, and interannual climatic variability.

2.0 Variation in NUE due to Irrigation and Interannual Climatic Variability

Highlights Need for Optimal N Rates, not N Source, to Increase NUE in Semi-Arid

Southern Alberta

2.1 Introduction

Meeting the rising global food demand while reducing nitrogen (N) losses from N fertilizer use is of great global concern, and effective N fertilizer management is needed to maintain crop productivity and protect human and environmental health (Cassman et al. 2002; United Nations Environment Programme 2014; Steffen et al. 2015). The production and use of synthetic nitrogen fertilizers have allowed for a 40 – 60% increase in crop yields, which has contributed to meeting global food demand and increasing food security (Stewart et al. 2005). However, globally the nitrogen use efficiency (NUE), which is the amount of N fertilizer taken up by the crop, is 30 – 50% (Cassman et al. 2002). The remaining 50 – 70% of applied N fertilizer is immobilized in soil organic matter or is lost to the surrounding environment via leaching (NO_3^-), volatilization (NH_3), or denitrification (NO , NO_2 , N_2O , N_2), resulting in contamination of ground and surface water, acidification, eutrophication, declining air quality, ozone layer depletion, and the production of greenhouse gases (GHGs) (e.g., N_2O) (Cassman et al. 2002; Cameron et al. 2013). These N losses from synthetic N fertilizers have resulted in excessive amounts of N inputs into the earth's ecosystems, interfering with the N cycle and disrupting ecosystem functioning (Steffen et al. 2015). As a result, the planetary boundary for nitrogen cycling has been exceeded, which may greatly affect the stability of the earth system (Steffen et al. 2015).

In Canada, despite an increase in NUE from 46.7 to 50.8% from 1996 to 2016, there has been an increase in N loading to the environment of 52% (Karimi et al. 2020). Since 2005, nitrogen fertilizer use has risen by 89%, accompanied by a 92% increase in N_2O emissions, making up 75% of Canada's national N_2O emissions (Environment and Climate Change Canada 2022). The Western Canadian prairies make up

80% of farmland in Canada, and since 1981 fertilizer use has doubled in this region (Grant and Wu 2008; Agriculture and Agri-Food Canada 2022). As part of a larger plan to address climate change issues, the Government of Canada announced the Fertilizer Emissions Reduction Target, with a goal to reduce fertilizer GHG emissions by 30% below 2020 levels by 2030 (Agriculture and Agri-Food Canada 2022). Low NUE occurs due to spatial and temporal asynchronization of N supply with crop N demand, and when N supply exceeds crop N demand, results in low N uptake efficiency and N losses (Zebarth et al. 2009; Setiyono et al. 2011; Udvardi et al. 2021). Improved synchronization between N supply and N demand may be accomplished using the 4Rs of nutrient stewardship (Right source at Right time, Right rate, and Right place) to increase NUE, obtain N loss reduction goals, and maintain crop productivity (Malhi et al. 2001; Cassman et al. 2002; Grant and Wu 2008; Udvardi et al. 2021).

2.1.1 Right Time

In Canada, fertilizer may be applied in the fall after harvest or in the spring before or at seeding. Compared to fall fertilizer application, spring fertilizer application reduces N losses and increases crop N recovery by improving synchronization between N availability and crop N demand and reducing soil mineral N accumulation which may be subject to N losses prior to crop growth (Hao et al. 2001; Soon et al. 2011; Mezbahuddin et al. 2020). A reported 90% of farmers in Canada apply fertilizer in the spring, with the remainder choosing fall applications to take advantage of lower fertilizer prices and to minimize the spring workload (Korol 2004; Grant and Wu 2008).

2.1.2 Right Place

Placing nitrogen fertilizer below the soil surface can reduce nitrogen losses and increase NUE compared to surface applications (Malhi et al. 2001; Grant and Wu 2008). Placement of nitrogen fertilizer below the soil surface reduces volatilization losses compared with surface broadcasting and reduces immobilization losses by reducing N fertilizer contact with crop residues and soil

microorganisms. In addition, N fertilizer applied in highly concentrated bands below the surface slows ammonification and nitrification rates, which can reduce early-season denitrification and leaching losses (Malhi et al. 2001; Grant and Wu 2008). In Canada, surface broadcasting accounted for 1/3 of fertilizer applications, and in-soil placement accounted for the remaining 2/3 (Korol 2004).

2.1.3 Right Source

Urea (46-0-0) is Canada's most used nitrogen fertilizer, followed by ammonium and nitrate-based fertilizers (Korol 2004). In contrast to conventional urea, which hydrolyzes rapidly within the first few days or the first week (Agehara and Warncke 2005; Cahill et al. 2010a), polymer-coated urea (PCU) fertilizers have a semi-permeable polymer coating which acts as a physical barrier to urea dissolution and diffusion and allows for a more gradual N release (Cahill et al. 2010a; Golden et al. 2011; Chen et al. 2018). A delay in N release could better match early season crop N demand when crop N uptake is low, reducing inorganic N accumulation in the soil and allowing for more N to be available later in the growing season when crop N demand is higher, and thereby increase NUE (Grant and Wu 2008; Grant et al. 2012; Drury et al. 2012). Environmentally Smart Nitrogen (ESN) fertilizer is a PCU fertilizer and is the first commercially available agronomic PCU fertilizer available in Canada (Grant and Wu 2008). The effectiveness of ESN at increasing yields and NUE has been found to be inconsistent in Western Canada and varies interannually and regionally with climatic conditions, crop type, and soil properties (Malhi et al. 2010; McKenzie et al. 2010; Blackshaw et al. 2011a, 2011b; Grant et al. 2012; Mezbahuddin et al. 2020; Thilakarathna et al. 2020). Under the drier conditions of the Canadian prairies, N release from ESN may be delayed, and the potential for reducing N losses low, which may limit the benefits of ESN (Grant and Wu 2008; Nelson et al. 2008; Grant et al. 2012). However, under irrigated agricultural production, ESN may be more beneficial due to higher soil moisture and a greater potential for N losses (Nelson et al. 2008; Wilson et al. 2010; Malhi et al. 2010; Grant et al. 2012; Gagnon et al. 2012; Li et al. 2018). In semi-arid Southern Alberta, irrigated agriculture makes up approximately 70% of irrigated agriculture in

Canada (Statistics Canada 2022). However, there has been no published research to this date on the effects of ESN on yields and NUE on irrigated lands compared to rainfed, dryland agriculture in Southern Alberta. Laboratory studies have found N release from ESN to be controlled by temperature and limited by soil moisture (Cahill et al. 2010a; Golden et al. 2011; Ransom et al. 2020). However, knowledge of N release from ESN under field conditions in relation to crop N demand would provide a greater understanding of how ESN fertilizer affects the synchronization between N availability and crop N uptake, and subsequent impacts on crop yields and NUE at dryland and irrigated sites in semi-arid agroecosystems (Cahill et al. 2010a; Golden et al. 2011; Ransom et al. 2020).

2.1.4 Right Rate

Selecting the appropriate nitrogen rate is one of the most important components of effective nitrogen management, and the amount of nitrogen applied should meet crop N requirements while minimizing N losses (Zebarth et al. 2009). Nitrogen applied in excess of crop N requirements results in minimal yield gains and reduced NUE (Cassman et al. 2002; Malhi et al. 2010). Many factors influence crop N uptake of applied N fertilizer, such as climatic conditions (temperature, precipitation), management practices (crop type, tillage regime, residue management, previous N fertilizer applications), soil N supply, and other limiting factors for crop growth, which makes N rate recommendations a challenge (Zebarth et al. 2009; Malhi et al. 2010; Puntel et al. 2016). Soil N supply varies spatially and temporally (Sogbedji et al. 2001; Setiyono et al. 2011), and predicting soil N supply is one of the most challenging aspects of selecting the N rate (Zebarth et al. 2009). In addition, producers aim to maximize net returns for agricultural activities to be economically sustainable by applying N fertilizer at an economic optimum N rate (EONR) which varies with commodity pricing (Cassman et al. 2002; McKenzie et al. 2004b; Puntel et al. 2016). Accordingly, crop yield response to N rate applications, EONRs, and NUE may vary substantially between years and at different sites (McKenzie et al. 2004a, 2004b; Basso et al. 2019). Quantifying the spatial and temporal variability of N supply with increasing N

rates and the trade-offs between increasing N rates on yields and NUE would help inform N rate recommendations and improve our understanding of the many factors which control crop N uptake and NUE.

2.1.5 Computer Modelling to Inform N Management Practices

Due to the substantial variability in crop yield response, N uptake, and NUE, site-specific N management practices will be required to increase NUE (Basso et al. 2019; Karimi et al. 2020). However, comparing multiple management options and their effects on multiple outputs in field experiments is time-consuming, difficult, and expensive (Zebarth et al. 2009; Puntel et al. 2016). In addition, field measurements may not capture the spatial and temporal variability of crop N uptake and soil N supply or account for N transformations from biogeochemical cycling (Setiyono et al. 2011; Mezbahuddin et al. 2020; Congreves et al. 2021). Furthermore, current NUE indices are unable to account for N fertilization effects on crop N uptake from differences in root growth and subsequent N uptake or differences in soil N supply due to N fertilization effects on the mineralization of soil organic nitrogen (SON) (Burns 1980; Rasmussen et al. 2015; Mahal et al. 2019; Congreves et al. 2021). Rigorously validated computer models that simulate biogeochemical cycling and key ecosystem processes can be used to evaluate the effects of different N management strategies on the fate of N in the agroecosystem at high spatial and temporal resolutions (Grant et al. 2020; Mezbahuddin et al. 2020). Such computer models can be used as a tool to help inform effective N management strategies and grant insight into controls on crop N uptake and NUE (Zebarth et al. 2009; Puntel et al. 2016; Mezbahuddin et al. 2020; Udvardi et al. 2021). The process-based ecosystem model *ecosys* has been used extensively in the Western Canadian prairies to model N fertilization effects on agroecosystems (Grant et al. 2001, 2006, 2020; Mezbahuddin et al. 2020). Comparing the effects of multiple N management practices on crop yields and NUE would grant further insight into N management practices which balance economic and environmental sustainability (Puntel et al. 2016; Udvardi et al. 2021).

2.1.6 Objectives and Hypotheses

This study will model the effects of 2 of the 4 R's (right source and right rate) on barley grain yields, grain N, soil N stocks, and NUE at dryland and irrigated sites in semi-arid Southern Alberta using the model *ecosys*. Accordingly, the objectives of this study are:

- 1) Validate the N release parameters in the model *ecosys* for urea and ESN N fertilizer sources, and determine the effects of temperature and moisture on modelled N release in a laboratory simulation;
- 2) Assess how differing N release patterns of urea and ESN affect the synchronization between N supply and barley N demand under field conditions, and subsequent impacts on barley grain yields, grain N, and NUE at dryland and irrigated sites; and
- 3) Assess barley grain yield, grain N, NUE, and soil N response to increasing N rates at dryland and irrigated sites, and estimate the EONR.

The effects of different N sources and N rates on N losses will be addressed in Chapter 3. This study will test the following hypotheses: (1) Modelled N release will be controlled by temperature and soil moisture, and modelled N release from ESN will have a simulated lag period with respect to urea. (2) A simulated lag in modelled N release from ESN will improve synchronization between modelled N availability and crop N demand and allow for increased modelled barley N uptake, yields, and NUE. (3) Increasing N rates will increase modelled barley yields, but at diminishing rates of return as modelled barley N demand is met, and modelled barley yield response will result in accurate estimates of EONR. (4) As N rates increase, NUE will decrease, and modelled soil N supply and barley N uptake will differ between fertilized and unfertilized barley not only due to N fertilization but also to its effects on root growth and mineralization of SON, which will affect NUE. Testing these hypotheses will contribute to

understanding the effects of different N sources and N rates on crop N uptake, grain yields, NUE, and soil N stocks at dryland and irrigated sites in semi-arid agroecosystems.

2.2 Methods

2.2.1 Model Validation of N Release under Laboratory Conditions

2.2.1.1 Laboratory Dataset

Measured results for N release from urea and Environmentally Smart Nitrogen (ESN) used to test modelled N release to validate N release parameters in the model *ecosys* were obtained from a laboratory experiment conducted by Dowbenko (2016). A laboratory soil incubation experiment was conducted to compare the nitrogen release of urea and ESN under an increasing temperature regime and two soil moisture levels (Dowbenko, personal communication). The soil incubation experiment used a commercially available Greensmix sandy loam soil (80% loam, 20% sand) with a bulk density of 1 Mg m^{-3} and a pH of 6.6. Before fertilizer application, the soil was mixed thoroughly and then incubated in pots at $10 \text{ }^{\circ}\text{C}$ for 3 days in temperature-controlled growth chambers. Urea and ESN fertilizer granules were applied separately to compare nitrogen release from the different fertilizer sources, and fertilizer granules were scattered evenly on the soil surface and covered with a 0.6 cm layer of soil to resemble the incorporation of fertilizer into the soil (Dowbenko, personal communication). After fertilizer application, the experiment was incubated in growth chambers starting at $0 \text{ }^{\circ}\text{C}$, with an increase of $5 \text{ }^{\circ}\text{C}$ every 7 days up to $40 \text{ }^{\circ}\text{C}$ (9 weeks). The increasing temperature regime was meant to represent rising temperatures after fertilizer application in the spring (Dowbenko, personal communication). The experiment was carried out under two soil moisture levels of 50% and 70% field capacity, and moisture levels were checked daily to maintain the necessary moisture level. Every 7 days, the top layer of soil covering the fertilizer granules was carefully removed to prevent damage to the fertilizer granules, and granules were removed and rinsed with deionized water to remove loose soil particles. The remaining

nitrogen concentration in the granules was analyzed using colorimetry in aqueous solutions (Dowbenko, personal communication).

2.2.1.2 Modelling N Release under an Increasing Temperature Regime

The laboratory soil incubation experiment described in section 2.2.1.1 was simulated in the process-based model *ecosys* to compare modelled and measured N release and to validate the model's N release parameters for urea and ESN. Nitrogen release from urea in *ecosys* is determined by the rate of urea fertilizer dissolution, which is determined in turn by the rate of urea hydrolysis and the soil water concentration. The rate of urea hydrolysis is determined by a specific rate constant for urea fertilizer dissolution multiplied by microbial activity, governed by a Michaelis-Menten constant which determines the microbial concentration relative to urea concentration. Microbial activity is controlled by soil moisture and an Arrhenius function of soil temperature. Urea hydrolysis is also subject to inhibition that declines with time to simulate the initial lag and subsequent gradual increase in N release rates following urea application (Mezbahuddin et al. 2020). The rate of decline for urea hydrolysis inhibition was used in Grant and Pattey (2003) and subsequent N₂O emissions *ecosys* modelling studies to accurately simulate the time course of N₂O emissions generated from urea hydrolysis products. Therefore, the rate of decline in urea hydrolysis inhibition for conventional urea has been previously tested and validated in *ecosys* (Grant and Pattey 2003).

ESN has a polymer coating surrounding the urea granule, which allows for a delay in N release compared to conventional urea fertilizer (Cahill et al. 2010a; Golden et al. 2011; Chen et al. 2018). To simulate this in *ecosys*, the decline in urea hydrolysis inhibition for ESN was set to 1/10th that of urea, allowing for a prolonged lag in N release from ESN compared to urea. Parameters for urea hydrolysis inhibition for urea and ESN, and the specific rate constant for urea fertilizer dissolution were validated by comparing measured and modelled N release from urea and ESN.

To simulate the soil used in the laboratory soil incubation experiment, reported soil properties from section 2.2.1.1 such as pH (6.6), texture (silty loam), and bulk density (1.0 Mg m^{-3}) were input into *ecosys*. Field capacity ($0.337 \text{ m}^3 \text{ m}^{-3}$) and wilting point ($0.134 \text{ m}^3 \text{ m}^{-3}$) were estimated in *ecosys* from texture and organic matter. The model was initialized under laboratory conditions at $0 \text{ }^\circ\text{C}$ and under moisture levels of 50% and 70% field capacity and ran for a period of 9 months to allow for conditions in the model to reach equilibrium. After the initial spin-up period, the modelled soil was tilled to simulate thorough mixing of the soil, and the air temperature was set to $10 \text{ }^\circ\text{C}$ for a period of 3 days to simulate the conditions prior to fertilizer application in the laboratory experiment. Separate model runs for urea and ESN were conducted to compare the N release from both fertilizer sources, and fertilizer was broadcast applied and incorporated to a depth of 0.6 cm to simulate the fertilizer application in the laboratory experiment described in section 2.2.1.1. Irrigation was applied as necessary to maintain 50% and 70% field capacity in the model runs to simulate the two soil moisture levels in the laboratory experiment. Following fertilizer application, the air temperature was set at $0 \text{ }^\circ\text{C}$ with an increase of $5 \text{ }^\circ\text{C}$ every 7 days up to $40 \text{ }^\circ\text{C}$ (9 weeks) to follow the increasing temperature regime in the laboratory experiment (section 2.2.1.1). The remaining nitrogen amount in the fertilizer granules was reported as a model output for comparison with measured values recorded in section 2.2.1.1. Nitrogen release was determined by subtracting the remaining N in the granule from the initial N amount, which was divided by the initial N amount to determine the % N release.

2.2.1.3 Modelling Temperature and Moisture Effects on N Release

The laboratory modelling experiment under an increasing temperature regime (section 2.2.1.2) had time and temperature as confounding variables on N release, limiting inferences that could be made about temperature and moisture effects on N release. To assess the effects of temperature and moisture on modelled N release, separate laboratory modelling experiments at 10, 20, and $30 \text{ }^\circ\text{C}$ were conducted at 70% and 100% field capacity to determine the effect of temperature on modelled N release from urea

and ESN under laboratory conditions. Soil moisture levels of 70% and 100% field capacity were selected as these soil moisture levels are more representative of field conditions during N fertilizer application. Model runs were initialized under laboratory conditions at 10, 20, or 30 °C and under moisture levels of 70% and 100% field capacity for a period of 9 months to allow for conditions in the model to reach equilibrium. The same soil properties used in the previous laboratory soil incubation experiment (section 2.2.1.2) were input into the model. After the initial spin-up period, the soil was tilled to simulate thorough mixing of the soil, and fertilizer was broadcast applied and incorporated to a depth of 0.6 cm. Irrigation was applied as necessary to maintain 70% and 100% field capacity, and temperatures were held constant at 10, 20 or 30 °C throughout the duration of the experiment (92 days). Nitrogen release was determined as described above in section 2.2.1.2.

2.2.2 Modelling N Source and N Rate Effects on Barley Yields, NUE, and Soil N

2.2.2.1 Field Dataset

Field measurements from a field experiment conducted by Kryzanowski et al. (2009) were used for model inputs and to compare measured results against modelled results. The field experiment was conducted under a zero-tillage regime in the Dark Brown Chernozemic soil zone at a dryland and irrigated site in semi-arid Lethbridge, Alberta (49.69, -112.76) in 2008 – 2011 (Kryzanowski et al. 2009). Daily average air temperatures and daily total precipitation were obtained from the nearest meteorological station (ACIS 2021) and are depicted alongside irrigation amounts in Figure 2-1C. Average growing season temperature, total precipitation for 2008 – 2011, and monthly irrigation amounts are presented in Table 2-1 (irrigation schedule available in Supplementary Table 2-1) (Kryzanowski et al. 2009) along with the 30-year climate normal (1971 – 2000) (ACIS 2021) for mean temperature and total precipitation. The Sand-silt-clay content, pH, organic C, solution $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, exchangeable $\text{PO}_4\text{-P}$, K, and $\text{SO}_4\text{-S}$, and bulk density were determined from field measurements and laboratory analysis for 0 – 0.15, 0.15 – 0.30, 0.30 – 0.60, and 0.60 – 0.90 meters in the soil profile (Table 2-2) (Kryzanowski et al.

2009). Field capacity, wilting point, and saturated hydraulic conductivity were estimated using Saxton and Rawls (2006) (Table 2-2). At the irrigated site, soil temperature was measured at 0.05, and 0.10-meter depths using soil temperature sensors, and soil moisture measurements were taken at 0 – 0.05 meters depth using a time-domain reflectometry probe (Kryzanowski et al. 2009).

Seeding and N fertilizer application dates were May 2, 2008 (May 13 for the irrigated site), May 5, 2009, May 13, 2010, and May 2, 2011. Harvest dates were September 15 for all years, except for 2010 where harvest was September 24. Barley was seeded at 300 seeds m⁻² into standing stubble using a direct seeder with atom jet double shoot openers with 20 cm row spacing (Kryzanowski et al. 2009). Prior to seeding, glyphosate was applied to the fields as a pre-burn application. A 2-way factorial of N rate (0, 30, 60, 90, and 120 kg N ha⁻¹) and N source (Urea (46-0-0) and ESN (44-0-0)) was set up as a randomized complete block design of 4 replicates each at the dryland and irrigated sites. Nitrogen fertilizer was applied at the time of seeding and side banded below and to the side of the seed at a depth of 7.5 cm (Kryzanowski et al. 2009). Each year the experimental treatments were located in an area that had received no N fertilizer the year prior. Triple superphosphate (0-44-0) was applied at a rate of 25 kg P ha⁻¹ for all treatments to minimize P limitations. An area of 11.34 m² of barley grain was harvested, and 15 cm of straw was left as stubble. Yields were adjusted to 13.5% moisture content, and protein concentration was determined using near-infrared spectroscopy (Kryzanowski et al. 2009).

2.2.2.2 Model Set Up and Simulations

The process-based ecosystem model *ecosys* was used to simulate the field experiment described above (section 2.2.2.1) and to assess N source and N rate effects on barley grain yields, NUE, and soil N. *Ecosys* models the transport and transformation of nitrogen, carbon, and phosphorus along with heat, water, and energy on an hourly timestep to simulate ecosystem processes and functioning (Grant 2001). The key parameters and algorithms which simulate the scientific processes in *ecosys* have been determined by separate research studies and therefore, the model does not require calibration and

parameterization for each site-specific scenario (Grant 2001). Organic nitrogen may be mineralized to inorganic ammonium (NH_4^+) or NH_4^+ and nitrate (NO_3^-) may undergo immobilization and be converted to organic N by heterotrophic microorganisms to maintain a set microbial C:N ratio. Ammonium may be taken up by the plant, immobilized, converted to nitrate via nitrification by chemoautotrophic bacteria, sorbed to soil particles, or converted to ammonia (NH_3) and lost to the atmosphere via volatilization. Nitrate may be taken up by the plant, immobilized, or subject to denitrification and leaching losses. Nitrogen movement in soil is governed by mass flow and concentration gradients. Plant root N uptake occurs via convection, which is driven by water uptake when the plant transpires and concentration gradients between the soil solution and root and mycorrhizal surfaces. Further model descriptions and equations for soil microbial activity, N transformations, and crop growth are available in Grant (2001) (Appendices B, C, E, F, H, I).

Model runs for each combination of N rate (0, 30, 60, 90, 120 kg N ha⁻¹), N source (control (0 kg N ha⁻¹), urea, ESN), site (Dryland and Irrigated), and year (2008, 2009, 2010, 2011) were conducted to simulate the effect of different N rates, N sources, irrigated vs dryland, and interannual climatic variability on barley grain yields, grain N, NUE, and soil organic nitrogen. ESN was input as urea with a slower decline in hydrolysis inhibition to simulate the delayed N release from ESN compared to conventional urea fertilizer. Management options such as fertilizer, tillage, irrigation, and cropping inputs were entered into *ecosys* to simulate the management practices as described in the field dataset section 2.2.2.1. The fraction of protein allocated to rubisco has been found to range between 15 – 65% depending on the barley variety and growth stage (Blenkinsop and Dale 1974; Metodiev and Demirevska-Kepova 1992; Pancheva and Popova 1998; Simova-Stoilova et al. 2001), and was set as 30% in the barley plant functional type (PFT) according to modelled grain yield performance in relation to measured grain yields. The high yields obtained in the newer barley varieties are likely a result of the increased allocation of protein to rubisco (O'Donovan et al. 2015), as increased allocation of protein to

rubisco allows for greater CO₂ assimilation and hence greater crop productivity (Metodieva and Demirevska-Kepova 1992). The maturity group in the barley PFT was set so that the modelled anthesis dates corresponded with the measured anthesis dates. The grain filling rate was set to ensure grain fill was completed for the barley crop a week prior to harvest. Soil properties used in the model simulations were obtained from field measurements and laboratory analysis (Kryzanowski et al. 2009) or estimated using Saxton and Rawls (2006) (Table 2-2). Weather inputs (solar radiation, relative humidity, wind speed, temperature, and precipitation) were obtained from the nearest meteorological station to input into the model runs at an hourly timestep, with the exception of 2008 for which hourly data were not found (ACIS 2021). Daily weather data for 2008 were therefore input to the model and was downscaled to hourly weather data within the *ecosys* model.

Separate spin-up runs for dryland and irrigated sites were executed for 1998 – 2007 to allow conditions in the model to reach equilibrium prior to the experimental production runs. Spin-up runs had a continuous field crop, zero tillage, and a 100 kg N ha⁻¹ year⁻¹ of urea fertilizer and 25 kg P ha⁻¹ of triple superphosphate applied except in the year prior to the experimental production run to simulate the cropping and management history in the years leading up to the field experiment (section 2.2.2.1). Phosphorus fertilizer was also applied at a rate of 25 kg P ha⁻¹ in control runs (no N fertilizer) to reduce P limitations.

2.2.2.3 Data Processing and Analyses

To compare modelled and measured barley grain yields (kg C ha⁻¹), measured barley grain yields were converted to dry matter by accounting for a moisture content of 13.5%. Dry matter grain yields were converted to carbon (kg C ha⁻¹) by multiplying the dry matter grain yields by a conversion factor of 0.43. To compare modelled and measured barley grain N, measured barley grain protein (%) was converted to nitrogen (kg N ha⁻¹) by dividing by the correction factor of 5.8 (Jones 1941) and multiplied by dry matter grain yields to determine barley grain N uptake.

All statistical analyses were completed in the R software (version 4.1.1). To assess model performance, linear regression analyses for modelled vs measured grain yields (kg C ha⁻¹) and grain N (kg N ha⁻¹) were performed. The coefficient of determination (R²), linear regression slope and intercept, root mean square error (RMSE), and standard deviation (SD) were calculated to determine the accuracy of modelled results compared to measured results. Modelled and measured soil water content and soil temperature at the irrigated site for N rates of 0, 60, and 120 kg N ha⁻¹ were compared to assess model performance. Measured spring soil nitrate-N and ammonium-N tests for 0 – 0.9 meters in the soil profile were compared to modelled soil inorganic N levels to assess model performance. The nitrogen use efficiency (NUE) (% kg Grain N kg⁻¹ N Fertilizer) was determined using equation 1 for modelled and measured grain N.

$$(1) \text{ NUE} = \frac{\text{Fertilized Grain N} - \text{Unfertilized Grain N}}{\text{N Fertilizer Rate}} * 100$$

Quadratic regression equations (linear and quadratic coefficients, and the intercept), and the coefficient of determination (R²) were used to determine the relationship between N rate and modelled and measured barley grain yields (kg C ha⁻¹), grain N (kg N ha⁻¹), and NUE (kg Grain N kg⁻¹ N fertilizer). To estimate the EONR, the first derivative of the regression equations of N fertilizer with barley grain yield were set equal to the fertilizer to grain price ratios for urea (7.4 fertilizer to grain price ratio) and ESN (9.0 fertilizer to grain price ratio) (McKenzie et al. 2004b; Reussi Calvo et al. 2022). These ratios were using historical barley crop prices and urea fertilizer prices for 2008 (Statistics Canada 2023) and were kept fixed for the calculations in this study. The price of ESN is \$0.31 – 0.41 kg⁻¹ N more expensive than urea and was set as \$0.35 kg⁻¹ N more expensive than urea for this analysis (Khakbazan et al. 2013). Barley grain yield (kg C ha⁻¹) and NUE (kg Grain N kg⁻¹ Fertilizer N) at the EONR were determined by inserting the EONR as x into the regression equations of N fertilizer with barley grain yield and NUE, respectively.

The change in nitrate-N, ammonium-N, residue-N, and humus-N N stocks is the gain (positive) or loss (negative) at the year's end compared to the year's beginning. The change in soil organic nitrogen is determined by the sum of the changes in residue-N and humus-N, and the change in soil inorganic nitrogen is determined by the sum of the changes in nitrate-N and ammonium-N. Each year's N stocks were summed together and then averaged to determine the average change in N stocks for 2008 – 2011.

2.3 Results

2.3.1 Model Validation of N Release under Laboratory Conditions

2.3.1.1 Modelled vs Measured N Release

Modelled N release (%) from urea and ESN were in good agreement with measured N release (%) ($R^2 = 0.94$, RMSE = 11.1%, $p < 0.001$; Figure 2-2). Both modelled and measured N release increased with temperature and time (Figure 2-2). Modelled N release more closely matched measured N release at 70% than at 50% field capacity (Figure 2-2). Modelled and measured N release were initially slower at lower temperatures but increased rapidly as time progressed and temperatures increased, approaching sigmoidal patterns of N release (Figure 2-2). Modelled N release from urea was more rapid at 70% than at 50% field capacity, while measured N release from urea was similar regardless of soil moisture (Figure 2-2). Both modelled and measured N release from ESN had a lag in N release compared to that of urea (Figure 2-2). Modelled and measured N release from ESN were more rapid and had a shorter lag period at 70% compared to 50% field capacity (Figure 2-2). The difference in N release between urea and ESN was greater for measured than modelled N release (Figure 2-2). Prior to analysis of the measured N release, fertilizer granules were rinsed with deionized water (Dowbenko, personal communication), which may have contributed to greater soluble N loss from urea and a more rapid measured N release resulting in a greater difference in measured N release between urea and ESN than modelled results. A lower difference in modelled N release between urea and ESN compared to measured results also

suggests that the slower decline in modelled urea hydrolysis inhibition for ESN compared to that of urea did not fully capture the magnitude of the lag of the measured N release.

2.3.1.2 Effects of Temperature and Moisture on Modelled N Release

Modelled N release from urea and ESN increased rapidly with increasing 10 °C temperature increments from 10 to 30 °C and was more rapid at 100% field capacity than 70% field capacity (Figure 2-3). Modelled N release increased by 0.01 – 2.45% per 1 °C every 7 days between 10 and 30 °C and increased by 0.002 – 0.6% per 1% increase in soil moisture every 7 days between 70% and 100% field capacity (Figure 2-3). The initial delay in modelled N release from urea and prolonged delay in modelled N release from ESN in Figure 2-2 was due to low soil temperatures, as at temperatures ≥ 10 °C modelled N release from urea began immediately, and ESN had a lag period of 7 days before N release began (Figure 2-3). Following this lag period, modelled N release from ESN proceeded more rapidly at higher temperatures and higher soil moisture levels (Figure 2-3).

2.3.2 Modelling N Source and N Rate Effects on Barley Yields, NUE, and Soil N

2.3.2.1 Soil Moisture and Temperature

Modelled soil water content (SWC) was similar to measured SWC (Figure 2-1A), and modelled SWC closely followed precipitation and irrigation moisture inputs, as well as rises in soil temperature resulting in spring thaw and increased soil moisture (Figure 2-1B,C). Low SWCs below wilting point were not simulated in the model but are unlikely in an irrigated modelled landscape (Figure 2-1A). Fertilized treatments had more rapid declines in SWC than the unfertilized control (Figure 2-1A) due to greater barley productivity resulting in more rapid barley water uptake from increased transpiration. Modelled SWC was greater at the irrigated site than the dryland site due to higher moisture inputs from irrigation, particularly in 2008 and 2009 when greater amounts of irrigation were applied (Figure 2-1A,C, Table 2-1). Overall modelled soil temperature closely matched the measured soil temperature, but at times

measured soil temperature was slightly higher than modelled soil temperature (Figure 2-1B). During the growing season, modelled soil temperatures were 3 – 20 °C, and measured soil temperatures were 3 – 25 °C (Figure 2-1B).

2.3.2.2 Inorganic and Organic Soil N

Depending on the year and site, modelled and measured inorganic soil N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) prior to seeding in the top 0.90 meters of the soil profile ranged between 92 – 134 kg N ha⁻¹ and 63 – 115 kg N ha⁻¹, respectively, indicating there was substantial mineral N build-up prior to the experiment at this site (Supplementary Table 2-2). Greater modelled residual soil nitrate-N levels were observed with higher N fertilizer rates as nitrogen availability exceeded modelled barley N uptake (Figures 2-4, 2-5; Table 2-3). Low soil temperatures during urea hydrolysis following N fertilizer application (Figure 2-1B) resulted in a prolonged delay in modelled N release from ESN (Figures 2-2, 2-3, Supplementary Figure 2-3), slower modelled barley N uptake with ESN, and hence slightly higher modelled residual soil nitrate-N levels with ESN than urea (Figures 2-4, 2-5; Table 2-3). Modelled soil nitrate-N declined rapidly up to 0.60 meters in the soil profile during the modelled barley growth period and rapid modelled barley N uptake, but deeper in the soil profile, modelled soil nitrate-N levels only declined slightly (Figures 2-4, 2-5). At and below 0.60 meters in the soil profile, fertilized barley treatments had greater declines in modelled soil nitrate-N than the unfertilized control treatment (Figures 2-4, 2-5). Modelled soil nitrate-N below 1.2 meters in the soil profile rose in 2010, a wet year (Table 2-1), and the year following, 2011, with a greater increase in modelled soil nitrate-N below 1.2 meters at the irrigated site than at the dryland site (Figures 2-4, 2-5).

Higher N application rates resulted in higher modelled barley yields and greater amounts of organic matter inputs to the soil in the form of crop residues (Supplementary Figure 2-1; Table 2-3). Decomposition of products from greater amounts of modelled crop residues from higher N application rates allowed for slower depletion of modelled soil humus (Supplementary Figure 2-2; Table 2-3). Lower

N rates also had greater declines in modelled residue-N and humus-N during the growing season, particularly for the unfertilized control treatment (Supplementary Figures 2-1, 2-2; Table 2-3). The irrigated site had a slower decline in modelled soil humus due to greater modelled barley productivity at the irrigated site compared to the dryland site (Supplementary Figures 2-1, 2-2; Table 2-3).

2.3.2.3 Synchronization of Modelled N Release from Urea and ESN with Barley N Uptake

Modelled N release from urea was better synchronized with barley N uptake than modelled N release from ESN (Supplementary Figure 2-3). Low modelled soil temperatures at the time of N fertilizer application ($<5^{\circ}\text{C}$, Figure 2-1B) slowed modelled N release from urea and ESN and resulted in a prolonged lag period for modelled N release from ESN (Figures 2-2, 2-3; Supplementary Figure 2-3). Slowed modelled N release from urea early in the growing season closely matched initial barley N uptake ($\sim\text{DOY } 120 - 160$), while a prolonged lag period with modelled N release from ESN resulted in rapid barley N uptake occurring during a period of reduced modelled N release from ESN ($\sim\text{DOY } 160 - 200$) (Supplementary Figures 2-3, 2-4). However, differences in modelled N release between urea and ESN were small ($<7\text{ kg N ha}^{-1}$) throughout the growing season (Supplementary Figure 2-4), and modelled barley N uptake was similar regardless of N source (Supplementary Figure 2-3).

2.3.2.4 Barley Grain Yields and Grain N

Measured barley grain yields (kg C ha^{-1}) corroborated modelled barley grain yields (kg C ha^{-1}) ($R^2 = 0.64$, $\text{RMSE} = 404\text{ kg C ha}^{-1}$, $\text{SD} = 564\text{ kg C ha}^{-1}$) and measured barley grain N (kg N ha^{-1}) corroborated modelled barley grain N (kg N ha^{-1}) ($R^2 = 0.46$, $\text{RMSE} = 17\text{ kg N ha}^{-1}$, $\text{SD} = 25\text{ kg N ha}^{-1}$) (Figure 2-6). The residuals for modelled vs measured barley grain yields (kg C ha^{-1}) ($\text{RMSE} = 404\text{ kg C ha}^{-1}$) were less than the variability of measured barley grain yields ($\text{SD} = 564\text{ kg C ha}^{-1}$), and the residuals for modelled vs measured barley grain N ($\text{RMSE} = 17\text{ kg N ha}^{-1}$) were less than the variability of measured barley grain N ($\text{SD} = 25\text{ kg N ha}^{-1}$), indicating model results fell within the range of measured variability (Figure 2-6). Agreement between the modelled and measured barley grain yields and grain N varied between years

and sites (Table 2-4). Modelled and measured barley grain yields and grain N were similar regardless of N source and increased with increasing N rates but at diminishing rates of return (Figures 2-7, 2-8; Supplementary Table 2-6). Greater modelled barley grain yield response to N rates at 30 and 60 kg N ha⁻¹ compared to measured barley grain yields (Figure 2-7; Supplementary Table 2-6), was driven by low modelled grain yields at 0 kg N ha⁻¹ (2008; irrigated site in 2010) or by higher modelled barley grain yields at 30 and 60 kg N ha⁻¹ (irrigated site in 2009; 2011) (Figure 2-7). In 2010, greater spring precipitation (Table 2-1) led to greater modelled soil nitrate-N deep in the profile and less modelled soil nitrate-N in the top 0.15 meters of the soil profile available for early season modelled barley N uptake (Figures 2-4, 2-5; Supplementary Table 2-2), reducing modelled unfertilized barley grain yields (Figures 2-7). Modelled unfertilized barley grain yields in 2008 and 2010 had greater oxygen stress than fertilized barley grain yields (Supplementary Figure 2-5) as a result of reduced rooting densities (Supplementary Figures 2-6, 2-7) and higher SWC (Figure 2-1A), which likely also contributed to low modelled unfertilized barley grain yields (Figure 2-7).

2.3.2.5 EONR

Depending on the year, site, and N source, EONRs estimated based on modelled yield response to N rate (kg N ha⁻¹) (modelled EONRs) ranged between 44 – 88 kg N ha⁻¹, and EONRs estimated based on measured yield response to N rate (measured EONRs) ranged between 5 – 111 kg N ha⁻¹ (Table 2-5). Compared to modelled barley grain yields, measured barley grain yields had a more linear response to increasing N rates, resulting in lower EONRs than modelled results, except for 2011 at the irrigated site (Figure 2-7, Table 2-5). Due to the higher fertilizer cost for ESN, ESN had lower EONRs and, thereby, higher NUEs than urea at the EONR (Figure 2-9, Table 2-5). Modelled EONR was higher during years and sites with higher moisture inputs, and modelled EONR was positively correlated with May and June moisture inputs (precipitation + irrigation) ($r = 0.91$, $p = 0.002$). Modelled EONR was negatively

correlated with modelled soil nitrate-N levels prior to seeding in the top 0.15 meters of the soil profile ($r=-0.84$, $p = 0.009$).

2.3.2.6 NUE

Nitrogen use efficiency (NUE) (% kg Grain N kg⁻¹ N Fertilizer) calculated from modelled and measured barley grain N (Figure 2-8) (modelled and measured NUE) was similar regardless of N source and declined with increasing N rates as N availability exceeded barley N uptake (Figure 2-9). Low-modelled unfertilized control and high-modelled fertilized barley grain N (Figure 2-8) resulted in higher modelled NUE values compared to measured NUE, particularly at lower N rates of 30 and 60 kg N ha⁻¹ (Figure 2-9; section 2.3.2.4). At typical commercially applied N rates of 90 and 120 kg N ha⁻¹, modelled NUE values (27–53% at the dryland site, 33–68% at the irrigated site) were closer to measured NUE values (19–46% at the dryland site, 25–43% at the irrigated site) (Figure 2-9). Modelled NUE varied considerably between years, with modelled NUE differing by 2 – 51% at the dryland site, and 5 – 47% at the irrigated site for any given N rate between 30 to 120 kg N ha⁻¹ for 2008 – 2011 (Figure 2-9). Modelled NUE was greater at the irrigated site (53 – 107%) than at the dryland site (27 – 61%) in the drier years of 2008 and 2009 (Table 2-1) but was similar between dryland (39 – 63%) and irrigated sites (39 – 65%) in 2010, a wet year (Figure 2-9, Table 2-1). Following the wet year of 2010, in 2011, modelled NUE was greater at the dryland site (42 – 111%) than at the irrigated site (33 – 60%) (Figure 2-9, Table 2-1). The modelled NUE at the modelled EONRs ranged between 44 – 71%, and the measured NUE at the measured EONRs ranged between 11 – 51% depending on the year, site, and N source (Table 2-5). Unlike the modelled NUE, which declined with increases in N rate, modelled NUE at the EONR and the EONR had no observed trends, except for a weak positive correlation ($r = 0.18$, $p = 0.66$).

2.4 Discussion

2.4.1 Sensitivity of N Release to Temperature and Moisture

Modelled N release from urea and ESN were in good agreement with measured N release results, indicating parameters within the model for N release adequately simulated the N release from different N fertilizer sources at different temperatures and soil moisture levels ($R^2 = 0.94$, RMSE = 11.1%, $p < 0.001$; Figure 2-2). Modelled N release from urea and ESN were more rapid with increasing temperatures and soil moisture, but the temperature had a greater impact on modelled N release than soil moisture, which is in accordance with literature findings (Figures 2-2, 2-3). Temperature has the greatest impact on N release as it controls the rate of diffusion and urease activity (Agehara and Warncke 2005; Du et al. 2006; Golden et al. 2011; Ransom et al. 2020). Modelled sensitivity of N release to temperature was 0.01 – 2.45% per 1°C every 7 days (Figure 2-3), which is at the lower end of the temperature sensitivity range reported by Golden et al. (2011) of 2.0 – 4.6% per 1°C every 7 days, but similar to ranges reported by Agehara and Warncke (2005) of 0 – 1.44% and Du et al. (2006) of 0.34 – 0.7% per 1 °C every 7 days.

Modelled sensitivity of N release was lower for soil moisture than temperature, and modelled N release increased 0.004 – 0.58% per 1% increase in soil moisture every 7 days at 20 °C (Figure 2-3), which is similar to the range of 0.03 – 0.35% per 1% increase in soil moisture every 7 days at 20°C reported by Agehara and Warncke (2005). In contrast, Cahill et al. (2010a) found no significant soil moisture impact on N release from increasing the soil moisture from 60 to 80% field capacity, although this may have been due to the small difference in soil moisture levels. However, increasing soil moisture has been found to enhance microbial activity and urease enzyme production, thereby increasing the rate of urea hydrolysis (Agehara and Warncke, 2005). Nitrogen release in *ecosys* is affected by soil water concentration and microbial activity, which is controlled by soil moisture, leading to a more rapid N release from urea and ESN at higher soil moisture levels (Figures 2-2, 2-3).

2.4.2 Lag in N Release from ESN

Modelled N release from ESN approached a sigmoidal pattern of N release and had a lag in N release of approximately 7 days at $\geq 10^{\circ}\text{C}$, which is in accordance with literature findings (Figures 2-2, 2-3). Shaviv et al. (2003) described the first stage in N release from polymer-coated urea (PCU) fertilizers such as ESN as a lag period where no N is released from the granule, resulting in a sigmoidal pattern of N release. This lag period occurs as water must first diffuse through the polymer coating, dissolve the urea in the granule, and the urea must then diffuse out of the polymer coating before subsequent urea hydrolysis (Cahill et al. 2010a). In a laboratory soil incubation experiment, Cahill et al. (2010a) found that the lag in N release from ESN was between 3 to 7 days at $23 - 26^{\circ}\text{C}$. Golden et al. (2011) conducted a laboratory soil incubation experiment and measured the N release from ESN every 5 days and found that the N release from ESN began after 5 or 10 days at $15 - 30^{\circ}\text{C}$ (2011). In water-saturated sand at temperatures of 20, 30, or 40°C , Du et al. (2006) found the lag period to vary between 4 – 8 days depending on the PCU fertilizer type and temperature. In contrast to N release from ESN, modelled N release from urea at temperatures $\geq 10^{\circ}\text{C}$ proceeded immediately following N application (Figure 2-3) which is in accordance with findings reported by Cahill et al. (2010a) and Agehara and Warncke (2005). A lag period where no N is released from ESN and low initial crop N uptake at the beginning of the growing season may result in improved synchronization between crop N demand and N availability, thereby increasing N uptake and NUE compared to conventional urea fertilizer (Nelson et al. 2008; Cahill et al. 2010a; Golden et al. 2011; Soon et al. 2011).

Low temperatures of $< 10^{\circ}\text{C}$ markedly reduced modelled N release, resulting in a delayed N release from urea and a prolonged lag in N release from ESN (Figure 2-2). Golden et al. (2011) also found that lower temperatures reduced initial N release from ESN. In the first 10 days of a laboratory soil incubation experiment, initial N release from ESN was reduced by at least 50% when temperatures were decreased by 5°C between 15 and 25°C (Golden et al. 2011). A slower N release at lower temperatures

and soil moisture levels (Figures 2-2, 2-3) suggests that in cooler and drier conditions at the time of N fertilizer application, there will be a slower N release from urea and ESN, which will affect the synchronization between N supply and crop N demand.

2.4.3 Effectiveness of ESN in Increasing Barley Grain Yields, Grain N, and NUE

The lag in modelled N release from ESN did not improve synchronization of N availability with modelled barley N uptake (Supplementary Figure 2-3) and did not improve modelled barley grain yields, grain N, or NUE at this cool, semi-arid site (MAT = 5.8 °C; Figure 2-1C, Table 2-1) in Southern Alberta (Figures 2-7, 2-8, 2-9). Nitrogen release from ESN must better match crop N uptake than does that from urea to increase yields and NUE (Nelson et al. 2008; Golden et al. 2011; Soon et al. 2011). Cold soil temperatures at the beginning of the growing season (<5 °C, Figure 2-1B) resulted in a prolonged modelled lag period with ESN (Figure 2-2, Supplementary Figure 2-3), which did not match early season modelled barley N uptake (Supplementary Figure 2-3). The slower modelled N release from urea due to low spring soil temperatures closely matched the low initial modelled barley N uptake, while a prolonged modelled lag period with ESN resulted in rapid modelled N release from ESN beginning after rapid modelled barley N uptake began at around DOY 160 (Figures 2-2, 2-3; Supplementary Figure 2-3).

Model findings of a prolonged N release from ESN are consistent with findings from C. Grant et al. (2012) and Blackshaw et al. (2011 a,b), that early season growth and crop N accumulation was reduced with ESN which was attributed to N release from ESN being too delayed to match crop N demand in the cool, semi-arid Canadian prairies. While modelled barley N uptake was not lower early in the growing season with ESN compared to urea (Supplementary Figure 2-3), this was likely due to high levels of soil inorganic N (Figures 2-4, 2-5). Thilakarathna et al. (2020) also found that high levels of soil inorganic N may have masked the effects of different N sources on crop nitrogen recovery efficiency (NRE) and NUE. In addition, while modelled N release from ESN was slower than that from urea

throughout the growing season, differences in modelled N release between the N sources were small (<7 kg N ha⁻¹) and diminished throughout the growing season (Supplementary Figures 2-3, 2-4). Accordingly, modelled barley N uptake, barley grain yields, grain N, and NUE were similar for ESN and urea (Figures 2-7, 2-8, 2-9; Supplementary Figure 2-3).

In accordance with model results, other studies in Western Canada have reported similar or inconsistent effects of ESN on crop yields, grain nitrogen, and NUE (McKenzie et al. 2010; Malhi et al. 2010; Blackshaw et al. 2011b, 2011a; Grant et al. 2012; Mezbahuddin et al. 2020; Thilakarathna et al. 2020). Throughout Alberta's different climatic conditions and soil zones, Mezbahuddin et al. (2020) found that ESN lowered barley grain yields by 0.7 – 2.7% and lowered grain N content by 0.6 – 2.7% compared to urea. Across a range of climatic conditions in Western Canada, C. Grant et al. (2012) found that ESN did not offer consistent increases in crop yield, grain N accumulation, or NUE compared to urea. In semi-humid Central Alberta, wheat NUE and NRE were similar for urea and ESN over 2 years (Thilakarathna et al. 2020). At sub-humid sites in Western Canada, Malhi et al. (2010) found that under wetter than normal soil moisture levels, yields and NRE were higher with ESN than urea at 2 out of 7 site years. Under the semi-arid conditions of the Western Canadian prairies, ESN had inconsistent effects on barley and canola yields (Blackshaw et al. 2011a, 2011b). ESN increased barley and canola yields at 3/20 and 4/20 site-years, reduced barley and canola yields at 2/20 and 1/20 site-years, and the remaining site-years had similar barley and canola yields for urea and ESN (Blackshaw et al. 2011a, 2011b). In semi-arid Southern Alberta, ESN slightly increased winter wheat grain yields by 2.2% compared to urea and had no impact on grain protein concentrations (McKenzie et al. 2010). Inconsistent findings of the effects of ESN on yields and NUE may indicate that ESN has limited effectiveness in providing agronomic benefits in the cool, semi-arid Canadian prairies.

However, in warmer regions where urea would hydrolyze more rapidly, a delay in N release from ESN compared to urea could improve the synchronization between N supply and crop N demand,

increasing yields and NUE (Li et al. 2018; Yang et al. 2021). Results from global meta-analyses suggest that polymer-coated urea (PCU) fertilizer effectiveness at increasing crop N uptake increases with increasing MAT (Yang et al. 2021), and that PCU fertilizer may only be effective at increasing yields and NUE in cropping systems at MATs of 10 – 20 °C (Li et al. 2018). For instance, in maize cropping systems where planting and N fertilizer application occurs at soil temperatures > 10 °C (Cahill et al. 2010b; Gagnon et al. 2012), PCU fertilizers were found to increase maize yields by 5.3 % and NUE by 24.1% according to a meta-analysis (Zhang et al. 2019).

ESN may be more effective at increasing yields and NUE under wetter conditions where there is a higher potential for denitrification and leaching losses, such as under irrigation (Nelson et al. 2008; Wilson et al. 2010; Malhi et al. 2010; Grant et al. 2012; Gagnon et al. 2012). However, despite increased soil moisture at the irrigated site, barley grain yields, grain N, and NUE were similar for both N sources at this semi-arid site in Southern Alberta (Figures 2-7, 2-8, 2-9). At the time of irrigation inputs, there were minimal differences in modelled N release between urea and ESN, and likely a lower potential for N losses due to rapid modelled barley N uptake resulting in lower modelled soil nitrate levels (Figure 2-5; Supplementary Figure 2-3). The effectiveness of ESN at increasing yields and NUE depends on the timing of N availability with conditions prone to N losses, and therefore irrigation may not result in increased efficacy of ESN (Li et al. 2016; Thapa et al. 2016; Clément et al. 2021). Conditions at the site may have also been too cold and dry for increased efficacy of ESN, even with increased moisture from irrigation. In a global meta-analysis, Li et al. (2018) found that PCU fertilizers were more effective at irrigated sites but also found that PCU fertilizers were only effective in climates where annual precipitation was 800 – 1200 mm, and the MAT was 10 – 20 °C. At this site, total combined annual precipitation and irrigation ranged between 517 – 624 mm and the MAT was 5.0 – 5.4 °C for 2008 – 2011, which is colder and drier than the reported range for PCU effectiveness described by Li et al. (2018) (Table 2-1).

2.4.4 Modelled Barley Grain Yield Response to Increasing N Rates and Factors Affecting the EONR

Modelled barley grain yield response to increasing N rates agreed with literature findings on yield response to N rate and allowed for accurate estimates of EONRs (Figure 2-7, Table 2-5). Increasing the N application rate will increase crop yields but at diminishing rates of return as crop N demand is met (O'Donovan et al. 2015). Modelled increases in barley grain yields declined with increasing N rates, and minimal modelled barley grain yield responses (<3% yield gains, Supplementary Table 2-6) were observed from 90 to 120 kg N ha⁻¹ (Figure 2-7). In accordance with model findings, O'Donovan et al. (2015) also found minimal increases in barley yields from increasing the nitrogen rate from 90 to 120 kg N ha⁻¹ in Western Canada, and McKenzie et al. (2004a) found that most yield gains were achieved below 90 kg N ha⁻¹ in Central and Southern Alberta.

At a fertilizer-to-grain price ratio of 7.4 for urea, EONRs estimated based on modelled yield response to increasing N rates ranged between 51 – 88 kg N ha⁻¹ (average 75 kg N ha⁻¹) (Table 2-5), which falls within the range of EONR values reported in the literature. In a study on the EONR for barley in Southern and Central Alberta at a fertilizer-to-grain price ratio of 8, McKenzie et al. (2004b) reported the EONR for urea fertilizer to be 50 – 92 kg N ha⁻¹, depending on the barley cultivar. Furthermore, at sites in Southern Alberta, McKenzie et al. (2004b) found that the EONR ranged between 38 – 147 kg N ha⁻¹, with an average EONR of 75 kg N ha⁻¹. Using a stochastic simulation model which varied barley grain and N fertilizer prices, Smith et al. (2012) determined that the maximum net return for barley grain yields at sites across the Western Canadian prairies occurred at N rates of 60 – 90 kg N ha⁻¹. Compared to urea, ESN had a higher N fertilizer cost (fertilizer-to-grain price ratio of 9) and similar modelled barley grain yields, making ESN fertilizer less economical than urea (Khakbazan et al. 2013).

May and June moisture inputs (precipitation + irrigation) (Table 2-1) were strongly positively correlated with modelled EONRs, as higher soil moisture availability facilitated greater modelled barley N

uptake and barley productivity at this semi-arid site in Southern Alberta (Figures 2-1, 2-7; Supplementary Figure 2-3). McKenzie et al. (2004b) also found that EONRs were higher with increased precipitation inputs due to enhanced barley N uptake at sites in Southern Alberta. Modelled EONRs were strongly negatively correlated with soil nitrate-N levels prior to seeding, similar to results reported by McKenzie et al. (2004b) that EONRs were lower with higher soil nitrate-N. The variability of EONRs with soil nitrate-N levels prior to seeding highlights the importance of annual spring soil testing, which is completed annually by only 20% of Canadian farmers (Korol 2004).

2.4.5 Effects of N Fertilization on NUE

Modelled NUE declined with increasing N rates (Figure 2-9), and modelled soil N supply and barley N uptake differed between fertilized and unfertilized treatments due to differences in root density (Supplementary Figures 2-6, 2-7), the spatial distribution of nitrate-N in the soil profile (Figures 2-4, 2-5), and mineralization of SON (Table 2-3; Supplementary Figures 2-1, 2-2). Declines in modelled NUE with increasing N rates are consistent with findings reported by Malhi et al. (2010) and Donovan et al. (2015). Lassaletta et al. (2016) estimated NUE in North America to be 70% at an N fertilizer rate of 76 kg N ha⁻¹, compared to modelled NUE which ranged between 31 – 71% (average 53%) for 2008 – 2011 at the same N fertilizer rate (Figure 2-9). Karimi et al. (2020) estimated NUE in Canada to be 51% at an average N fertilizer rate of 62 kg N ha⁻¹, compared to modelled NUE which ranged between 37 – 78% (average 60%) at 62 kg N ha⁻¹ for 2008 – 2011 (Figure 2-9). At N rates of 75 – 92 kg N ha⁻¹, McKenzie et al. (2004b) reported NUE to be 41 – 48% in Southern and Central Alberta, and modelled NUE values were 27 – 71% (average 47 – 53%) for 2008 – 2011 at corresponding N rates (Figure 2-9). Modelled NUE values were higher than results reported by McKenzie et al. (2004b) at lower N rates (<60 kg N ha⁻¹) but were similar at N rates greater than 90 kg N ha⁻¹ where modelled NUE approached ~50% (Figure 2-9). Higher modelled NUE in this study at lower N rates is likely due to the low modelled unfertilized barley grain N

values used to calculate the modelled NUE, which in some cases were lower than measured unfertilized barley grain N values (Figures 2-8, 2-9).

In some years and sites (2008 Irrigated, 2009 Irrigated, and 2011 Dryland), at 30 kg N ha⁻¹, modelled NUE exceeded 100% (Figure 2-9). At sites in Southern Alberta with 33 – 170 kg N ha⁻¹ of fertilizer applied, McKenzie et al. (2004a) also reported NUE values of greater than 100% and hypothesized this was due to increased N uptake or reduced leaching from increased crop transpiration with fertilized compared to unfertilized barley. Modelled fertilized barley treatments had greater modelled root densities than unfertilized barley, which increased soil N uptake efficiency and increased NUE (Burns 1980) (Supplementary Figures 2-6, 2-7). In addition, lower productivity in unfertilized barley led to reduced transpiration and higher soil water content (Figure 2-1A), which led to greater downward movement of soil nitrate-N deeper in the soil profile with unfertilized compared to fertilized barley (Figures 2-4, 2-5). While unfertilized barley had greater declines in SON during the growing season, and therefore greater soil N supply from mineralization (Table 2-3; Supplementary Figures 2-1, 2-2), reduced rooting density (Supplementary Figures 2-6, 2-7), higher SWC (Figure 2-1A) and a higher potential for N leaching and denitrification losses, and increased nitrate-N deeper in the soil profile (Figures 2-4, 2-5) indicates that this increased N supply from SON relative to fertilized barley may not have been taken up by the unfertilized crop. Current NUE indices do not account for how fertilization affects crop N uptake, such as by increasing root density and proliferation in the soil profile or reducing mineralization of SON (Burns 1980; Mahal et al. 2019; Congreves et al. 2021) (Table 2-3; Supplementary Figures 2-6, 2-7). Therefore, while the unfertilized control is meant to represent soil N uptake in the calculation of NUE (sec. 2.2.3; eq. 1), it may not represent soil N uptake of the fertilized crop and could result in an over or underestimation of NUE (Mahal et al. 2019; Congreves et al. 2021).

2.4.6 Variation in NUE with Irrigation and Interannual Climatic Variability

Modelled NUE at a specified N rate varied by as much as 51% depending on the irrigation and year (Figure 2-9), highlighting the challenges of increasing NUE. In semi-arid Southern Alberta, water is often a limiting factor for crop production and water availability influences crop N uptake and NUE (McKenzie et al. 2004a; Zebarth et al. 2009; Djaman et al. 2013; Maharjan et al. 2014). Depending on the timing and amount of precipitation and irrigation inputs, increased moisture inputs from irrigation may increase NUE by reducing water stress and enhancing crop N uptake (Djaman et al. 2013; Maharjan et al. 2014). Conversely, increased moisture inputs from irrigation may reduce NUE because of higher N leaching and denitrification losses from the higher soil moisture (Djaman et al. 2013; Maharjan et al. 2014). In the drier years of 2008 and 2009, modelled NUE was greater at the irrigated site than at the dryland site due to greater barley N uptake from increased water availability (Figure 2-1, 2-9). McKenzie et al. (2004a) also found that barley N uptake and NUE were higher at irrigated than dryland sites in Southern Alberta due to enhanced N uptake. In 2010, the study's wettest year, modelled NUE was similar at dryland and irrigated sites (Figure 2-9). Maharjan et al. (2014) found that in a wet year, NUE was similar between irrigated and dryland sites due to increased N leaching losses at the irrigated site (see Chapter 3 for N losses). In 2011, a dry year following a wet year, there was a carryover effect from the increased moisture in 2010, as evidenced by the higher soil nitrate-N levels deeper in the soil profile in 2011 (Figure 2-5). As a result, despite 2011 being a dry year, modelled NUE was higher at the dryland site than at the irrigated site (Figure 2-9). Similarly, in the drier year of their study, Maharjan et al. (2014) also found that NUE was higher at the dryland site than at the irrigated site. While NUE may be increased in drier years with irrigation due to enhanced N uptake, wet years, or the year following wet years, may result in increased N losses and reduced NUE (McKenzie et al. 2004a; Djaman et al. 2013; Maharjan et al. 2014) (see Chapter 3 for N losses). Accordingly, proper irrigation and N management are essential for

optimizing crop productivity, managing water resources, and reducing N losses (Djaman et al. 2013; Maharjan et al. 2014).

While estimates of NUE at national and continental scales (Lassaletta et al. 2016; Karimi et al. 2020) give insight into general NUE values, modelled NUE values and site-specific NUE values reported in the literature varied considerably between years and at different sites (Nyborg and Malhi 1986; McKenzie et al. 2004a, 2004b; Thilakarathna et al. 2020) (Figure 2-9). For a given N rate, modelled NUE varied by 2 – 51% between 2008 and 2011 at dryland and irrigated sites in Southern Alberta due to interannual climatic variability and irrigation (Figure 2-9). Yang et al. (2023) found that crop N uptake of applied fertilizer varied between 26 – 76% in the Western Canadian prairies due to regional and interannual climatic variability, particularly due to total annual precipitation. Nyborg and Malhi (1986) found that NUE of barley ranged between 27 – 97% at 56 kg N ha⁻¹ due to interannual climatic variability over a 7-year period and differing soil properties at sites in northern and central Alberta. Thilakarathna et al. (2020) found that NUE of wheat ranged between 25 – 42% at 100 kg N ha⁻¹ due to interannual climatic variability over a 2-year period in Central Alberta. McKenzie et al. (2004a,b) found that NUE of barley ranged between 29 – 48% at economically optimum N rates of 11 – 147 kg N ha⁻¹, and that NUE ranged between 35 – 134% at EONRs of 31 – 170 kg N ha⁻¹ in Southern and Central Alberta due to variable moisture inputs (precipitation and irrigation) and spring soil nitrate-N levels. The substantial variability in NUE showcases the challenge of increasing NUE across different regions and environmental conditions and highlights the need for site-specific N management practices (Karimi et al. 2020). By determining the variability in NUE, regions and conditions with low NUE could be identified and improved management practices and policy directives could be focused on these situations (Mezbahuddin et al. 2020; Udvardi et al. 2021). In addition, knowledge of the variability in NUE could allow for a systems approach to increasing NUE so that gains in NUE in one context would not be offset by decreases in NUE in another context (Karimi et al. 2020; Udvardi et al. 2021). Long-term studies will

also be crucial to account for the effect of repeated N applications on NUE (Congreves et al. 2021). As conducting numerous field studies to determine the variability of NUE under different management practices, soil properties, and environmental conditions would be expensive and time-consuming, the use of computer models such as *ecosys* will be an effective tool in informing effective N management decisions for various conditions and in different regions (Puntel et al. 2016; Mezbahuddin et al. 2020).

2.4.7 Economic and Environmental Sustainability: NUE at the EONR

Unlike the relationship between the N rate and modelled NUE, modelled NUE at the EONR (Table 2-5) did not decline with increases in EONR at a constant fertilizer-to-grain price ratio, which is a trend also reported by McKenzie et al. (2004b), where EONR and NUE were positively correlated. Greater yield response to N fertilizer allowed for higher EONRs and increased N uptake and NUE (McKenzie et al. 2004b; Basso et al. 2019). Therefore, it is important to identify regions and conditions with high and low yield potential and to adjust N rates accordingly to increase NUE (Basso et al. 2019). Modelled NUE values at EONR (44 – 71%, Table 2-5) were relatively high, but a lower fertilizer-to-grain price ratio would allow for higher N rates to be more economical but would decrease NUE (Figure 2-9). Variability in commodity pricing and, thereby, the EONR is another challenge associated with increasing NUE, as increases, or decreases in N rates will be driven by economic factors rather than agricultural productivity or environmental concerns. While the EONR is important to allow producers to make a profit and thus be economically sustainable (Cassman et al. 2002), it does not account for the environmental effects of increases in N application rates, such as reductions in NUE and increases in N losses (see Chapter 3). To account for the hidden environmental costs, Millar et al. (2010) suggested that a nutrient market be used to compensate producers for applying N rates slightly below EONR, as these rates provided comparable economic returns and agricultural productivity while reducing N losses. Accordingly, to increase NUE, it is important to account for economic factors in N rate decisions and variability in NUE response to increasing N rates for different sites and environmental conditions.

2.5 Conclusion

The process-based ecosystem model *ecosys* successfully simulated the effects of N source, N rate, irrigation, and interannual climatic variability on barley grain yields, grain N, NUE, and EONRs. Compared to conventional urea fertilizer, ESN did not increase modelled barley grain yields, grain N, or NUE as cool soil temperatures slowed modelled N release from ESN and, as a result, did not match early season modelled barley N uptake. Under the cool, semi-arid conditions of the Western Canadian prairies, conditions are too dry and cold for ESN to provide agronomic benefits, even with increased moisture inputs at irrigated sites. Nitrogen rate had a larger impact on modelled barley yields, grain N, and NUE than differences in N sources (Urea and ESN), with barley grain yields and grain N increasing with increasing N rates but at diminishing rates of return. Furthermore, the negative correlation of EONRs with spring soil nitrate-N levels indicates that improvements in N rate recommendations, such as ensuring annual spring soil testing, should be a priority for increasing NUE. Modelled NUE declined with increases in N rate but varied substantially between years and with different irrigation amounts, indicating site-specific N management practices will be necessary to increase NUE. While EONRs may account for the economic sustainability of agricultural production, EONRs do not account for environmental considerations such as NUE, and these external costs need to be addressed in policymaking. The use of computer models such as *ecosys* could be used to model other site-specific scenarios to identify conditions with low NUE while also considering economic factors such as EONR to aid in selecting N management practices which balance both environmental and economic considerations.

2.6 References

- ACIS 2021. Alberta Climate Information Service. [Online] Available: <https://agriculture.alberta.ca/acis/> [2021 Oct. 1].
- Agehara, S., and Warncke, D.D. 2005. Soil Moisture and Temperature Effects on Nitrogen Release from Organic Nitrogen Sources. *Soil Science Society of America Journal* **69**: 1844–1855. doi:10.2136/sssaj2004.0361.
- Agriculture and Agri-Food Canada 2022. Discussion Document: Reducing emissions arising from the application of fertilizer in Canada's agriculture sector - agriculture.canada.ca. [Online] Available: <https://agriculture.canada.ca/en/about-our-department/transparency-and-corporate-reporting/public-opinion-research-and-consultations/share-ideas-fertilizer-emissions-reduction-target/discussion-document-reducing-emissions-arising-application-fertilizer-canadas-agriculture-sector> [2022 Sep. 22].
- Basso, B., Shuai, G., Zhang, J., and Robertson, G.P. 2019. Yield stability analysis reveals sources of large-scale nitrogen loss from the US Midwest. *Sci Rep* **9**. Nature Publishing Group. doi:10.1038/s41598-019-42271-1.
- Blackshaw, R.E., Hao, X., Brandt, R.N., Clayton, G.W., Harker, K.N., O'Donovan, J.T., Johnson, E.N., and Vera, C.L. 2011a. Canola response to ESN and urea in a four-year no-till cropping system. *Agron J* **103**: 92–99. doi:10.2134/agronj2010.0299.
- Blackshaw, R.E., Hao, X., Harker, K.N., O'Donovan, J.T., Johnson, E.N., and Vera, C.L. 2011b. Barley productivity response to polymer-coated urea in a no-till production system. *Agron J* **103**: 1100–1105. doi:10.2134/agronj2010.0494.
- Blenkinsop, P.G., and Dale, J.E. 1974. The Effects of Nitrate Supply and Grain Reserves on Fraction I Protein Level in the First Leaf of Barley. *J Exp Bot* **25**: 913–926. doi:10.1093/jxb/25.5.913.
- Burns, I.G. 1980. Influence of the Spatial Distribution of Nitrate on the Uptake of N by Plants: A Review and a Model for Rooting Depth. *Journal of Soil Science* **31**: 155–173. doi:10.1111/j.1365-2389.1980.tb02073.x.
- Cahill, S., Osmond, D., and Israel, D. 2010a. Nitrogen release from coated urea fertilizers in different soils. *Commun Soil Sci Plant Anal* **41**: 1245–1256. doi:10.1080/00103621003721437.
- Cahill, S., Osmond, D., Weisz, R., and Heiniger, R. 2010b. Evaluation of alternative nitrogen fertilizers for corn and winter wheat production. *Agron J* **102**: 1226–1236. doi:10.2134/agronj2010.0095.
- Cameron, K.C., Di, H.J., and Moir, J.L. 2013. Nitrogen losses from the soil/plant system: A review. *Annals of Applied Biology* **162**: 145–173. doi:10.1111/aab.12014.
- Cassman, K.G., Dobermann, A., and Walters, D.T. 2002. Agroecosystems, Nitrogen-use Efficiency and Nitrogen management. *Amibio* **31**: 132–139. doi:10.1579/0044-7447-31.2.132.
- Chen, J., Lü, S., Zhang, Z., Zhao, X., Li, X., Ning, P., and Liu, M. 2018. Environmentally friendly fertilizers: A review of materials used and their effects on the environment. *Science of the Total Environment* **613–614**: 829–839. Elsevier B.V. doi:10.1016/j.scitotenv.2017.09.186.
- Clément, C.C., Cambouris, A.N., Ziadi, N., Zebarth, B.J., and Karam, A. 2021. Potato yield response and seasonal nitrate leaching as influenced by nitrogen management. *Agronomy* **11**. MDPI. doi:10.3390/agronomy11102055.
- Congreves, K.A., Otchere, O., Ferland, D., Farzadfar, S., Williams, S., and Arcand, M.M. 2021. Nitrogen Use Efficiency Definitions of Today and Tomorrow. *Front Plant Sci* **12**. Frontiers Media S.A. doi:10.3389/fpls.2021.637108.

- Djaman, K., Irmak, S., Martin, D.L., Ferguson, R.B., and Bernards, M.L. 2013. Plant nutrient uptake and soil nutrient dynamics under full and limited irrigation and rainfed maize production. *Agron J* **105**: 527–538. doi:10.2134/agronj2012.0269.
- Drury, C.F., Reynolds, W.D., Yang, X.M., McLaughlin, N.B., Welacky, T.W., Calder, W., and Grant, C.A. 2012. Nitrogen Source, Application Time, and Tillage Effects on Soil Nitrous Oxide Emissions and Corn Grain Yields. *Soil Science Society of America Journal* **76**: 1268–1279. Wiley. doi:10.2136/sssaj2011.0249.
- Du, C.W., Zhou, J.M., and Shaviv, A. 2006. Release characteristics of nutrients from polymer-coated compound controlled release fertilizers. *J Polym Environ* **14**: 223–230. doi:10.1007/s10924-006-0025-4.
- Environment and Climate Change Canada 2022. National Inventory Report 1990–2022: Greenhouse Gas Sources and Sinks in Canada.
- Gagnon, B., Ziadi, N., and Grant, C. 2012. Urea fertilizer forms affect grain corn yield and nitrogen use efficiency. *Can J Soil Sci* **92**: 341–351. doi:10.4141/cjss2011-074.
- Golden, B., Slaton, N., Norman, R., Gbur, E., and Wilson, C. 2011. Nitrogen release from environmentally smart nitrogen fertilizer as influenced by soil series, temperature, moisture, and incubation method. *Commun Soil Sci Plant Anal* **42**: 1809–1824. doi:10.1080/00103624.2011.587568.
- Grant, C., and Wu, R. 2008. Enhanced-Efficiency Fertilizers for Use on the Canadian Prairies. *Crop Management* **7**: 1–15. American Society of Agronomy. doi:10.1094/cm-2008-0730-01-rv.
- Grant, C.A., Wu, R., Selles, F., Harker, K.N., Clayton, G.W., Bittman, S., Zebarth, B.J., and Lupwayi, N.Z. 2012. Crop yield and nitrogen concentration with controlled release urea and split applications of nitrogen as compared to non-coated urea applied at seeding. *Field Crops Res* **127**: 170–180. doi:10.1016/j.fcr.2011.11.002.
- Grant, R. 2001. A Review of the Canadian Ecosystem Model - ecosys. Pages 173–263 in M. Shaffer, L. Ma, and S. Hansen, eds. *Modeling Carbon and Nitrogen Dynamics for Soil Management*. CRC Press, Boca Raton, Florida.
- Grant, R.F., Dyck, M., and Puurveen, D. 2020. Nitrogen and phosphorus control carbon sequestration in agricultural ecosystems: Modelling carbon, nitrogen, and phosphorus balances at the breton plots with ecosys under historical and future climates1. *Can J Soil Sci* **100**: 408–429. Agricultural Institute of Canada. doi:10.1139/cjss-2019-0132.
- Grant, R.F., Juma, N.G., Robertson, J.A., Izaurralde, R.C., and McGill, W.B. 2001. Long-Term Changes in Soil Carbon under Different Fertilizer, Manure, and Rotation. *Soil Science Society of America Journal* **65**: 205–214. Wiley. doi:10.2136/sssaj2001.651205x.
- Grant, R.F., and Pattey, E. 2003. Modelling variability in N₂O emissions from fertilized agricultural fields. *Soil Biol Biochem* **35**: 225–243. doi:10.1016/S0038-0717(02)00256-0.
- Grant, R.F., Pattey, E., Goddard, T.W., Kryzanowski, L.M., and Puurveen, H. 2006. Modeling the Effects of Fertilizer Application Rate on Nitrous Oxide Emissions. *Soil Science Society of America Journal* **70**: 235–248. Wiley. doi:10.2136/sssaj2005.0104.
- Hao, X., Chang, C., Carefoot, J.M., Janzen, H.H., and Ellert, B.H. 2001. Nitrous oxide emissions from an irrigated soil as affected by fertilizer and straw management. *Nutr Cycl Agroecosyst* **60**: 1–8. doi:10.1023/A:1012603732435.
- Jones, D.B. 1941. *Factors for Converting Percentages of Nitrogen in Foods and Feeds into Percentages of Proteins*. Washington, DC.

- Karimi, R., Pogue, S.J., Kröbel, R., Beauchemin, K.A., Schwinghamer, T., and Henry Janzen, H. 2020. An updated nitrogen budget for Canadian agroecosystems. *Agric Ecosyst Environ* **304**. Elsevier B.V. doi:10.1016/j.agee.2020.107046.
- Khakbazan, M., Grant, C.A., Finlay, G., Wu, R., Malhi, S.S., Selles, F., Clayton, G.W., Lupwayi, N.Z., Soon, Y.K., and Harker, K.N. 2013. An economic study of controlled release urea and split applications of nitrogen as compared with non-coated urea under conventional and reduced tillage management. *Canadian Journal of Plant Science* **93**: 523–534. doi:10.4141/CJPS2012-107.
- Korol, M. 2004. Fertilizer and pesticide management, Canada. Statistics Canada, Agriculture Division.
- Kryzanowski, L., Mckenzie, R., Middleton, A., Sprout, C., Henriquez, B., and O'Donovan, J. 2009. Enabling Adoption of Environmentally Smart Nitrogen (ESN) Technology to Maximize Economic Returns and Environmental Benefits in Alberta Progress Report.
- Lassaletta, L., Billen, G., Garnier, J., Bouwman, L., Velazquez, E., Mueller, N.D., and Gerber, J.S. 2016. Nitrogen use in the global food system: Past trends and future trajectories of agronomic performance, pollution, trade, and dietary demand. *Environmental Research Letters* **11**. Institute of Physics Publishing. doi:10.1088/1748-9326/11/9/095007.
- Li, C., Hao, X., Blackshaw, R.E., Clayton, G.W., O'Donovan, J.T., and Harker, K.N. 2016. Nitrous Oxide Emissions in Response to ESN and Urea Application in a No-Till Barley Cropping System. *Commun Soil Sci Plant Anal* **47**: 692–705. Taylor & Francis. doi:10.1080/00103624.2016.1146745.
- Li, T., Zhang, W., Yin, J., Chadwick, D., Norse, D., Lu, Y., Liu, X., Chen, X., Zhang, F., Powlson, D., and Dou, Z. 2018. Enhanced-efficiency fertilizers are not a panacea for resolving the nitrogen problem. *Glob Chang Biol* **24**: e511–e521. Blackwell Publishing Ltd. doi:10.1111/gcb.13918.
- Mahal, N.K., Osterholz, W.R., Miguez, F.E., Poffenbarger, H.J., Sawyer, J.E., Olk, D.C., Archontoulis, S. V., and Castellano, M.J. 2019. Nitrogen Fertilizer Suppresses Mineralization of Soil Organic Matter in Maize Agroecosystems. *Front Ecol Evol* **7**. Frontiers Media S.A. doi:10.3389/fevo.2019.00059.
- Maharjan, B., Venterea, R.T., and Rosen, C. 2014. Fertilizer and irrigation management effects on nitrous oxide emissions and nitrate leaching. *Agron J* **106**: 703–714. doi:10.2134/agronj2013.0179.
- Malhi, S.S., Grant, C.A., Johnston, A.M., and Gill, K.S. 2001. Nitrogen fertilization management for no-till cereal production in the Canadian Great Plains: a review. *Soil Tillage Res* **60**: 101–122. doi:10.1016/S0167-1987(01)00176-3.
- Malhi, S.S., Soon, Y.K., Grant, C.A., Lemke, R., Lupwayi, N., and Lemke, C.A. 2010. Influence of controlled-release urea on seed yield and N concentration, and N use efficiency of small grain crops grown on Dark Gray Luvisols *Can J Soil Sci* **90**: 363–372. doi:10.4141/CJSS09102.
- McKenzie, R.H., Middleton, A.B., DeMulder, J., and Bremer, E. 2004a. Fertilizer response of barley silage in southern and central Alberta. *Can J Soil Sci* **84**: 133–147. doi:10.4141/S03-042.
- McKenzie, R.H., Middleton, A.B., Hall, L., Demulder, J., Bremer, E., and Bremer, J. 2004b. Fertilizer response of barley grain in south and central Alberta. *Can J Soil Sci*: 513–523.
- McKenzie, R.H., Middleton, A.B., Piffner, P.G., and Bremer, E. 2010. Evaluation of polymer-coated urea and urease inhibitor for winter wheat in Southern Alberta. *Agron J* **102**: 1210–1216. doi:10.2134/agronj2009.0194.
- Metodiev, M., and Demirevska-Kepova, K. 1992. Rubisco Quantitation in Leaves of Different Barley Varieties by Enzyme-Linked Immunosorbent Assay. *J Exp Bot* **43**: 155–158. doi:10.1093/jxb/43.2.155.

- Mezbahuddin, S., Spiess, D., Hildebrand, D., Kryzanowski, L., Itenfisu, D., Goddard, T., Iqbal, J., and Grant, R. 2020. Assessing Effects of Agronomic Nitrogen Management on Crop Nitrogen Use and Nitrogen Losses in the Western Canadian Prairies. *Front Sustain Food Syst* **4**: 1–21. doi:10.3389/fsufs.2020.512292.
- Millar, N., Robertson, G.P., Grace, P.R., Gehl, R.J., and Hoben, J.P. 2010. Nitrogen fertilizer management for nitrous oxide (N₂O) mitigation in intensive corn (Maize) production: an emissions reduction protocol for US Midwest agriculture. *Mitig Adapt Strateg Glob Chang* **15**: 185–204. doi:10.1007/s11027-010-9212-7.
- Nelson, K.A., Scharf, P.C., Bundy, L.G., and Tracy, P. 2008. Agricultural Management of Enhanced-Efficiency Fertilizers in the North-Central United States. *Crop Management* **7**: 1–12. doi:10.1094/cm-2008-0730-03-rv.
- Nyborg, M., and Malhi, S.S. 1986. Comparison of Fall and Spring Application of Nitrogen Fertilizers in Northern and Central Alberta. *Can J Soil Sci* **66**: 225–236. doi:10.4141/cjss86-025.
- O'Donovan, J.T., Anbessa, Y., Grant, C.A., Macleod, A.L., Edney, M.J., Izydorczyk, M.S., Turkington, T.K., Juskiw, P.E., Lafond, G.P., May, W.E., Harker, K.N., Johnson, E.N., Beres, B.L., McAllister, T.A., Smith, E.G., and Chapman, W. 2015. Relative responses of new malting barley cultivars to increasing nitrogen rates in western Canada. *Canadian Journal of Plant Science* **95**: 831–839. Agricultural Institute of Canada. doi:10.4141/cjps-2014-415.
- Pancheva, T. v., and Popova, L.P. 1998. Effect of salicylic acid on the synthesis of ribulose-1,5-bisphosphate carboxylase/oxygenase in barley leaves. *J Plant Physiol* **152**: 381–386. doi:10.1016/S0176-1617(98)80251-4.
- Puntel, L.A., Sawyer, J.E., Barker, D.W., Dietzel, R., Poffenbarger, H., Castellano, M.J., Moore, K.J., Thorburn, P., and Archontoulis, S. V. 2016. Modeling long-term corn yield response to nitrogen rate and crop rotation. *Front Plant Sci* **7**. Frontiers Research Foundation. doi:10.3389/fpls.2016.01630.
- Ransom, C.J., Jolley, V.D., Blair, T.A., Sutton, L.E., and Hopkins, B.G. 2020. Nitrogen release rates from slow- And controlled-release fertilizers influenced by placement and temperature. *PLoS One* **15**: 1–21. doi:10.1371/journal.pone.0234544.
- Rasmussen, I.S., Dresbøll, D.B., and Thorup-Kristensen, K. 2015. Winter wheat cultivars and nitrogen (N) fertilization—Effects on root growth, N uptake efficiency and N use efficiency. *European Journal of Agronomy* **68**: 38–49. Elsevier B.V. doi:10.1016/j.eja.2015.04.003.
- Reussi Calvo, N.I., Carciochi, W.D., Prystupa, P., Queirolo, I., and Sainz Rozas, H.R. 2022. Economic optimum nitrogen rate analysis for feed and malting barley. *Crop Sci* **62**: 1997–2010. John Wiley and Sons Inc. doi:10.1002/csc2.20808.
- Saxton, K.E., and Rawls, W.J. 2006. Soil Water Characteristic Estimates by Texture and Organic Matter for Hydrologic Solutions. *Soil Science Society of America Journal* **70**: 1569–1578. Wiley. doi:10.2136/sssaj2005.0117.
- Setiyono, T.D., Yang, H., Walters, D.T., Dobermann, A., Ferguson, R.B., Roberts, D.F., Lyon, D.J., Clay, D.E., and Cassman, K.G. 2011. Maize-N: A decision tool for nitrogen management in maize. *Agron J* **103**: 1276–1283. doi:10.2134/agronj2011.0053.
- Shaviv, A., Raban, S., and Zaidel, E. 2003. Modeling controlled nutrient release from polymer coated fertilizers: Diffusion release from single granules. *Environ Sci Technol* **37**: 2251–2256. doi:10.1021/es011462v.
- Simova-Stoilova, L., Stoyanova, Z., and Demirevska-Kepova, K. 2001. Ontogenic Changes in Leaf Pigments, Total Soluble Protein and Rubisco in Two Barley Varieties in Relation to Yield. *Bulgarian Journal of Plant Physiology* **27**: 15–24.
- Smith, E.G., Clayton, G.W., O'Donovan, J.T., Turkington, T.K., Harker, K.N., Henderson, W.J., McKenzie, R.H., Juskiw, P.E., Lafond, G.P., May, W.E., Grant, C.A., Brandt, S., Johnson, E.N., and Edney, M.J. 2012. Net return risk for

- malting barley production in Western Canada as influenced by production strategies. *Agron J* **104**: 1374–1382. American Society of Agronomy. doi:10.2134/agronj2011.0416.
- Sogbedji, J.M., van Es, H.M., Klausner, S.D., Bouldin, D.R., and Cox, W.J. 2001. Spatial and temporal processes affecting nitrogen availability at the landscape scale. *Soil Tillage Res* **58**: 233–244. doi:10.1016/S0167-1987(00)00171-9.
- Soon, Y.K., Malhi, S.S., Lemke, R.L., Lupwayi, N.Z., and Grant, C.A. 2011. Effect of polymer-coated urea and tillage on the dynamics of available N and nitrous oxide emission from Gray Luvisols. *Nutr Cycl Agroecosyst* **90**: 267–279. doi:10.1007/s10705-011-9428-2.
- Statistics Canada 2022. September 29. 2016 Census of Agriculture. [Online] Available: <https://www.statcan.gc.ca/en/ca2016> [2022 Nov. 12].
- Statistics Canada 2023. February 7. Table 32-10-0077-01 Farm product prices, crops and livestock. [Online] Available: <https://www150.statcan.gc.ca/t1/tbl1/en/tv.action?pid=3210007701&cubeTimeFrame.startMonth=07&cubeTimeFrame.startYear=2007&cubeTimeFrame.endMonth=11&cubeTimeFrame.endYear=2022&referencePeriods=20070701%2C20221101> [2023 Feb. 6].
- Steffen, W., Richardson, K., Rockström, J., Cornell, S.E., Fetzer, I., Bennett, E.M., Biggs, R., Carpenter, S.R., De Vries, W., De Wit, C.A., Folke, C., Gerten, D., Heinke, J., Mace, G.M., Persson, L.M., Ramanathan, V., Reyers, B., and Sörlin, S. 2015. Planetary boundaries: Guiding human development on a changing planet. *Science* (1979) **347**. American Association for the Advancement of Science. doi:10.1126/science.1259855.
- Stewart, W.M., Dibb, D.W., Johnston, A.E., and Smyth, T.J. 2005. The contribution of commercial fertilizer nutrients to food production. *Agron J* **97**: 1–6. American Society of Agronomy. doi:10.2134/agronj2005.0001.
- Thapa, R., Chatterjee, A., Awale, R., McGranahan, D.A., and Daigh, A. 2016. Effect of Enhanced Efficiency Fertilizers on Nitrous Oxide Emissions and Crop Yields: A Meta-analysis. *Soil Science Society of America Journal* **80**: 1121–1134. doi:10.2136/sssaj2016.06.0179.
- Thilakarathna, S.K., Hernandez-Ramirez, G., Puurveen, D., Kryzanowski, L., Lohstraeter, G., Powers, L.A., Quan, N., and Tenuta, M. 2020. Nitrous oxide emissions and nitrogen use efficiency in wheat: Nitrogen fertilization timing and formulation, soil nitrogen, and weather effects. *Soil Science Society of America Journal* **84**: 1910–1927. John Wiley and Sons Inc. doi:10.1002/saj2.20145.
- Udvardi, M., Below, F.E., Castellano, M.J., Eagle, A.J., Giller, K.E., Ladha, J.K., Liu, X., Maaz, T.M.C., Nova-Franco, B., Raghuram, N., Robertson, G.P., Roy, S., Saha, M., Schmidt, S., Tegeder, M., York, L.M., and Peters, J.W. 2021. May 31. A Research Road Map for Responsible Use of Agricultural Nitrogen. *Frontiers Media S.A.* doi:10.3389/fsufs.2021.660155.
- United Nations Environment Programme 2014. UNEP Year Book 2014 Emerging Issues in our Global Environment. [Online] Available: <https://www.unep.org/resources/year-books> [2022 Jan. 9].
- Wilson, M.L., Rosen, C.J., and Moncrief, J.F. 2010. Effects of Polymer-coated Urea on Nitrate Leaching and Nitrogen Uptake by Potato. *J Environ Qual* **39**: 492–499. doi:10.2134/jeq2009.0265.
- Yang, J.Y., Drury, C.F., Jiang, R., Yang, X.M., Worth, D.E., Bittman, S., Grant, B.B., Smith, W.N., and Reid, K. 2023. Simulating nitrogen balance in Canadian agricultural soils from 1981 to 2016. *J Environ Manage* **341**: 118015. doi:10.1016/j.jenvman.2023.118015.

- Yang, M., Zhu, X., Bai, Y., Sun, D., Zou, H., Fang, Y., and Zhang, Y. 2021. Coated controlled-release urea creates a win-win scenario for producing more staple grains and resolving N loss dilemma worldwide. *J Clean Prod* **288**. Elsevier Ltd. doi:10.1016/j.jclepro.2020.125660.
- Zebarth, B.J., Drury, C.F., Tremblay, N., and Cambouris, A.N. 2009. Opportunities for improved fertilizer nitrogen management in production of arable crops in eastern Canada: A review. *Can J Soil Sci* **89**: 113–132. doi:10.4141/CJSS07102.
- Zhang, W., Liang, Z., He, X., Wang, X., Shi, X., Zou, C., and Chen, X. 2019. The effects of controlled release urea on maize productivity and reactive nitrogen losses: A meta-analysis. *Environmental Pollution* **246**: 559–565. Elsevier Ltd. doi:10.1016/j.envpol.2018.12.059.

2.7 Tables

Table 2-1. Monthly mean air temperature (°C) for the growing season (May – September), mean annual temperature (°C)(MAT) for 2008 – 2011, monthly total precipitation (mm) for the growing season (May – September) and total annual precipitation (mm) for 2008 – 2011 at Lethbridge, Alberta compared to the 30-year climate normal (1971 – 2000) (ACIS 2021). Monthly irrigation amounts (mm) for the growing season (May – September), and total growing season irrigation + precipitation for 2008 – 2011 at the irrigated site in Lethbridge, Alberta (Kryzanowski et al. 2009).

Mean Air Temperature (°C)						Total Precipitation (mm)						Total Irrigation (Irrigated Site Only)				
Month(s)	2008	2009	2010	2011	30 Year Climate Normal (1971-2000)	Month(s)	2008	2009	2010	2011	30 Year Climate Normal (1971 - 2000)	Month(s)	2008	2009	2010	2011
May	11.4	10.9	8.1	9.8	11.4	May	70.9	29.0	114.8	87.6	48.3	May	-	24.0	-	-
June	14.4	14.0	14.3	13.9	15.6	June	88.3	57.1	127.8	76.4	53.0	June	47.5	40.4	-	-
July	17.0	16.8	16.9	17.7	18.2	July	84.7	42.0	43.6	42.0	37.2	July	89.4	143.9	63	36.4
August	16.6	15.9	15.5	17.5	17.7	August	28.6	81.2	65.8	33.9	47.4	August	45.3	-	-	40.6
September	11.5	15.4	10.5	15.1	12.3	September	60.4	6.4	41.2	11.3	38.3	September	-	-	-	-
May - September	14.2	14.6	13.1	14.8	15.0	May - September	332.9	215.7	393.2	251.2	224.2	May - September	182.2	208.3	63	77
Mean Annual Air Temperature	5.4	5.0	5.2	5.3	5.8	Total Annual Precipitation	419	341.5	560.6	440.4	365	Total Growing Season Irrigation + Precipitation	515.1	424	456.2	328.2

Table 2-2. Model inputs for the soil properties at Lethbridge, Alberta obtained from field and laboratory measurements (Kryzanowski et al. 2009). *Estimated from Saxton and Rawls (2006).

Depth (m)	0.01	0.05	0.10	0.15	0.30	0.45	0.60	0.90	1.20	2.00
Bulk Density (Mg m ⁻³)	1.4	1.4	1.4	1.41	1.42	1.42	1.49	1.49	1.5	1.5
Field Capacity (m ³ m ⁻³)*	0.293	0.293	0.293	0.288	0.29	0.29	0.282	0.282	0.27	0.27
Wilting Point (m ³ m ⁻³)*	0.157	0.157	0.157	0.155	0.159	0.159	0.156	0.156	0.13	0.13
Saturated Hydraulic Conductivity (mm hr ⁻¹)*	16.65	16.65	16.65	13.83	9.78	9.78	8.99	8.99	5.4	5.4
Sand Content (kg kg ⁻¹)	456	456	456	450	442	442	452	452	410	410
Silt Content (kg kg ⁻¹)	318	318	318	320	310	310	302	302	370	370
Clay Content (kg kg ⁻¹)	226	226	226	230	248	248	246	246	220	220
pH	8.15	8.15	8.15	8.08	7.93	7.93	7.95	7.95	7.5	7.5
Cation Exchange Capacity (CEC) (cmol kg ⁻¹)	25.5	25.5	25.5	24.4	24.4	24.1	23	23	11	11
Anion Exchange Capacity (AEC) (cmol kg ⁻¹)	3	3	3	3	3	3	3	3	3	3
Organic Carbon (g kg ⁻¹)	21.5	21.5	21.5	17.3	12.4	12.4	9.4	9.4	0.7	0
Organic Nitrogen (g Mg ⁻¹)	1933	1933	1933	1557	1115	1115	850	850	70	0
Organic Phosphorus (g Mg ⁻¹)	213	213	213	171	123	123	93	93	7	0
NO ₃ -N (g Mg ⁻¹)	8.25	8.25	8.25	6.5	1.75	1.75	4.25	4.25	0	0
NH ₄ -N (g Mg ⁻¹)	3.6	3.6	3.6	2.53	2.08	2.08	2.9	2.9	0	0
Exchangeable PO ₄ -P (g Mg ⁻¹)	35.25	35.25	35.25	17.5	5.75	5.75	5.5	5.5	2	2
K (g Mg ⁻¹)	460.5	460.5	460.5	373.75	340	340	248	248	3.9	3.9
SO ₄ -S (g Mg ⁻¹)	18.75	18.75	18.75	62.75	200	200	200	200	48	48

Table 2-3. Average change in modelled soil organic and inorganic N stocks ($\text{kg N ha}^{-1}\text{year}^{-1}$) over a 4-year period (2008 – 2011) for N rates (0, 30, 60, 90, and 120 kg N ha^{-1}), and N sources (Control (0 kg N ha^{-1}), Urea, ESN), at dryland and irrigated sites in Lethbridge, Alberta. The change in N stocks is the gain (positive) or loss (negative) at the year's end compared to the year's beginning. *Change in soil organic nitrogen is the sum of the average change in residue and humus N. **Change in soil inorganic nitrogen is the sum of the average change in nitrate-N and ammonium-N.

Years	Site	N Source	N Rate	Δ in Residue N	Δ in Humus N	Δ in Soil Organic Nitrogen*	Δ in $\text{NO}_3\text{-N}$	Δ in $\text{NH}_4\text{-N}$	Δ in Soil Inorganic Nitrogen**
2008 - 2011	Dryland	Control	0	-67.7	-3.0	-70.7	-11.5	22.1	10.6
		ESN	30	-58.0	-1.0	-59.1	-21.4	25.3	3.9
			60	-52.6	-0.4	-53.1	-9.2	26.4	17.2
			90	-48.8	0.2	-48.7	9.1	27.2	36.3
			120	-47.2	0.8	-46.4	30.6	27.7	58.3
		Urea	30	-57.3	-1.0	-58.3	-22.8	25.8	3.0
			60	-50.7	-0.3	-51.1	-11.6	26.9	15.2
			90	-47.2	0.2	-46.9	6.0	27.6	33.6
	120		-45.4	0.9	-44.5	27.0	28.1	55.1	
	Irrigated	Control	0	-63.5	-5.6	-69.0	-9.7	21.5	11.8
		ESN	30	-51.7	-3.5	-55.2	-23.2	22.9	-0.4
			60	-44.9	-2.3	-47.2	-15.5	23.0	7.5
			90	-39.8	-1.6	-41.3	-0.7	23.2	22.4
			120	-37.6	-1.0	-38.6	19.3	23.3	42.5
		Urea	30	-50.7	-3.4	-54.1	-24.4	23.1	-1.3
			60	-43.5	-2.2	-45.7	-17.5	23.4	5.9
90			-37.7	-1.4	-39.1	-3.7	23.6	19.9	
120	-35.4		-0.8	-36.2	15.4	23.8	39.2		

Table 2-4. Modelled vs measured barley grain yields (kg C ha⁻¹) and modelled vs measured barley grain N (kg N ha⁻¹) coefficient of determination (R²), p-value, linear regression intercept, linear regression slope, root mean square error (RMSE); and standard deviation (SD) of measured results for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta. Measured barley grain yields and barley grain N obtained from a field experiment by Kryzanowski et al. (2009).

Year	Site	R ²	P Value	Intercept	Slope	RMSE	SD of Measured Results
Barley Grain Yield (kg C ha⁻¹)							
2008	Dryland	0.96	<0.001	-3804.3	2.3	289	274
2008	Irrigated	0.67	0.01	-1995.5	1.7	282	394
2009	Dryland	0.22	0.21	452.5	0.9	203	303
2009	Irrigated	0.94	<0.001	-1767.8	1.8	467	387
2010	Dryland	0.64	0.01	216.0	1.1	537	377
2010	Irrigated	0.83	<0.001	-1811.1	1.7	358	580
2011	Dryland	0.85	<0.001	445.0	1.0	558	449
2011	Irrigated	0.86	<0.001	289.6	1.0	401	382
Overall		0.64	<0.001	588	0.82	404	564
Barley Grain N (kg N ha⁻¹)							
2008	Dryland	0.97	<0.001	-26.6	1.0	23	19
2008	Irrigated	0.94	<0.001	-39.6	1.4	9	20
2009	Dryland	0.82	<0.001	44.2	0.6	10	17
2009	Irrigated	0.78	<0.001	-16.3	1.3	17	18
2010	Dryland	0.70	0.01	4.2	1.1	13	14
2010	Irrigated	0.88	<0.001	-51.1	1.3	22	22
2011	Dryland	0.69	0.01	26.5	0.8	16	17
2011	Irrigated	0.87	<0.001	24.1	0.9	19	14
Overall		0.46	<0.001	36.0	0.6	17	25

Table 2-5. Nitrogen rate (kg N ha⁻¹) to obtain the economic optimum N rate (EONR) (kg N ha⁻¹), barley grain yield at EONR (kg C ha⁻¹), and the nitrogen use efficiency (NUE) (% kg Grain N kg⁻¹ N Fertilizer) at the EONR for modelled and measured results for N sources of urea and ESN for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta. EONR was estimated by setting the first derivative of the regression equations of N fertilizer with barley grain yield equal to the fertilizer-to-grain price ratios for urea and ESN (7.4 for urea, 9.0 for ESN) (McKenzie et al. 2004; Calvo et al. 2022). Barley grain yield at EONR was determined by the regression equations of N fertilizer with barley grain yield (Supplementary Table 3). NUE at EONR was determined by inserting the EONR as x into the regression equation of N fertilizer with the NUE (% kg Grain N kg⁻¹ Fertilizer N) (Supplementary Table 5). Measured 2010 Dryland results were not listed as there was no N fertilizer required due to a highly linearized relationship between the N rate and measured barley grain yields.

Data Type	Year	Site	N Source	Economic Optimum N Rate (EONR) (kg N ha ⁻¹)	Yield at EONR (kg C ha ⁻¹)	NUE at EONR (% kg Grain N kg ⁻¹ N Fertilizer)
Modelled	2008	Dryland	ESN	70	2815	49
			Urea	81	2909	46
		Irrigated	ESN	78	3037	70
			Urea	82	3075	68
	2009	Dryland	ESN	44	2747	48
			Urea	51	2810	44
		Irrigated	ESN	72	3482	71
			Urea	75	3486	69
	2010	Dryland	ESN	72	2403	51
			Urea	85	2515	48
		Irrigated	ESN	75	2315	52
			Urea	88	2427	49
	2011	Dryland	ESN	67	2663	66
			Urea	73	2731	62
		Irrigated	ESN	63	2387	48
			Urea	74	2490	45
Measured	2008	Dryland	ESN	5	2479	48
			Urea	15	2572	41
		Irrigated	ESN	61	2750	48
			Urea	63	2743	41
	2009	Dryland	ESN	38	2473	41
			Urea	41	2491	42
		Irrigated	ESN	30	2477	11
			Urea	49	2811	39
	2010	Dryland	ESN	-	-	-
			Urea	68	1544	15
		Irrigated	ESN	-	-	-
			Urea	38	2203	51
	2011	Dryland	ESN	78	2146	50
			Urea	73	1960	35
		Irrigated	ESN	51	1842	43
			Urea	111	2222	29

2.8 Figures

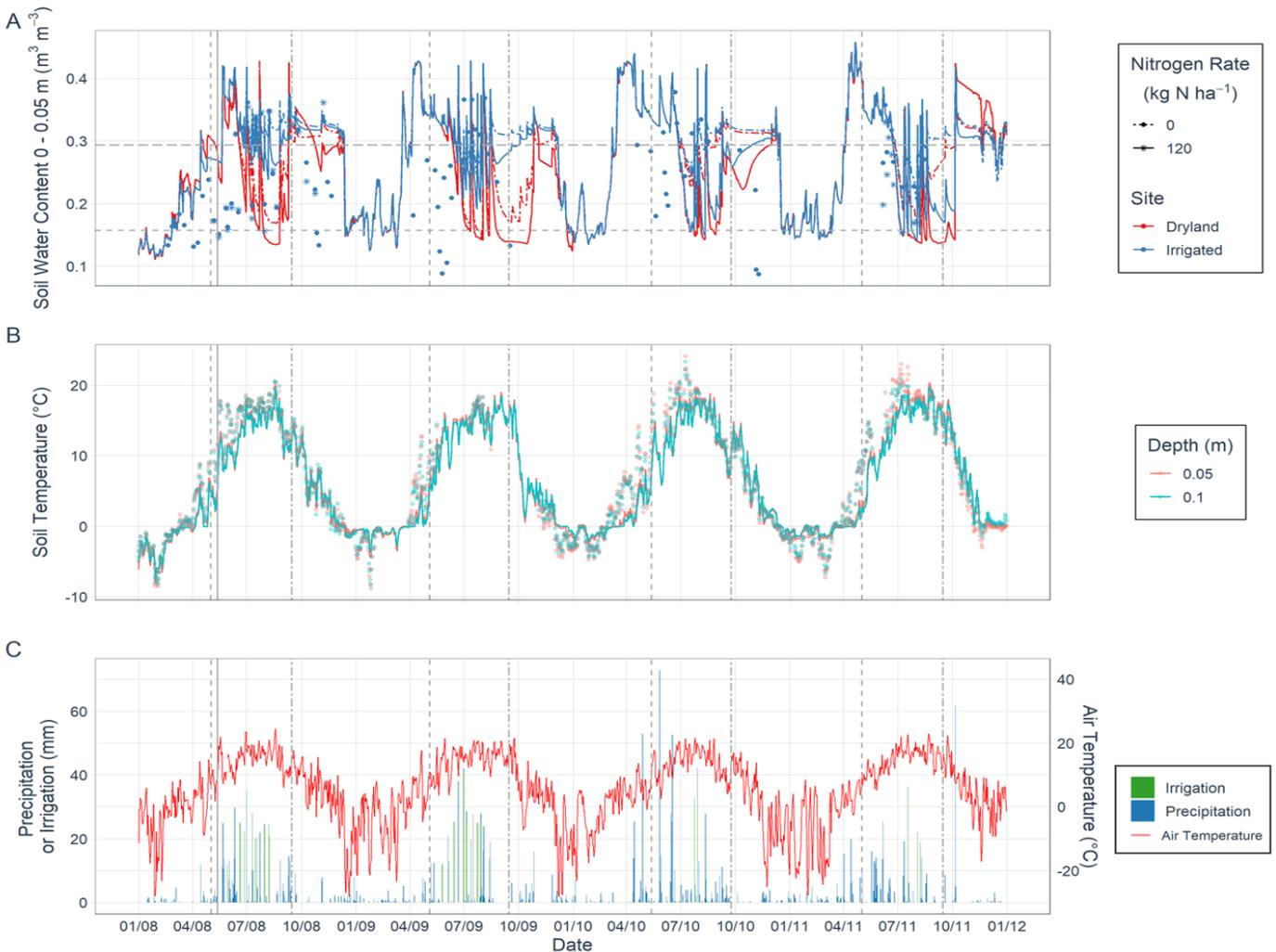


Figure 2-1. A) Modelled (lines) and measured (points) volumetric soil water content ($\text{m}^3 \text{m}^{-3}$) (SWC) for dryland (red) and irrigated (blue) sites at N fertilizer application rates of 0 kg N ha^{-1} (two dashed line, circle symbol) and 120 kg N ha^{-1} (solid line, star symbol) for 2008 – 2011 in Lethbridge, AB. Measured SWC was only available for the irrigated site. The field capacity ($0.293 \text{ m}^3 \text{m}^{-3}$) and wilting point ($0.157 \text{ m}^3 \text{m}^{-3}$) are represented by long dashed and short dashed horizontal lines, respectively. **B)** Modelled (lines) and measured (points) soil temperature ($^{\circ}\text{C}$) at 0.05 (orange) and 0.1 (green) meters for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. **C)** Daily average air temperature ($^{\circ}\text{C}$) (red line), daily total precipitation (mm) (blue bars), or total daily irrigation (mm) (green bars) for 2008 – 2011 in Lethbridge, Alberta. For all panels, vertical dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). The solid vertical line is the seeding/fertilizer application date for the irrigated site in 2008. Daily average air temperature and total precipitation data were obtained from ACIS (2021) and measured soil moisture, soil temperature, and irrigation data from Kryzanowski et al. (2009).

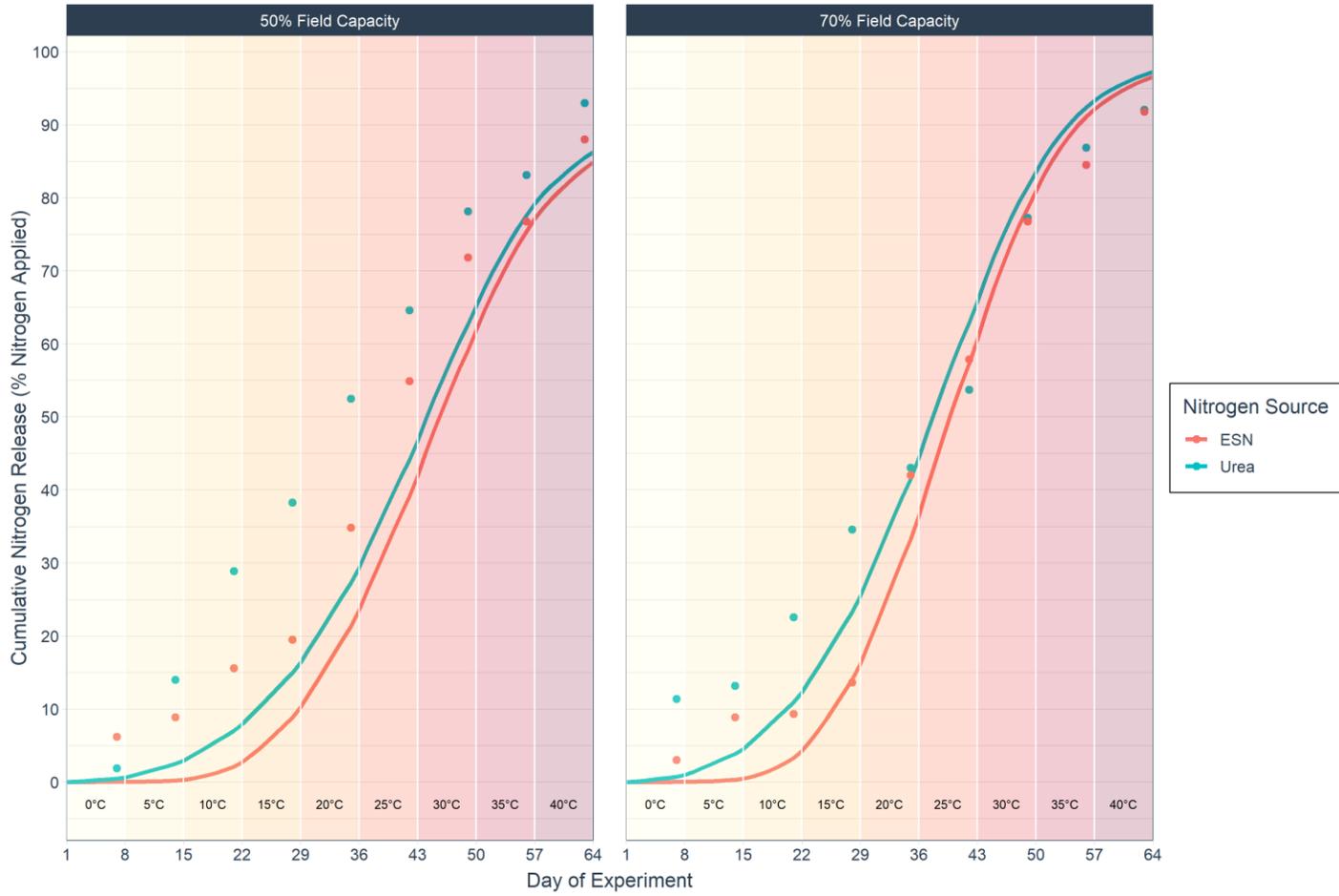


Figure 2-2. Cumulative nitrogen release (% nitrogen applied) for Environmentally Smart Nitrogen (ESN) (orange) and Urea (green) nitrogen sources for measured (points) and modelled (lines) results at 50% and 70% field capacity, with an increase of 5 °C every 7 days of the experiment.

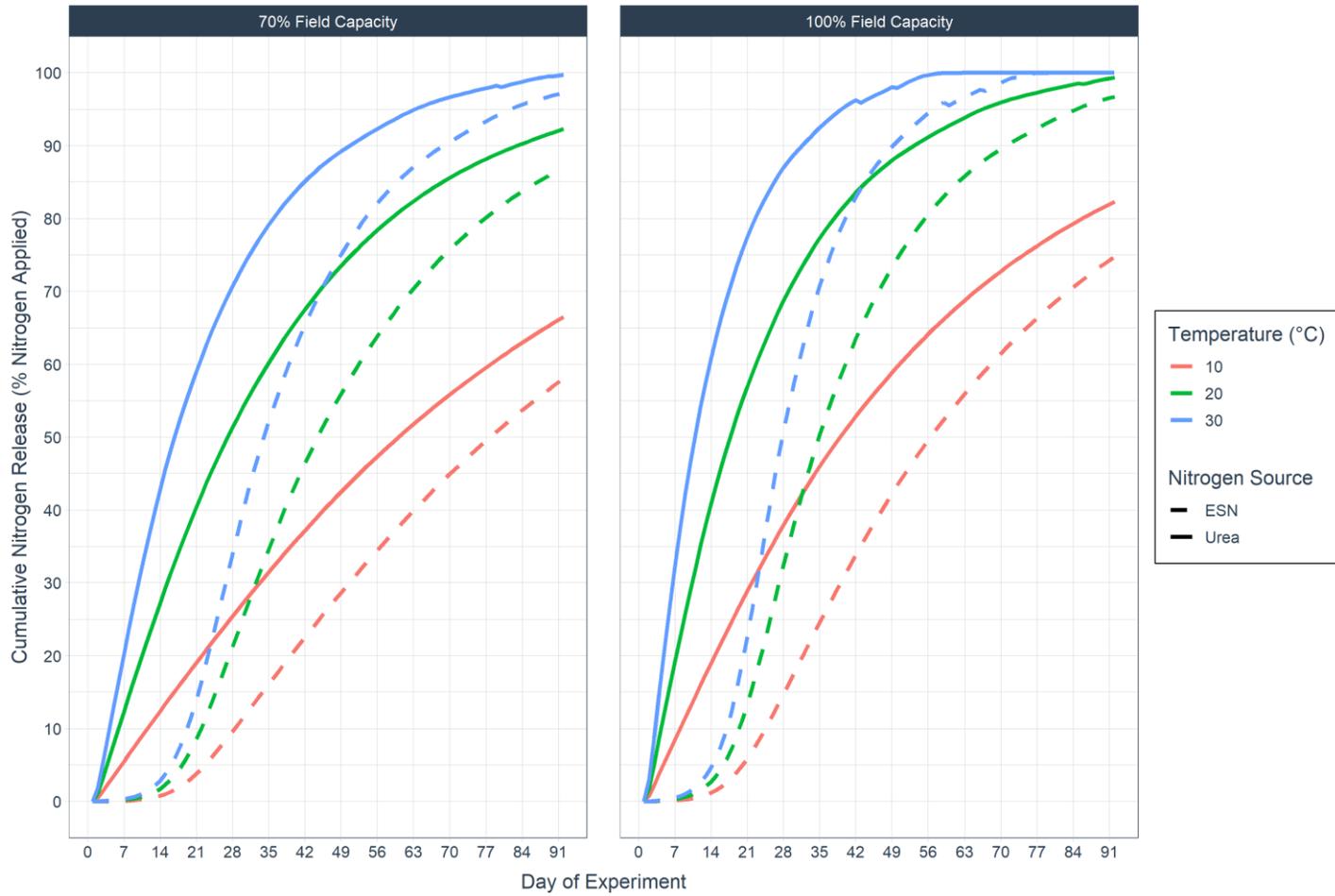


Figure 2-3. Cumulative nitrogen release (% nitrogen applied) for modelled Environmentally Smart Nitrogen (ESN) (dashed) and Urea (solid) nitrogen sources at 70% and 100% field capacity at temperatures of 10 °C (orange), 20 °C (green) and 30 °C (blue) over a period of 92 days.



Figure 2-4. Modelled (lines) and measured (points) soil nitrate + nitrite N (kg N ha^{-1}) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at the dryland site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). Measured soil nitrate is obtained from a field experiment by Kryzanowski et al. (2009).

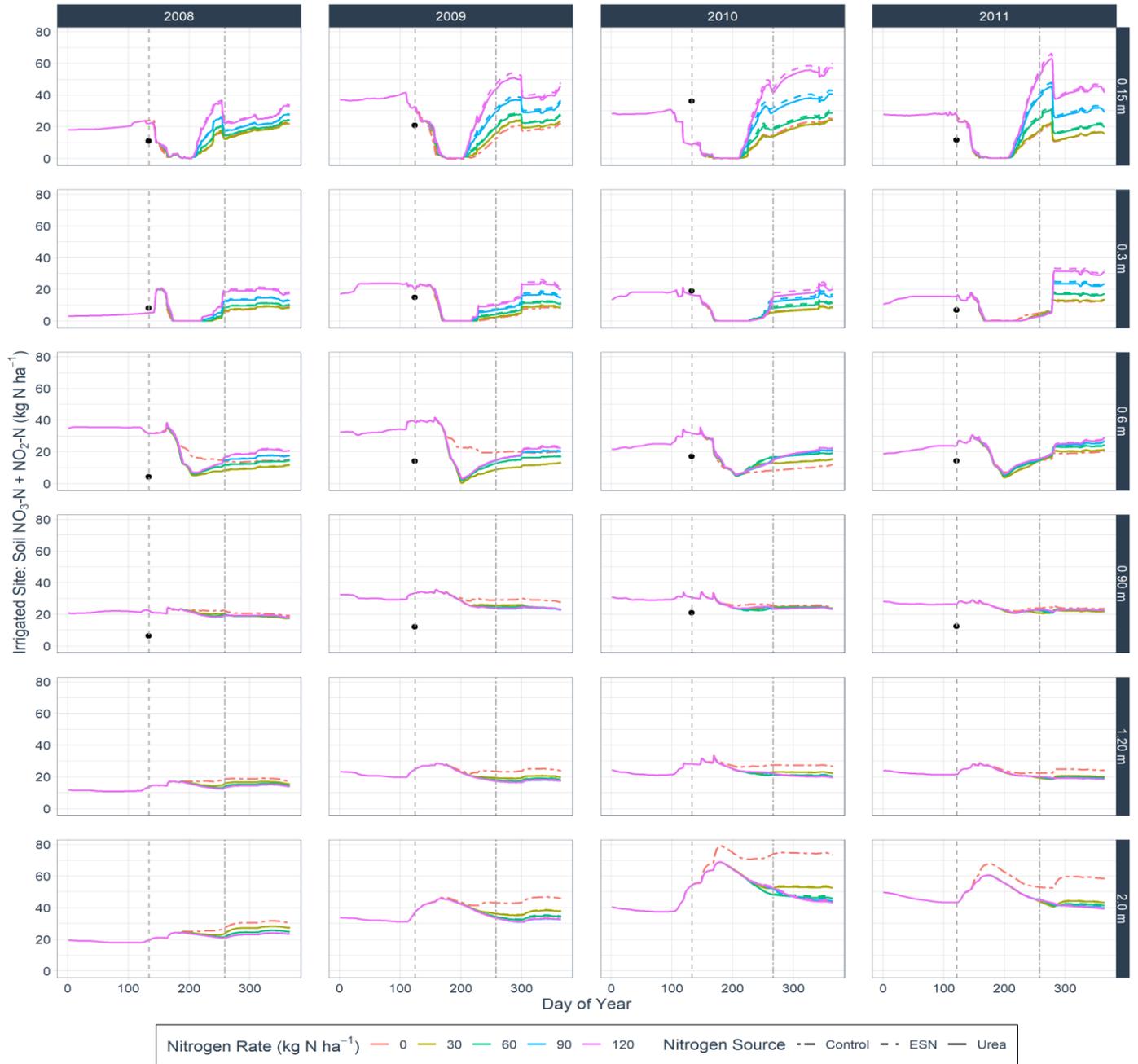


Figure 2-5. Modelled (lines) and measured (points) soil nitrate + nitrite N (kg N ha⁻¹) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha⁻¹ for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). Measured soil nitrate is obtained from a field experiment by Kryzanowski et al. (2009).

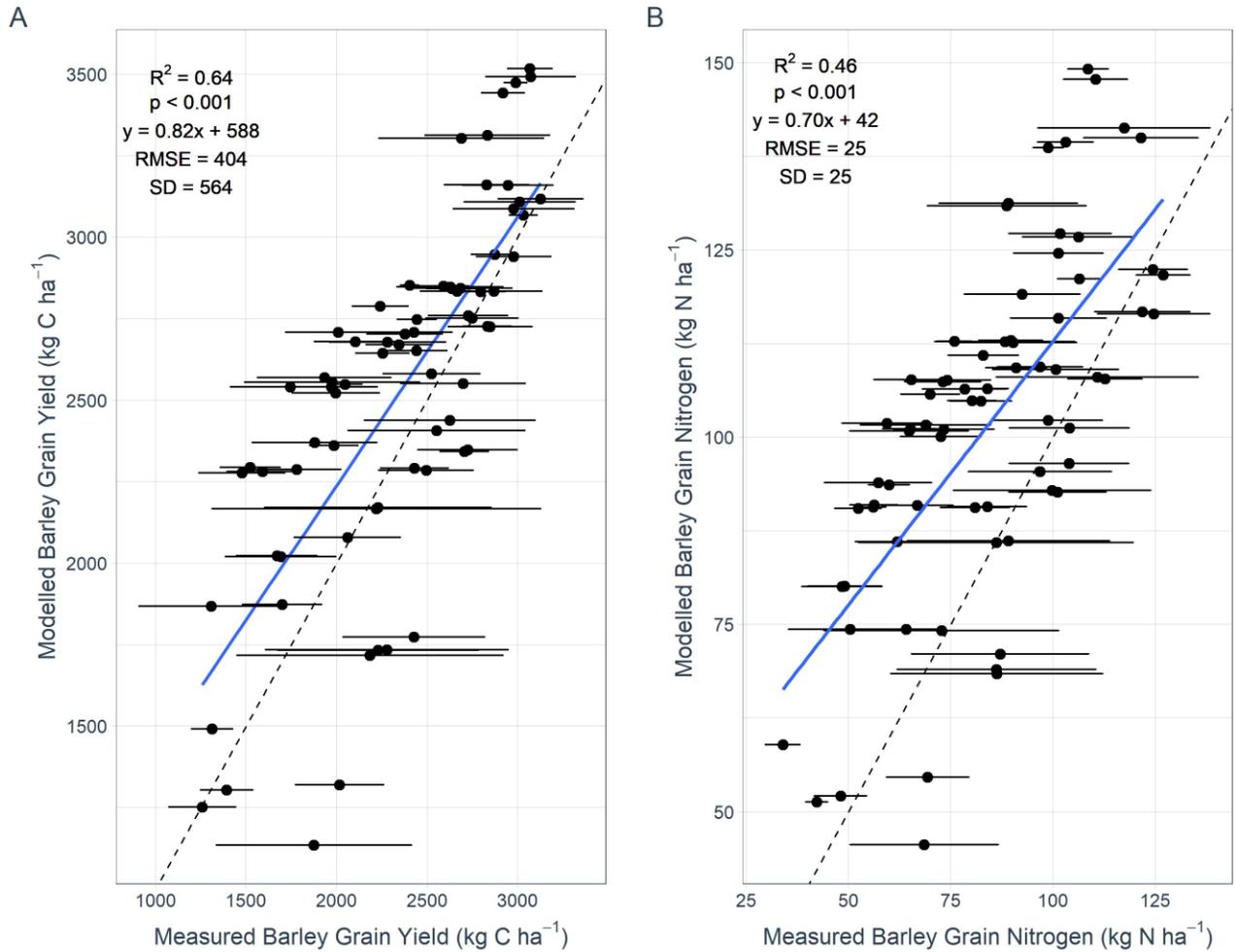


Figure 2-6. A) Modelled vs measured barley grain yields (kg C ha^{-1}) and **B)** Modelled vs measured barley grain nitrogen (kg N ha^{-1}) for all sites (Dryland and Irrigated) and years (2008 – 2011) in Lethbridge, Alberta. The solid blue line represents the linear regression between modelled vs measured results. The dashed line is a 1:1 line representing a perfect relationship between modelled and measured results. Error bars represent the standard deviation of mean barley grain yields or grain nitrogen due to variability among replicates in the field experiment. Measured barley grain yields and grain N obtained from a field experiment by Kryzanowski et al. (2009).

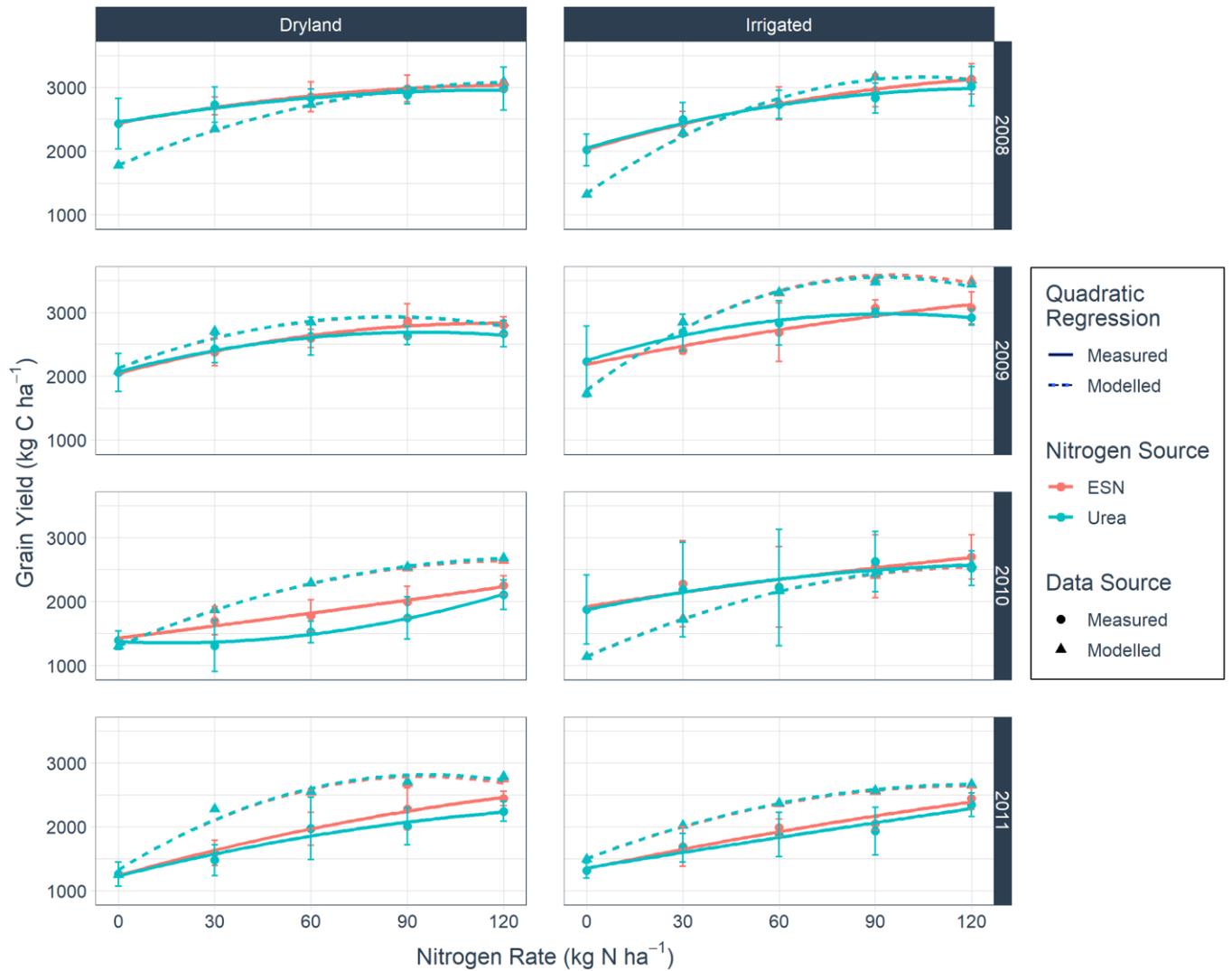


Figure 2-7. Modelled (triangles) and mean measured (circles) barley grain yield (kg C ha^{-1}) response to increasing nitrogen rates of 30, 60, 90 and 120 kg N ha^{-1} for urea (green) and Environmentally Smart Nitrogen (ESN) (orange) at dryland and irrigated sites for 2008 – 2011 in Lethbridge, Alberta. Error bars represent the standard deviation of mean barley grain yields due to variability among replicates in the field experiment. Measured barley grain yields obtained from a field experiment by Kryzanowski et al. (2009). Quadratic regression lines for measured (solid) and modelled (dashed) barley grain yield (kg C ha^{-1}) response to increasing nitrogen rates (kg N ha^{-1}) for urea (green) and ESN (orange) are shown above. Quadratic regression results are presented in Supplementary Table 2-3.

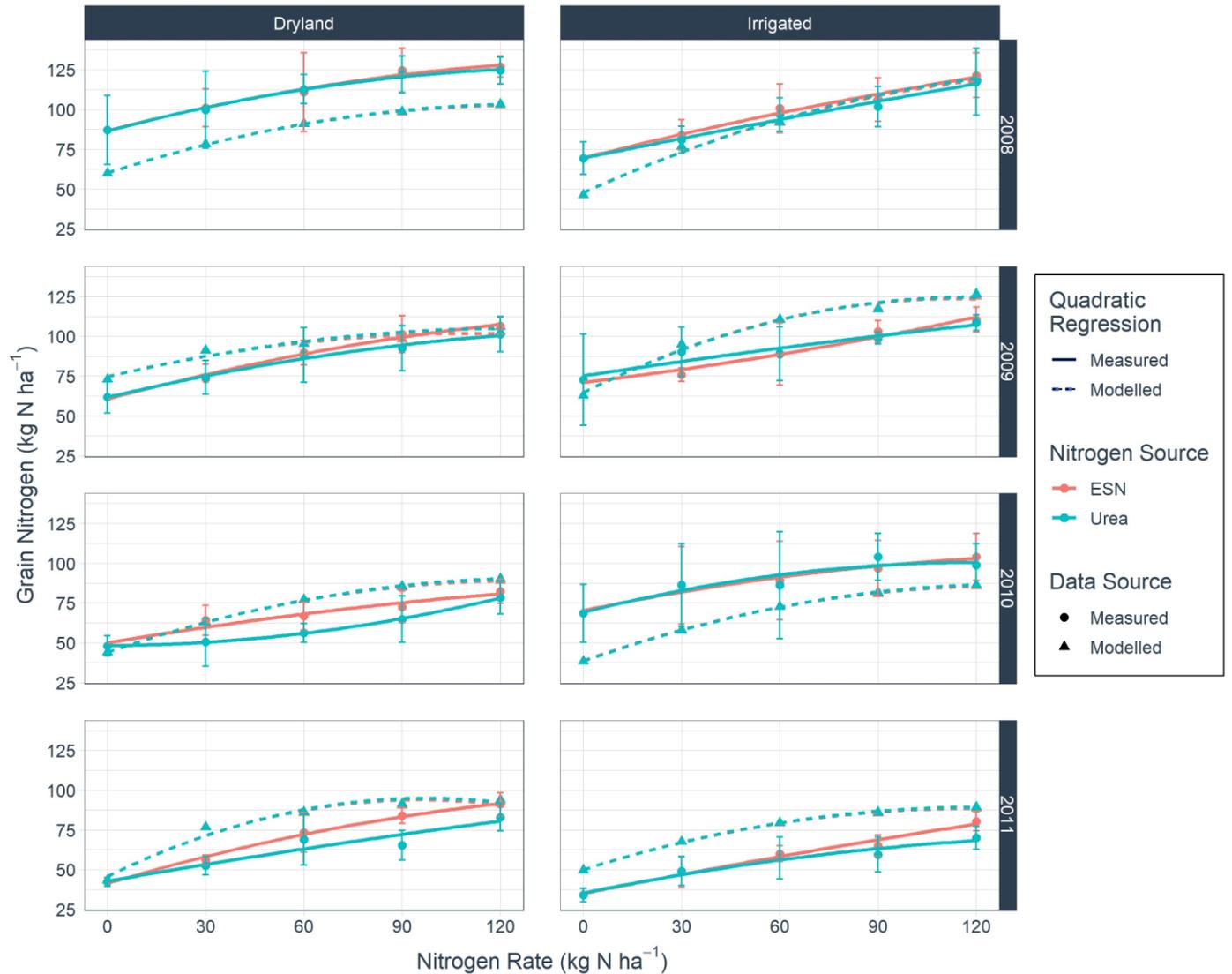


Figure 2-8. Modelled (triangles) and mean measured (circles) barley grain nitrogen (kg N ha^{-1}) response to increasing nitrogen rates of 30, 60, 90 and 120 kg N ha^{-1} for urea (green) and Environmentally Smart Nitrogen (ESN) (orange) at dryland and irrigated sites for 2008 – 2011 in Lethbridge, Alberta. Error bars represent the standard deviation of mean grain nitrogen due to variability among replicates in the field experiment. Measured barley grain nitrogen obtained from a field experiment by Kryzanowski et al. (2009). Quadratic regression lines for measured (solid) and modelled (dashed) barley grain nitrogen (kg N ha^{-1}) response to increasing nitrogen rates (kg N ha^{-1}) for urea (green) and ESN (orange) are shown above. Quadratic regression results are presented in Supplementary Table 2-4.

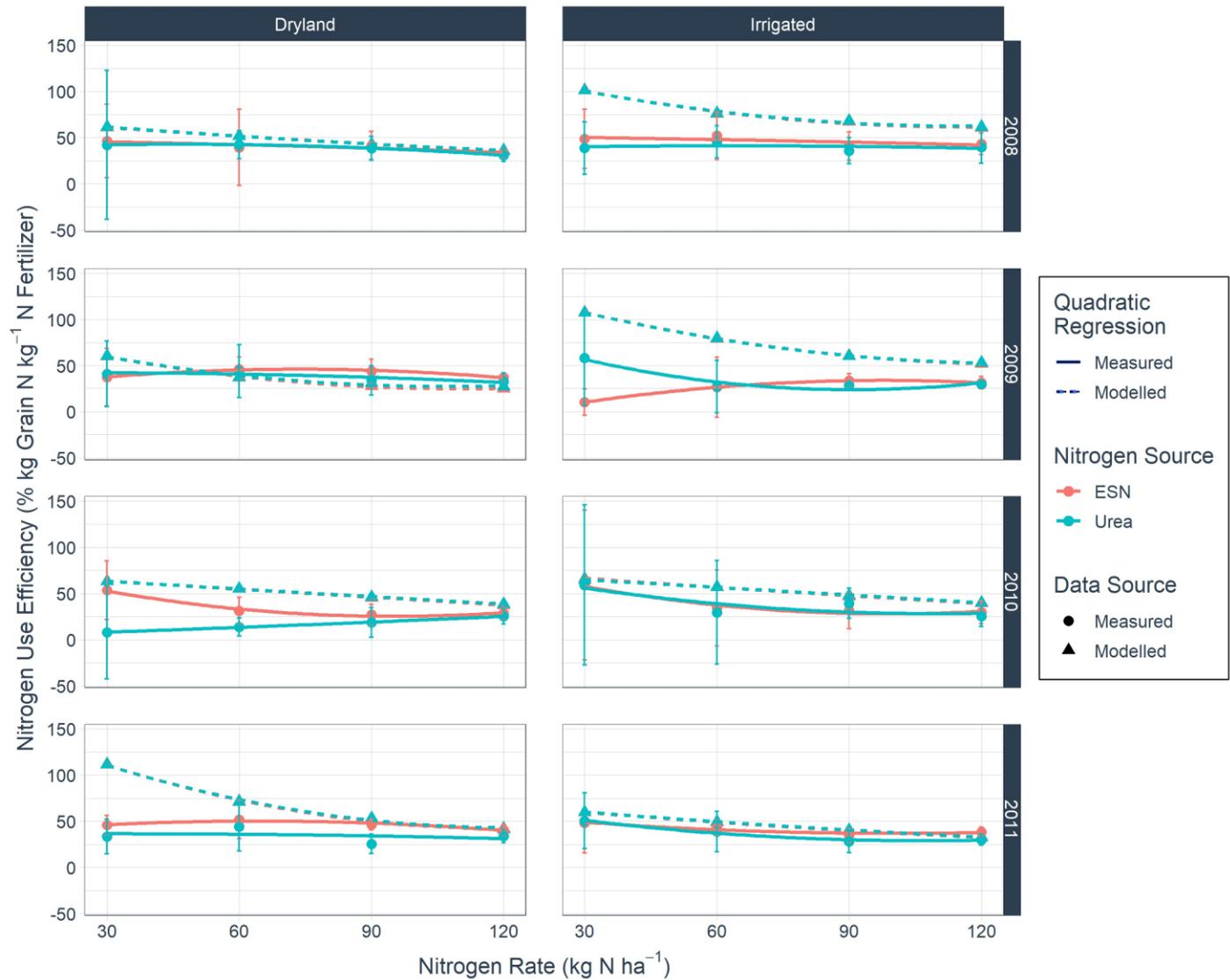


Figure 2-9. Modelled (triangles) and mean measured (circles) barley nitrogen use efficiency (% kg Grain N kg⁻¹ N Fertilizer) (NUE) response to increasing N rates of 30, 60, 90 and 120 kg N ha⁻¹ for urea (green) and Environmentally Smart Nitrogen (ESN) (orange) at dryland and irrigated sites for 2008 – 2011 in Lethbridge, Alberta. Error bars represent the standard deviation of the mean measured NUE due to variability among replicates in the field experiment. Measured NUE values obtained from a field experiment by Kryzanowski et al. (2009). Quadratic regression lines for measured (solid) and modelled (dashed) NUE (% kg Grain N kg⁻¹ N Fertilizer) response to increasing nitrogen rates (kg N ha⁻¹) for urea (green) and ESN (orange) are shown above. Quadratic regression results are presented in Supplementary Table 2-5.

2.9 Appendix

Supplementary Tables

Supplementary Table 2-1. Irrigation schedule (mm) and total irrigation (mm) for 2008 – 2011 at the irrigated site in Lethbridge, Alberta (Kryzanowski et al. 2009).

Year	Month/Day	DOY	Irrigation (mm)	Total Irrigation (mm)
2008	June 20	172	25	182.2
	June 27	179	22.5	
	July 10	192	25	
	July 15	197	19.5	
	July 18	200	20.5	
	July 31	213	24.4	
	Aug. 7	220	24.5	
Aug. 8	221	20.8		
2009	May 26	146	12	208.3
	May 29	150	12	
	June 5	156	15.4	
	June 15	166	25	
	July 1	182	41.3	
	July 6	187	25	
	July 17	198	27.6	
	July 24	205	25	
July 30	211	25		
2010	July 24	205	32.6	63
	July 29	210	30.4	
2011	July 19	200	36.4	77
	Aug. 3	215	22.2	
	Aug. 8	220	18.4	

Supplementary Table 2-2. Modelled and measured soil ammonium-N (NH₄-N), soil nitrate-N (NO₃-N), and total inorganic N (NH₄-N + NO₃-N) (kg N ha⁻¹) in 0 – 0.15, 0.15 – 0.30, 0.30 – 0.60, and 0.60 – 0.90 meters in the soil profile after spin up but prior to seeding/fertilizer application in 2008 – 2011 at Dryland and Irrigated sites in Lethbridge, Alberta. Measured soil N is obtained from a field experiment by Kryzanowski et al. (2009).

Year	Site	Depth in Soil Profile (m)	Measured Soil NH ₄ -N (kg N ha ⁻¹)	Modelled Soil NH ₄ -N (kg N ha ⁻¹)	Measured Soil NO ₃ -N (kg N ha ⁻¹)	Modelled Soil NO ₃ -N (kg N ha ⁻¹)	Measured Total Inorganic N (NO ₃ -N + NH ₄ -N) (kg N ha ⁻¹)	Modelled Total Inorganic N (NH ₄ -N + NO ₃ -N) (kg N ha ⁻¹)
2008	Dryland	0-0.15	7.6	6.8	17	22.2	24.9	29.0
		0.15-0.30	5.3	2.2	14	0.5	19.1	2.7
		0.30-0.60	8.9	3.8	7	24.1	16.3	27.9
		0.60-0.90	13.0	1.0	19	31.7	32.0	32.7
	Irrigated	0-0.15	7.1	5.0	11	24.0	18.1	29.0
		0.15-0.30	5.6	0.9	8	5.0	13.8	5.9
		0.30-0.60	7.9	1.7	4	31.7	12.1	33.4
		0.60-0.90	12.6	1.0	6	22.3	19.0	23.3
2009	Dryland	0-0.15	5.0	6.1	21	38.8	26.3	44.9
		0.15-0.30	4.4	1.1	13	21.4	17.8	22.5
		0.30-0.60	6.7	1.6	14	34.7	20.8	36.3
		0.60-0.90	12.1	0.9	14	22.5	26.3	23.4
	Irrigated	0-0.15	4.4	5.3	21	32.5	25.4	37.8
		0.15-0.30	3.7	1.3	15	20.2	18.6	21.5
		0.30-0.60	6.2	1.8	14	38.7	20.3	40.5
		0.60-0.90	8.8	0.9	12	33.4	20.9	34.3
2010	Dryland	0-0.15	4.7	6.7	19	10.3	23.2	17.1
		0.15-0.30	5.6	1.4	10	19.5	15.3	20.9
		0.30-0.60	9.5	2.3	9	35.0	18.0	37.3
		0.60-0.90	14.0	1.1	12	25.4	25.8	26.5
	Irrigated	0-0.15	3.7	5.6	36	8.9	40.0	14.5
		0.15-0.30	2.8	1.5	19	16.4	21.7	17.9
		0.30-0.60	4.5	2.2	17	31.6	21.7	33.9
		0.60-0.90	7.1	1.1	21	30.7	28.1	31.7
2011	Dryland	0-0.15	4.0	4.0	20	33.8	24.2	37.8
		0.15-0.30	3.3	1.3	11	20.7	14.7	22.1
		0.30-0.60	4.8	1.9	28	32.8	32.5	34.7
		0.60-0.90	7.4	0.9	36	26.7	43.6	27.6
	Irrigated	0-0.15	3.4	3.4	12	27.0	15.1	30.4
		0.15-0.30	3.5	1.3	7	15.8	10.4	17.0
		0.30-0.60	6.2	1.9	14	24.4	20.6	26.4
		0.60-0.90	7.9	0.9	12	26.6	20.4	27.4

Supplementary Table 2-3. Quadratic Regression results for modelled and measured (Kryzanowski et al. 2009) barley grain (kg C ha⁻¹) yield response to increasing N rates (0, 30, 60, 90, and 120 kg N ha⁻¹) for N sources of urea and ESN for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta.

Date Type	Year	Site	N Source	Intercept	Linear Coefficient	Quadratic Coefficient	R ²	P Value
Modelled	2008	Dryland	ESN	1782.1	20.6	-0.083	0.99	<0.001
			Urea	1784.4	20.5	-0.082	0.99	0.001
		Irrigated	ESN	1338.3	34.7	-0.165	0.99	0.005
			Urea	1335.1	34.9	-0.167	0.99	0.004
	2009	Dryland	ESN	2130.3	18.9	-0.112	0.94	0.06
			Urea	2130.6	19.0	-0.113	0.94	0.06
		Irrigated	ESN	1781.8	38.0	-0.201	0.99	0.010
			Urea	1780.6	38.2	-0.206	0.99	0.010
	2010	Dryland	ESN	1306.2	21.3	-0.085	0.99	<0.001
			Urea	1304.8	21.2	-0.082	0.99	<0.001
		Irrigated	ESN	1139.6	22.3	-0.088	0.99	<0.001
			Urea	1133.6	22.1	-0.084	0.99	<0.001
2011	Dryland	ESN	1330.1	30.7	-0.162	0.96	0.04	
		Urea	1326.8	30.9	-0.160	0.97	0.03	
	Irrigated	ESN	1500.9	19.1	-0.080	0.99	0.001	
		Urea	1499.5	19.3	-0.080	0.99	<0.001	
Measured	2008	Dryland	ESN	2436.8	9.3	-0.037	0.99	0.004
			Urea	2452.9	8.5	-0.036	0.96	0.04
		Irrigated	ESN	2023.5	14.7	-0.046	0.99	0.001
			Urea	2048.6	14.6	-0.057	0.98	0.02
	2009	Dryland	ESN	2044.2	13.4	-0.057	0.97	0.03
			Urea	2076.4	13.0	-0.069	0.98	0.02
		Irrigated	ESN	2187.8	10.2	-0.020	0.95	0.05
			Urea	2246.0	15.6	-0.083	0.99	0.01
	2010	Dryland	ESN	1427.8	6.3	0.003	0.98	0.02
			Urea	1372.0	-2.4	0.071	0.99	0.01
		Irrigated	ESN	1923.6	7.7	-0.011	0.91	0.09
			Urea	1874.6	10.1	-0.036	0.89	0.1
2011	Dryland	ESN	1239.0	14.1	-0.033	0.99	0.004	
		Urea	1231.2	12.5	-0.035	0.96	0.04	
	Irrigated	ESN	1345.4	10.6	-0.016	0.96	0.04	
		Urea	1357.2	8.2	-0.003	0.95	0.05	

Supplementary Table 2-4. Quadratic Regression results for modelled and measured (Kryzanowski et al. 2009) barley grain nitrogen (kg N ha^{-1}) response to increasing N rates (0, 30, 60, 90, and 120 kg N ha^{-1}) for N sources of urea and ESN for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta.

Date Type	Year	Site	N Source	Intercept	Linear Coefficient	Quadratic Coefficient	R ²	P Value
Modelled	2008	Dryland	ESN	60.1	0.67	-0.0027	0.99	<0.001
			Urea	60.2	0.67	-0.0026	0.99	<0.001
		Irrigated	ESN	47.7	0.94	-0.0029	0.99	0.006
			Urea	47.7	0.93	-0.0028	0.99	0.006
	2009	Dryland	ESN	74.7	0.49	-0.0022	0.95	0.05
			Urea	74.6	0.49	-0.0020	0.97	0.03
		Irrigated	ESN	64.6	1.04	-0.0046	0.99	0.01
			Urea	64.7	1.02	-0.0043	0.98	0.02
	2010	Dryland	ESN	44.0	0.72	-0.0029	0.99	<0.001
			Urea	44.0	0.71	-0.0027	0.99	<0.001
		Irrigated	ESN	38.6	0.74	-0.0029	0.99	<0.001
			Urea	38.5	0.73	-0.0028	0.99	<0.001
	2011	Dryland	ESN	45.8	1.01	-0.0053	0.97	0.03
			Urea	45.7	1.01	-0.0052	0.97	0.03
Irrigated		ESN	50.0	0.65	-0.0028	0.99	0.001	
		Urea	49.9	0.65	-0.0027	0.99	<0.001	
Measured	2008	Dryland	ESN	86.8	0.53	-0.0015	0.99	0.01
			Urea	86.5	0.55	-0.0019	0.99	0.005
		Irrigated	ESN	69.6	0.52	-0.0008	0.99	0.01
			Urea	69.5	0.42	-0.0002	0.98	0.02
	2009	Dryland	ESN	60.6	0.55	-0.0014	0.99	0.01
			Urea	61.8	0.48	-0.0013	0.99	0.01
		Irrigated	ESN	71.1	0.25	0.0008	0.97	0.03
			Urea	75.2	0.31	-0.0004	0.92	0.08
	2010	Dryland	ESN	50.0	0.35	-0.0008	0.95	0.05
			Urea	48.2	0.01	0.0020	0.99	<0.001
		Irrigated	ESN	70.3	0.43	-0.0013	0.96	0.04
			Urea	69.1	0.53	-0.0022	0.89	0.11
	2011	Dryland	ESN	41.4	0.61	-0.0016	0.99	0.005
			Urea	42.8	0.36	-0.0004	0.91	0.09
Irrigated		ESN	35.0	0.41	-0.0004	0.98	0.02	
		Urea	35.3	0.42	-0.0012	0.96	0.04	

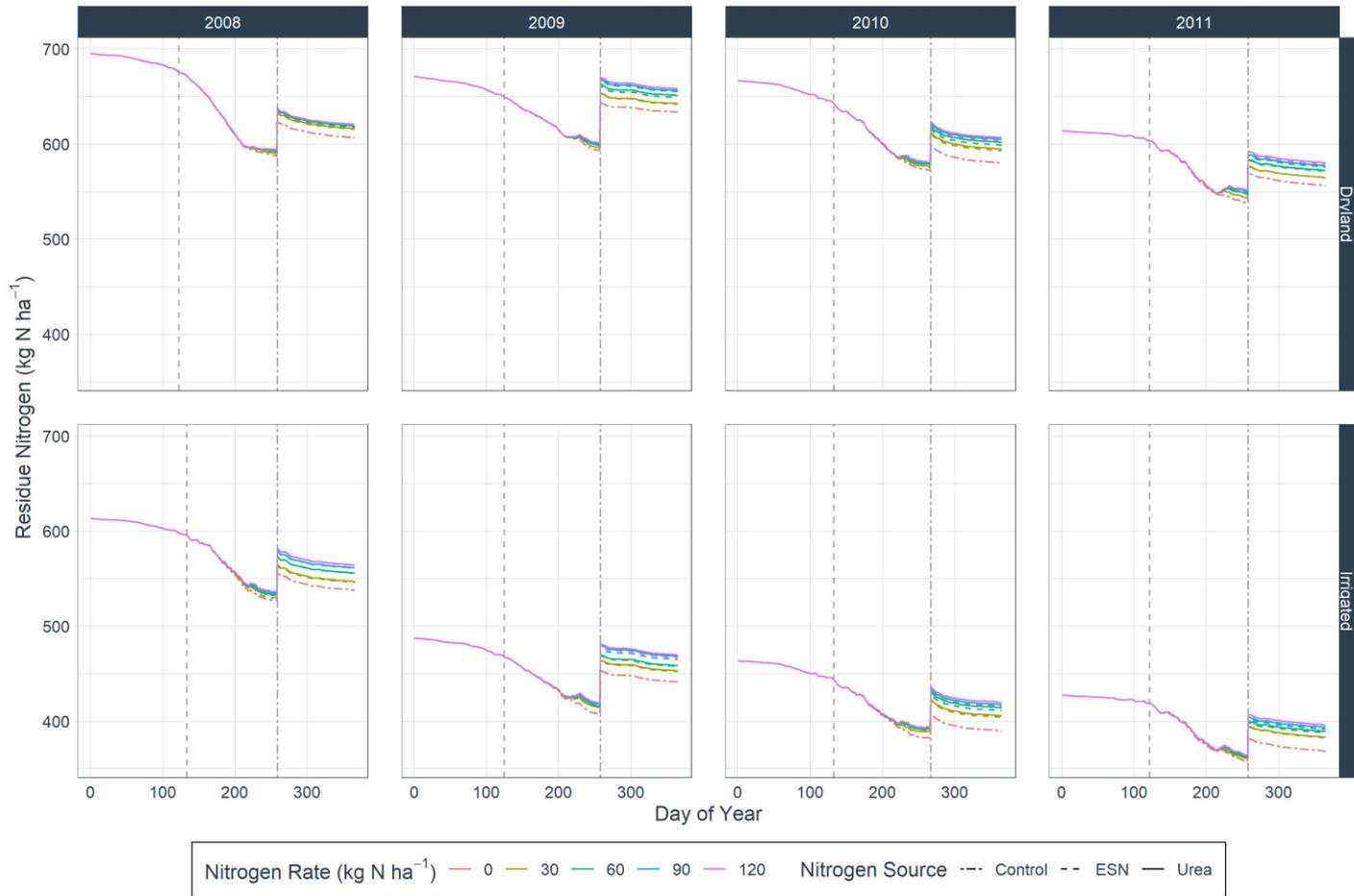
Supplementary Table 2-5. Quadratic Regression results for modelled and measured nitrogen use efficiency (NUE) (% kg Grain N kg⁻¹ N fertilizer) in response to increasing N rates (30, 60, 90, and 120 kg N ha⁻¹) for N sources of urea and ESN for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta.

Date Type	Year	Site	N Source	Intercept	Linear Coefficient	Quadratic Coefficient	R ²	P Value
Modelled	2008	Dryland	ESN	71.4	-0.36	4.9E-04	0.99	0.04
			Urea	73.3	-0.41	8.5E-04	0.99	0.01
		Irrigated	ESN	132.7	-1.22	5.2E-03	0.99	0.1
			Urea	131.8	-1.19	5.1E-03	0.99	0.10
	2009	Dryland	ESN	90.6	-1.19	5.4E-03	0.99	0.05
			Urea	90.0	-1.17	5.5E-03	0.99	0.1
		Irrigated	ESN	145.8	-1.43	5.4E-03	0.99	<0.001
			Urea	146.1	-1.46	5.7E-03	0.99	0.02
	2010	Dryland	ESN	71.9	-0.29	8.6E-06	0.99	0.04
			Urea	71.9	-0.29	1.2E-04	0.99	0.03
		Irrigated	ESN	77.0	-0.36	3.7E-04	0.99	0.05
			Urea	72.7	-0.26	-8.0E-05	0.99	0.03
	2011	Dryland	ESN	164.3	-2.02	8.3E-03	0.99	0.06
			Urea	162.1	-1.95	8.0E-03	0.99	0.06
		Irrigated	ESN	72.5	-0.45	9.5E-04	0.99	0.009
			Urea	72.0	-0.42	8.3E-04	0.99	0.006
Measured	2008	Dryland	ESN	48.04	-0.07	-3.9E-04	0.79	0.5
			Urea	38.08	0.21	-2.2E-03	0.99	0.03
		Irrigated	ESN	52.00	-0.05	-2.6E-04	0.48	0.7
			Urea	37.87	0.10	-8.3E-04	0.08	0.96
	2009	Dryland	ESN	22.49	0.64	-4.3E-03	0.96	0.21
			Urea	41.48	0.06	-1.1E-03	0.73	0.52
		Irrigated	ESN	-14.96	1.00	-5.1E-03	0.99	0.005
			Urea	97.24	-1.62	8.9E-03	0.91	0.29
	2010	Dryland	ESN	84.22	-1.24	6.5E-03	0.98	0.13
			Urea	3.25	0.15	2.7E-04	0.99	0.04
		Irrigated	ESN	89.53	-1.25	6.3E-03	0.96	0.20
			Urea	80.98	-0.96	4.4E-03	0.70	0.54
	2011	Dryland	ESN	36.74	0.42	-3.2E-03	0.90	0.31
			Urea	35.63	0.05	-7.0E-04	0.10	0.95
		Irrigated	ESN	61.81	-0.50	2.5E-03	0.87	0.36
			Urea	71.73	-0.80	3.7E-03	0.98	0.14

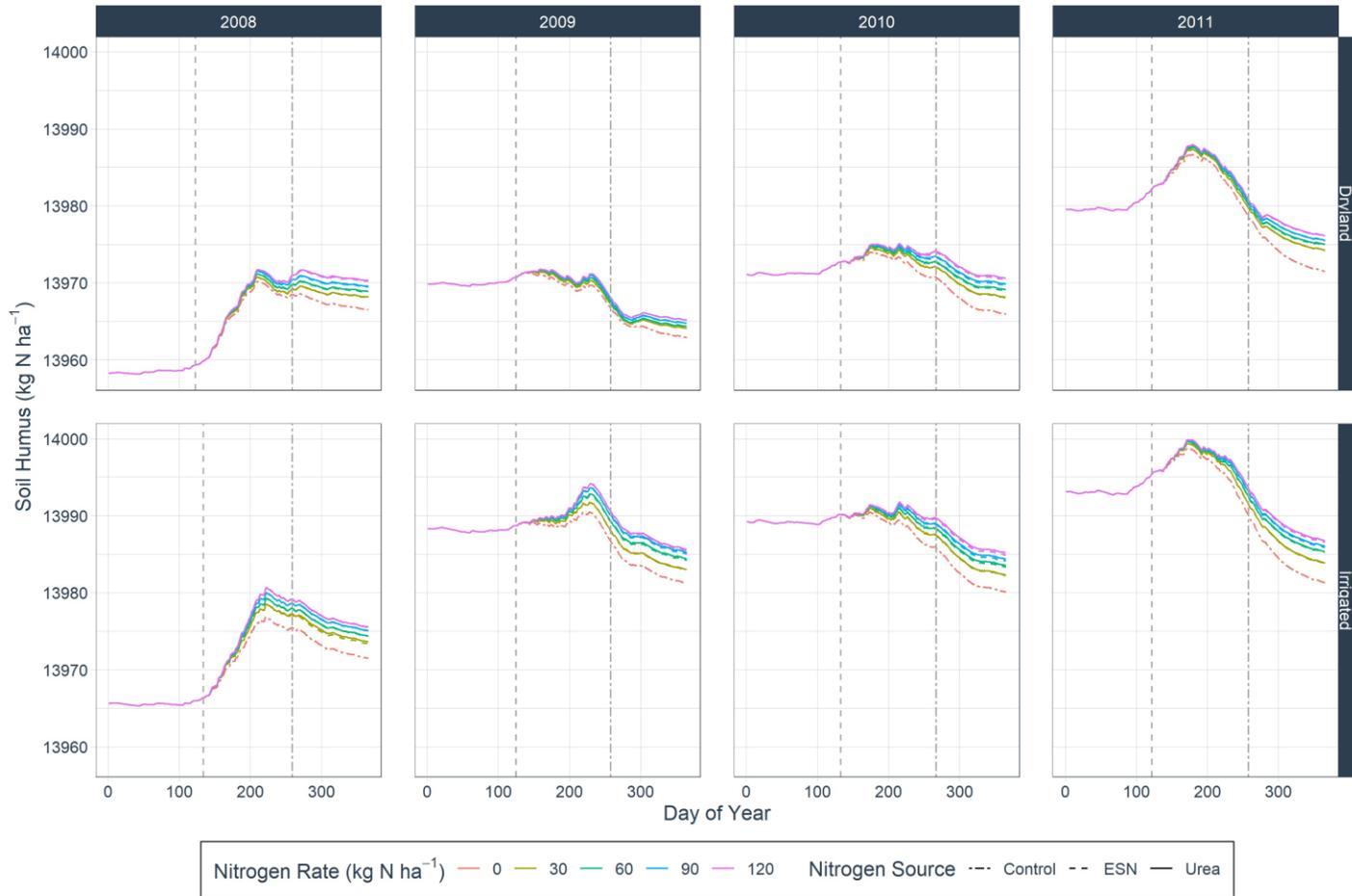
Supplementary Table 2-6. Mean barley grain yields (kg C ha⁻¹) and mean grain yield gains (%) from an additional 30 kg N ha⁻¹ increments of N fertilizer for 2008 – 2011 for modelled and measured (Kryzanowski et al. 2009) results at 30, 60, 90, and 120 kg N ha⁻¹ for urea and ESN N sources at dryland and irrigated sites in Lethbridge, Alberta. Grain yield gains with an additional 30 kg N ha⁻¹ increments of N fertilizer are calculated by taking the difference in yields between N fertilizer rates and dividing it by the grain yield at the lower N fertilizer rate.

Data Type	Site	N Source	N Amount (kg N ha ⁻¹)	Mean Grain Yields (kg C ha ⁻¹) for 2008-2011	Mean Grain Yield Gains (%) with an additional 30 kg N ha ⁻¹ increments of N Fertilizer for 2008-2011
Modelled	Dryland	Control	0	1602	-
			30	2299	44
		ESN	60	2601	13
			90	2744	5
			120	2823	3
		Urea	0	1602	-
			30	2300	44
			60	2605	13
	90		2759	6	
	Irrigated	Control	0	1419	-
			30	2225	57
			60	2646	19
			90	2908	10
		Urea	0	1419	-
			30	2217	56
			60	2652	20
90			2910	10	
Measured	Dryland	Control	0	1786	-
			30	2094	17
		ESN	60	2298	10
			90	2532	10
			120	2632	4
		Urea	0	1786	-
			30	1985	11
			60	2240	13
	90		2316	3	
	Irrigated	Control	0	1859	-
			30	2202	18
			60	2413	10
			90	2654	10
		Urea	0	1859	-
			30	2259	22
			60	2415	7
90			2595	7	
			120	2701	4

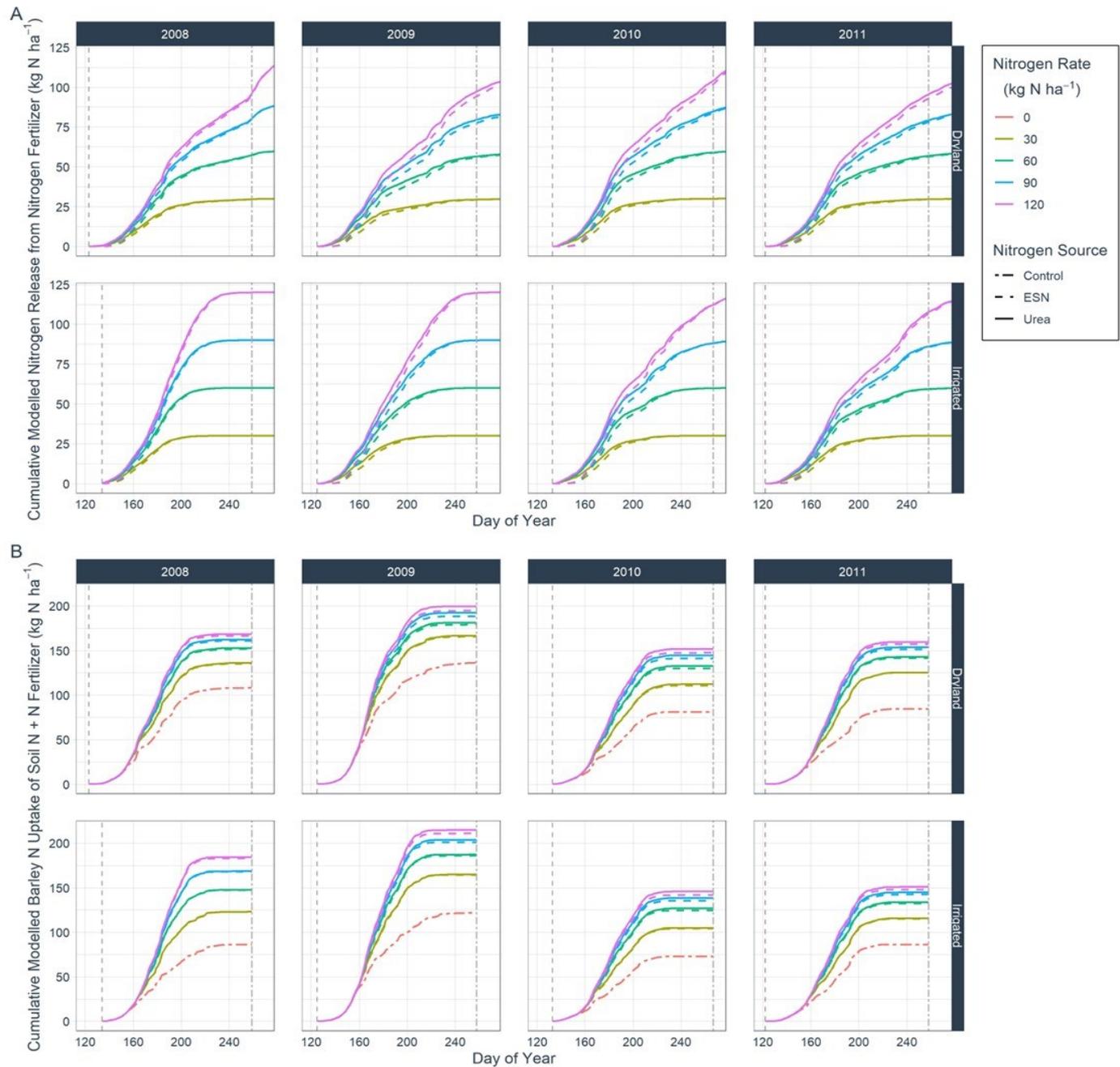
Supplementary Figures



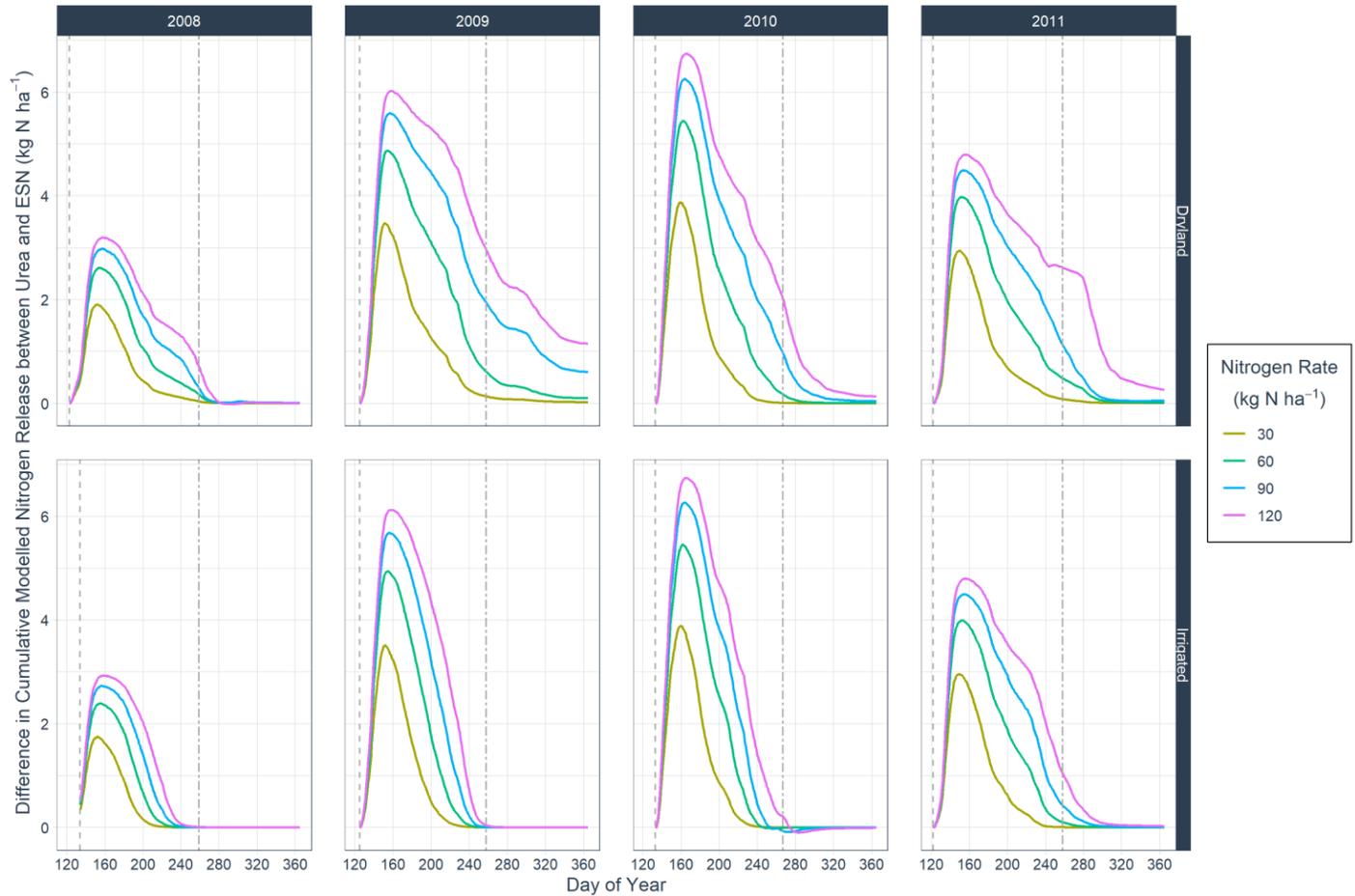
Supplemental Figure 2-1. Residue nitrogen (kg N ha⁻¹) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha⁻¹ for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta. Residue nitrogen declines with mineralization and rises after harvest as crop residues are left behind on the soil surface.



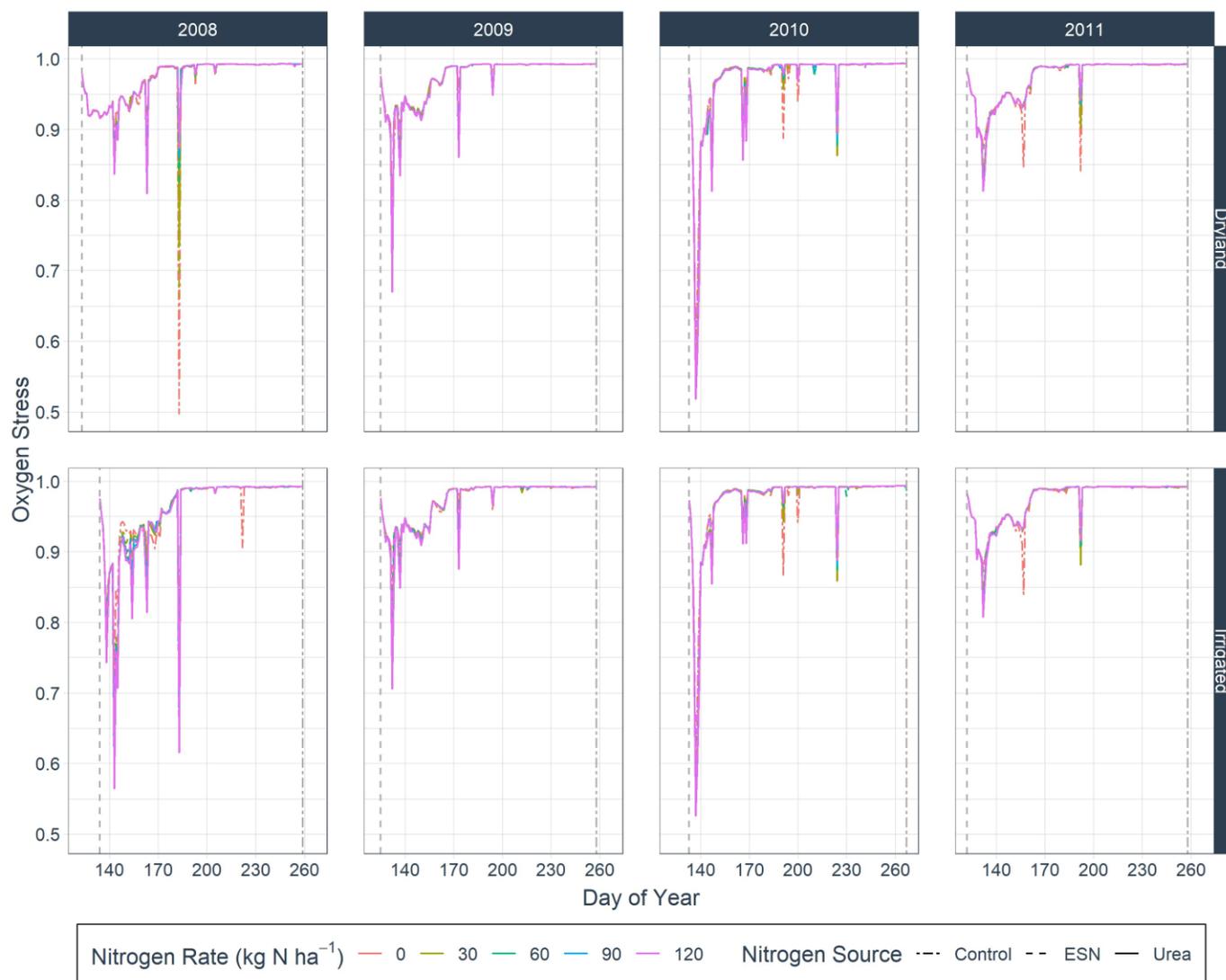
Supplemental Figure 2-2. Soil humus (kg N ha^{-1}) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta. Soil humus rises with immobilization and declines with mineralization.



Supplementary Figure 2-3. A) Modelled cumulative nitrogen release (kg N ha^{-1}) and **B)** Modelled barley N uptake of soil N + N fertilizer (kg N ha^{-1}) over the growing season for control (no N fertilizer applied, two-dashed line), urea (solid line) and Environmentally Smart Nitrogen (ESN) (dashed line) N sources at 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for Dryland and Irrigated Sites for 2008 – 2011 in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines).



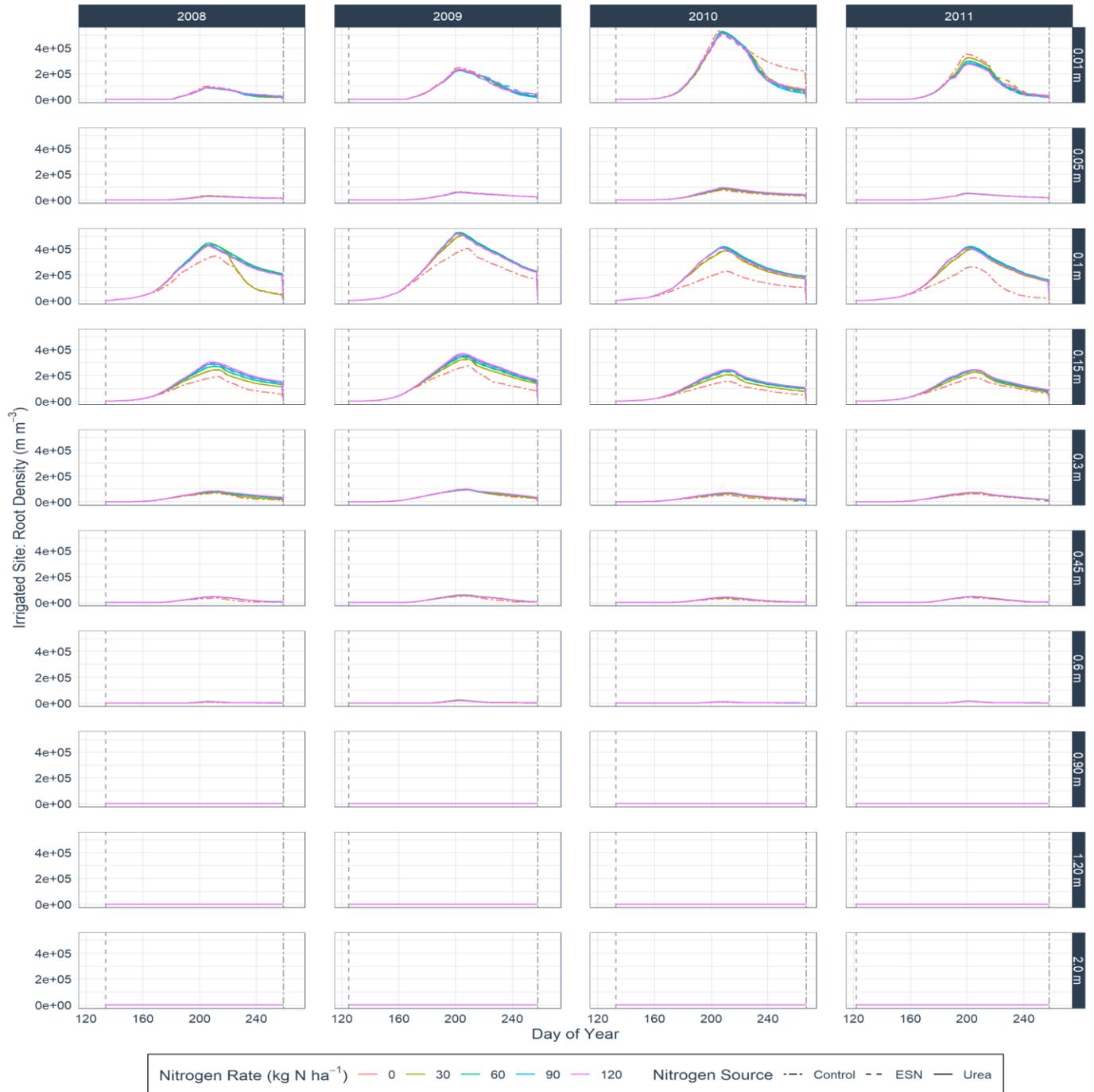
Supplementary Figure 2-4. The difference in cumulative modelled nitrogen release between urea and Environmentally Smart Nitrogen (ESN) at 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for Dryland and Irrigated Sites for 2008 – 2011 in Lethbridge, Alberta. Positive results indicate ESN has a lower N release than that of urea, while negative results indicate that N release from ESN is greater than that of urea. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines).



Supplementary Figure 2-5. Modelled oxygen stress (ratio of total root O₂ uptake to total root O₂ demand) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha⁻¹ for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta. Oxygen stress values <1 indicate an oxygen constraint for root growth and N uptake. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines).



Supplementary Figure 2-6. Root Density ($\text{m}^3 \text{m}^{-3}$) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at the dryland site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines).



Supplementary Figure 2-7. Root Density ($\text{m}^3 \text{m}^{-3}$) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines).

3.0 Development of a Comprehensive Nitrogen Budget Indicates Need for Optimal N Rate, not N source, to Reduce Direct and Indirect N₂O Emissions at Dryland and Irrigated Sites in Semi-Arid Southern Alberta

3.1 Introduction

Improved nitrogen (N) fertilizer management is necessary to meet the rising global food demand and reduce N fertilizer losses which negatively impact human and environmental health and affect the stability of the earth system (Cassman et al. 2002; United Nations Environment Programme 2014; Steffen et al. 2015). The use of synthetic N fertilizer has increased crop yields by 40 to 60% (Stewart et al. 2005), but crop N uptake efficiency of applied N fertilizer (NUE; nitrogen use efficiency) is as low as 30 to 50% (Cassman et al. 2002). The remaining 50 – 70% of applied N fertilizer not taken up by the crop may be immobilized in soil organic matter, retained as residual inorganic N, or lost to the surrounding environment via leaching (NO₃⁻), volatilization (NH₃), or denitrification (NO, NO₂, N₂O, N₂). These N losses have resulted in contamination of ground and surface water, acidification, eutrophication, declining air quality, ozone layer depletion, and the production of greenhouse gases (GHGs) (e.g., N₂O) (Cassman et al. 2002; Cameron et al. 2013). Of particular concern is the production of nitrous oxide (N₂O) emissions from N fertilizers, as N₂O has a global warming potential 298 times that of CO₂, making N₂O an important gaseous N loss in terms of climate change (Forster et al. 2007).

In Canada, N₂O emissions have risen by 92% since 2005 due to an increase in N fertilizer use of 89%, and agricultural N₂O emissions account for 75% of Canada's national N₂O emissions (Environment and Climate Change Canada 2022). The Western Canadian prairies make up 80% of farmland in Canada, and the increase in fertilizer use has been driven by Western Canada, where fertilizer use has doubled since 1981 (Grant and Wu 2008; Agriculture and Agri-Food Canada 2022). Recent policy targets in

Canada to reduce fertilizer GHG emissions by 30% below 2020 levels by 2030 have increased the urgency to continue to develop effective N fertilizer management strategies to reduce N losses (Agriculture and Agri-Food Canada 2022). Nitrogen losses occur due to N application rates exceeding crop N demand, and spatial and temporal asynchronization of N supply with crop N uptake; combined with environmental conditions which promote N losses (Zebarth et al. 2009; Setiyono et al. 2011; Cameron et al. 2013; Udvardi et al. 2021). Improved synchronization between N supply and N demand may be accomplished using the 4R's of nutrient stewardship (Right source at Right time, Right rate, and Right place) to reduce N losses (Malhi et al. 2001; Cassman et al. 2002; Grant and Wu 2008; Udvardi et al. 2021).

In the Canadian prairies, N fertilizer application in spring at the time of seeding (right time) and below the soil surface (right place) have been established as effective N fertilizer management practices which reduce N losses and increase NUE (Hao et al. 2001; Malhi et al. 2001; Grant and Wu 2008; Soon et al. 2011; Mezbahuddin et al. 2020). In contrast to conventional urea fertilizer, polymer-coated urea (PCU) fertilizers (right source) such as Environmentally Smart Nitrogen (ESN) have a delay in N release, which may better match early season crop N demand when crop N uptake is low (Grant and Wu 2008; Cahill et al. 2010a; Golden et al. 2011; Chen et al. 2018). Therefore, ESN may improve the synchronization between N availability and crop N demand, thereby reducing inorganic N accumulation in the soil and reducing the potential for N losses (Grant and Wu 2008; Grant et al. 2012; Drury et al. 2012). However, N release from ESN is controlled by soil temperature and limited by soil moisture (Cahill et al. 2010a; Golden et al. 2011; Ransom et al. 2020); therefore, ESN may not improve synchronization with crop N uptake in all regions due to climatic variability (Venterea et al. 2012; Li et al. 2018). Under the drier conditions of the Canadian prairies, N release from ESN may be delayed, and the effectiveness of ESN at reducing N losses has been found to be inconsistent (Burton et al. 2008; Soon et al. 2011; Li et al. 2012, 2016; Mezbahuddin et al. 2020; An et al. 2020; Thilakarathna et al. 2020). Selecting the optimal N rate (right rate) is one of the most important components of effective N fertilizer management as insufficient

N reduces crop productivity and increases the depletion of SOM, but N applied in excess of crop N demand results in minimal yield gains and increased N losses (Grant et al. 2006; Zebarth et al. 2009; Snyder et al. 2009; Malhi et al. 2010; Mahal et al. 2019). Crop response to N rate varies considerably with climatic conditions, management practices, soil N supply, and other limiting factors for crop growth, making N rate recommendations a challenge and variable between sites and years (Zebarth et al. 2009; Malhi et al. 2010; Puntel et al. 2016; Udvardi et al. 2021).

In semi-arid Southern Alberta, irrigated agriculture makes up approximately 70% of irrigated agriculture in Canada (Statistics Canada 2022) and is likely to be expanded due to the increasing demand for agricultural products (David et al. 2018). Higher soil moisture levels in irrigated agroecosystems may increase the potential for N leaching and denitrification losses (Maharjan et al. 2014; Liang et al. 2020; Guo et al. 2022). However, reduced water stress may also increase crop productivity due to enhanced crop N uptake and thereby reduce N losses (Djaman et al. 2013; Maharjan et al. 2014). Assessing the differences in the type and magnitude of N losses at dryland versus irrigated sites would provide insight into effective N fertilizer management strategies in irrigated semi-arid agroecosystems (Maharjan et al. 2014; David et al. 2018; Mezbahuddin et al. 2020).

Comprehensive N budgets can be developed to determine the fate of N in the agroecosystem by accounting for all N inputs, N outputs, and changes in soil N stocks. Such N budgets may therefore be used to assess the effects of different N management practices on denitrification, volatilization, leaching and runoff N losses (Mezbahuddin et al. 2020; Karimi et al. 2020; Yang et al. 2023). In addition, determining all forms of N losses would allow for an estimation of indirect N₂O losses in addition to direct N₂O emissions (Venterea et al. 2012; Hergoualc'h et al. 2019). Compared to field experiments, computer models can be used as low-cost and time-efficient estimates to determine the fate of N in the agroecosystem (Zebarth et al. 2009; Puntel et al. 2016; Mezbahuddin et al. 2020). Canadian agricultural N budgets have been developed by Karimi et al. (2020) and Yang et al (2023). However, due to the

variability in climatic conditions, soil properties, and cropping systems throughout Canada, site-specific N management practices will be required to reduce N losses (Karimi et al. 2020). Rigorously validated process-based models that simulate biogeochemical cycling and key ecosystem processes can be used to evaluate the effects of different N management strategies on the fate of N in the agroecosystem at high spatial and temporal resolutions (Grant et al. 2020; Mezbahuddin et al. 2020). One such model, *ecosys*, has been used extensively in the Western Canadian prairies to model N fertilization effects on agroecosystems and develop N budgets (Grant et al. 2001, 2006, 2020; Mezbahuddin et al. 2020).

Accordingly, the objectives of this study are:

- 1) Develop a comprehensive N budget to assess the fate of N at a site in the semi-arid Canadian prairies for different N sources (Urea vs ESN), N rates (0 – 120 kg N ha⁻¹), irrigation (irrigated vs dryland), and interannual climatic variability (2008 – 2011);
- 2) Determine area-based emission factors and yield-scaled emissions for direct and indirect N₂O losses.

This study will test the following hypotheses: (1) A simulated lag in N release with ESN with respect to that of urea will allow for improved synchronization between modelled N availability and crop N uptake, thereby reducing modelled inorganic N accumulation in the soil and lowering modelled N losses. (2) Increasing N rates will reduce the depletion of modelled soil organic nitrogen but increase modelled N losses and modelled residual soil nitrate-N. (3) If increased soil moisture from irrigation facilitates enhanced modelled crop N uptake, the irrigated site will have lower modelled N losses. (4) Otherwise, increased moisture inputs at the irrigated site will facilitate greater modelled N leaching and denitrification losses than the dryland site due to wetter conditions. Testing these hypotheses will contribute to our understanding of the effects of different N management practices (2 of the 4 R's, right source and right rate) on the fate of N at dryland and irrigated sites in semi-arid agroecosystems.

3.2 Methods

3.2.1 Field Dataset

Measurements from a field experiment conducted by Kryzanowski et al. (2009) were used for model inputs and to compare measured and modelled results. The field experiment was conducted under a zero-tillage regime in the Dark Brown Chernozemic soil zone at an irrigated site in semi-arid Lethbridge, Alberta (49.69, -112.76) in 2008 – 2011 with no dryland treatment (Kryzanowski et al. 2009). Daily average air temperatures and daily total precipitation were obtained from the nearest meteorological station (ACIS 2021) and are depicted alongside irrigation amounts in Figure 3-1D. Average growing season temperature, total precipitation for 2008 – 2011, and monthly irrigation amounts are presented in Table 3-1 (daily irrigation schedule available in Supplementary Table 3-1) (Kryzanowski et al. 2009) along with the 30-year climate normal (1971 – 2000) (ACIS 2021) for mean temperature and total precipitation. The Sand-silt-clay content, pH, organic C, solution $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, exchangeable $\text{PO}_4\text{-P}$, K, and $\text{SO}_4\text{-S}$, and bulk density were determined from field measurements and laboratory analysis for 0 – 0.15, 0.15 – 0.30, 0.30 – 0.60, and 0.60 – 0.90 meters in the soil profile (Table 3-2) (Kryzanowski et al. 2009). Field capacity, wilting point, and saturated hydraulic conductivity were estimated using Saxton and Rawls (2006) (Table 3-2). Soil temperature was measured at 0.05, and 0.10-meter depths using soil temperature sensors, and soil moisture measurements were taken at 0 – 0.05 meters depth using a time-domain reflectometry probe (Kryzanowski et al. 2009).

Nitrogen fertilizer was applied at the time of seeding on May 13, 2008, May 5, 2009, May 13, 2010, and May 2, 2011, and side banded below and to the side of the seed at a depth of 7.5 cm (Kryzanowski et al. 2009). Harvest dates were September 15 for all years, except for 2010 where harvest was September 24. Barley was seeded at 300 seeds m^{-2} into standing stubble using a direct seeder with atom jet double shoot openers with 20 cm row spacing (Kryzanowski et al. 2009). Prior to seeding, glyphosate was applied to the fields as a pre-burn application. A 2-way factorial of N rate (0, 60, and 120

kg N ha⁻¹) and N source (Urea (46-0-0) and ESN (44-0-0)) was set up as a randomized complete block design with 4 replicates. Each year the experimental treatments were located in an area that had received no N fertilizer the year prior. Triple superphosphate (0-44-0) was applied at a rate of 25 kg P ha⁻¹ for all treatments to minimize P limitations. An area of 11.34 m² of barley grain was harvested, and 15 cm of straw was left as stubble (Kryzanowski et al. 2009). Nitrous oxide measurements were taken at midday every 1 to 2 weeks from April to November. Measurements were taken from plexiglass vented chambers which covered 0.1 m² and had a 10 L headspace. Samples from the N₂O chambers were taken at 15, 30, and 45-minute intervals, and ambient air samples were taken for background N₂O levels for a time-zero N₂O concentration (Kryzanowski et al. 2009). The change in N₂O concentration with time was used to determine the N₂O flux, and N₂O measurements were extrapolated over a 24-hour period to determine daily fluxes (g ha⁻¹ day⁻¹). The N₂O fluxes in between sampling events were assumed to be the average of the fluxes between the 2 sampling times, and daily flux values were summed together to estimate annual N₂O losses (Kryzanowski et al. 2009).

3.2.2 Model Set Up and Simulations

The process-based ecosystem model *ecosys* was used to simulate the field experiment described above (with the addition of a dryland site and N fertilizer rates of 30 and 90 kg N ha⁻¹) (see section 3.2.1), and to assess the effects of N source, N rate, and dryland vs irrigated on the fate of N in the agroecosystem (soil N stocks, N inputs, N outputs). *Ecosys* models the transport and transformation of nitrogen, carbon, and phosphorus along with heat, water, and energy on an hourly timestep to simulate ecosystem processes and functioning (Grant 2001). The key parameters and algorithms which simulate the scientific processes in *ecosys* have been determined by separate research studies and therefore, the model does not require calibration and parameterization for each site-specific scenario (Grant 2001). Organic nitrogen may be mineralized to inorganic ammonium (NH₄⁺) or NH₄⁺ and nitrate (NO₃⁻) may undergo immobilization and be converted to organic N by heterotrophic microorganisms to maintain a

set microbial C:N ratio. Ammonium may be taken up by the plant, immobilized, converted to nitrate via nitrification by chemoautotrophic bacteria, sorbed to soil particles, or converted to ammonia (NH_3) and lost to the atmosphere via volatilization. Nitrate may be taken up by the plant, immobilized, or subject to denitrification and leaching losses. Under low O_2 conditions, nitrite may be reduced to nitrous oxide (N_2O) by nitrifying bacteria, or nitrate may be reduced by facultative anaerobic bacteria sequentially to nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O), and dinitrogen (N_2). Nitrate is highly mobile and may leach down the soil profile during drainage events. Nitrogen movement in soil is governed by mass flow and concentration gradients. Plant root N uptake occurs via convection, which is driven by water uptake when the plant transpires and concentration gradients between the soil solution and root and mycorrhizal surfaces. Further model descriptions and equations for soil microbial activity, N transformations and losses, and crop growth are available in Grant (2001) (Appendices B, C, D, E, F, H, I).

Model runs for each combination of N rate (0, 30, 60, 90, 120 kg N ha^{-1}), N source (control (0 kg N ha^{-1}), urea, ESN), site (Dryland and Irrigated), and year (2008, 2009, 2010, 2011) were conducted to simulate the effects of different N rates, N sources, dryland vs irrigated and interannual climatic variability on the fate of N in the agroecosystem and develop a comprehensive N budget. ESN was input as urea with a slower decline in hydrolysis inhibition to simulate the delayed N release from ESN compared to conventional urea fertilizer (see Chapter 2). Management options such as fertilizer, tillage, irrigation, and cropping inputs were entered into *ecosys* to simulate the management practices as described in the field dataset section 3.2.1. Soil properties used in the model simulations were obtained from field measurements and laboratory analysis (Kryzanowski et al. 2009) or estimated using Saxton and Rawls (2006) (Table 3-2). Weather inputs (solar radiation, relative humidity, wind speed, temperature, and precipitation) were obtained from the nearest meteorological station to input into the model runs at an hourly timestep, except for 2008 for which hourly data was not found (ACIS 2021).

Daily weather data for 2008 was therefore input to the model and was downscaled to hourly weather data within the *ecosys* model.

Separate spin-up runs for dryland and irrigated sites were executed for 1998 – 2007 to allow conditions in the model to reach equilibrium prior to the experimental production runs. Spin-up runs had a continuous field crop, zero tillage, and a 100 kg N ha⁻¹ year⁻¹ of urea fertilizer and 25 kg P ha⁻¹ of triple superphosphate applied except in the year prior to the experimental production run to simulate the cropping and management history in the years leading up to the field experiment (section 3.2.2.1). Phosphorus fertilizer was also applied at a rate of 25 kg P ha⁻¹ in control runs (no N fertilizer) to reduce P limitations.

3.2.3 Data Processing and Analyses

All statistical analyses were completed in the R software (version 4.1.1). To assess model performance, linear regression analyses for modelled vs measured grain yields (kg C ha⁻¹) and grain N (kg N ha⁻¹) (see Chapter 2), and for modelled vs measured annual N₂O emissions (kg N ha⁻¹ yr⁻¹) were performed. The coefficient of determination (R²), linear regression slope and intercept, root mean square error (RMSE), and standard deviation (SD) were calculated to determine the accuracy of modelled results compared to measured results. Modelled and measured soil water content and soil temperature at the irrigated site for N rates of 0, 60, and 120 kg N ha⁻¹ were compared to assess model performance. Measured spring soil nitrate-N and ammonium-N tests for 0 – 0.9 meters in the soil profile were compared to modelled soil inorganic N levels to assess model performance. Modelled annual N₂O-N emissions, area-based emissions factors (eq. 1), and yield-scaled emissions (eq. 2) at the irrigated site at N rates of 0, 60, and 120 kg N ha⁻¹ were compared against measured results to assess model performance. Area-based emission factors (%) (EF area) and yield-scaled emissions (g N₂O-N kg⁻¹ Grain

Yield Dry Matter (DM)) were calculated using equations 1 and 2 for modelled and measured results (Thilakarathna et al. 2020).

(1)

$$EF \text{ area} = \frac{\textit{Fertilized Emissions} - \textit{Unfertilized Emissions}}{\textit{N Fertilizer Rate}} * 100$$

(2)

$$\textit{Yield Scaled Emissions} = \frac{\textit{Treatment Emissions}}{\textit{Grain Yield}}$$

Indirect N₂O emissions from modelled subsurface N losses, N runoff, and N volatilization losses were estimated using the 2019 IPCC default emission factors of 0.011 for N subsurface and N runoff losses, and 0.010 for N volatilization losses (Hergoualc'h et al. 2019). Indirect area-based EFs and yield-scaled emissions were estimated using equations 1 and 2, and summed together with direct area-based EFs and yield-scaled emissions to determine direct + indirect EFs and yield-scaled emissions.

Nitrogen budgets developed from modelled results were made up of soil N stocks (inorganic (nitrate-N and ammonium-N) and organic (residue-N and humus-N) soil N), N inputs (N₂ fixation, N in seed, N from deposition, fertilizer N), and N outputs (Surface and subsurface dissolved inorganic and organic N, N₂O-N, N₂, and NH₃-N losses, and removal in grain N) (Sainju 2017). The change in modelled nitrate-N, ammonium-N, residue-N, and humus-N N stocks is the gain (positive) or loss (negative) at the year's end compared to the year's beginning. The change in soil organic nitrogen is determined by the sum of the changes in modelled residue-N and humus-N. Nitrogen inputs and outputs were the modelled values at the year's end. Each year's N stocks were summed together and then averaged to determine the average change in N stocks for 2008 – 2011.

3.3 Results

3.3.1 Modelled Soil Temperature, Soil Moisture and Discharge

Modelled soil water content (SWC) was similar to measured SWC (Figure 3-1A), and modelled SWC closely followed precipitation and irrigation moisture inputs, as well as rises in soil temperature resulting in spring thaw and increased soil moisture (Figure 3-1C, 3-1D). Low SWCs below wilting point were not simulated in the model but are unlikely in an irrigated landscape (Figure 3-1A). Fertilized treatments had more rapid declines in SWC than the unfertilized control (Figure 3-1A) due to greater barley productivity resulting in more rapid barley water uptake from increased transpiration. Modelled SWC was greater at the irrigated site than the dryland site due to higher moisture inputs from irrigation, particularly in 2008 and 2009 when greater amounts of irrigation were applied (Figure 3-1A, 3-1D, Table 3-1). Modelled daily water discharge events were greater at the irrigated site than at the dryland site, and greater during the wet year of 2010, and the year following, 2011 (Figure 3-1B). Overall modelled soil temperature closely matched the measured soil temperature, but at times measured soil temperature was slightly higher than modelled soil temperature (Figure 3-1C). During the growing season, modelled soil temperatures were 3 – 20 °C, and measured soil temperatures were 3 – 25 °C (Figure 3-1C).

3.3.2 Nitrogen Budget

3.3.2.1 Modelled Inorganic and Organic Soil N

Inorganic N levels ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) at seeding in 0 – 0.9 meters of the soil profile were 92 – 134 kg N ha⁻¹ for modelled results and 63 – 115 kg N ha⁻¹ for measured results, indicating substantial mineral N build-up at this site (Supplementary Table 3-2). On average for 2008 – 2011, modelled residual soil nitrate-N levels declined compared to initial levels at the beginning of the year for N rates of 0 – 60 kg N ha⁻¹ at the dryland site, and N rates of 0 – 90 kg N ha⁻¹ at the irrigated site. At higher N rates (≥ 90 kg N ha⁻¹

¹ at the dryland site and 120 kg N ha⁻¹ at the irrigated site), modelled residual soil nitrate-N levels increased 9 – 31 kg N ha⁻¹ in 0 – 2.0 meters of the soil profile compared to initial modelled nitrate-N levels (Figures 3-2, 3-3; Table 3-3). Compared to initial modelled ammonium-N levels at the beginning of the year, residual modelled soil ammonium-N levels increased with increasing N rates (Table 3-3; Supplementary Figure 3-1). Modelled soil nitrate-N and ammonium-N were similar regardless of N source (Table 3-3). End-of-year modelled residual nitrate-N levels with ESN were 0.5 – 5.3 kg N ha⁻¹ year⁻¹ (+0.4% to +3.5%) greater than those with urea (1.1 – 6.8% of applied N fertilizer), due to a delayed modelled N release and hence slower modelled crop N uptake with ESN (see Chapter 2) (Table 3-3; Supplementary Figure 3-2). Due to a delayed modelled urea hydrolysis and subsequent N release with ESN (see Chapter 2), end-of-year residual modelled ammonium-N levels with ESN were 0.2 – 0.9 kg N ha⁻¹ lower (-0.85 to -3.6%) than those with urea (0.2 – 3.0 % of applied N fertilizer) (Table 3-3; Supplementary Figure 3-1). The irrigated site had smaller gains in modelled residual nitrate-N and ammonium-N levels compared to the dryland site (Figures 3-2, 3-3; Table 3-3; Supplementary Figure 3-1).

Post-harvest modelled soil nitrate-N levels in 0.9 – 2.0 meters of the soil profile ranged between 48.8 – 126.8 kg N ha⁻¹ depending on the year, and N rate at dryland and irrigated sites (Figures 3-2, 3-3). Modelled post-harvest deep soil nitrate-N levels increased after N fertilizer application and with downwards nitrate-N movement in the soil profile, particularly in the wet year (2010), and the year following (2011) (Figures 3-2, 3-3), and at the irrigated site (Figure 3-3). Modelled post-harvest deep soil nitrate-N levels were lower during the drier years of 2008 and 2009 (49 – 81 kg N ha⁻¹), and higher during the wet year of 2010 and the year following in 2011 (73 – 127 kg N ha⁻¹). Post-harvest modelled soil nitrate-N levels in 0.9 – 2.0 meters of the soil profile were greater at the irrigated site with modelled nitrate-N levels of 53.3 – 126.8 kg N ha⁻¹, and lower at the dryland site with modelled nitrate-N levels of 48.8 – 85.4 kg N ha⁻¹ (Figures 3-2, 3-3). Modelled deep soil nitrate-N levels were greatest during the

wettest year of the study (2010) at the irrigated site, where modelled nitrate-N was 93 – 127 kg N ha⁻¹ (Figure 3-3). The unfertilized treatment had greater modelled residual nitrate-N accumulation at the irrigated sites and in the wetter years of the study (2010 and 2011) due to reduced modelled crop productivity, reduced modelled transpiration, and increased SWC, which increased downward modelled nitrate-N movement (Figures 3-1A, 3-2, 3-3).

Each year modelled soil organic nitrogen (SON) declined by 0.12 to 0.63% compared to initial levels, with higher N rates reducing the decline in SON (Table 3-3). Higher N rates increased modelled crop productivity and resulted in greater amounts of organic matter inputs to the soil in the form of crop residues (Supplementary Figure 3-3). The decomposition of products from greater amounts of crop residues allowed for slower depletion of modelled soil humus-N, and lower declines in modelled SON (Table 3-3; Supplementary Figure 3-4). Lower N rates also had greater declines in modelled residue-N and humus-N during the growing season, particularly for the unfertilized control treatment due to increased mineralization (Table 3-3; Supplementary Figures 3-3, 3-4). Compared to urea, ESN had 0 – 3.9 kg N ha⁻¹ year⁻¹ greater declines in SON levels due to slightly lower crop productivity and thereby lower residue-N inputs (Table 3-3).

3.3.2.2 Modelled Nitrogen Losses: N₂O, N₂, NH₃, N Runoff, and Subsurface N Losses

Daily modelled nitrous oxide (N₂O) emission fluxes coincided with irrigation and precipitation events and increases in SWC, and the majority of N₂O fluxes occurred when soil temperatures rose above 0°C (Figures 3-1A, 3-1C, 3-4A, 3-5A). Daily modelled N₂O fluxes ranged between 0 – 0.057 kg N ha⁻¹ day⁻¹ (Figures 3-4A, 3-5A). Measured annual N₂O emissions estimated based on linear interpolation (see section 3.2.1) were only available at the irrigated site at N rates of 0, 60, and 120 kg N ha⁻¹ and were 0.09 – 1.53 kg N ha⁻¹ (Table 3-4). Modelled N₂O emissions for corresponding treatments for the above-mentioned measured results were 0.13 – 0.40 kg N ha⁻¹ year⁻¹ (Table 3-4). Measured annual N₂O emissions corroborated modelled annual N₂O emissions ($R^2 = 0.21$, $y = 0.083x + 0.29$, $p = 0.04$, $RMSE =$

0.29 kg N ha⁻¹ yr⁻¹, SD = 0.30 kg N ha⁻¹ yr⁻¹). The residuals for modelled vs measured annual N₂O emissions (RMSE = 0.29 kg N ha⁻¹ yr⁻¹) were less than the variability of measured annual N₂O emissions (SD = 0.30 kg N ha⁻¹ yr⁻¹), indicating model results fell within the range of measured variability (Table 3-4). The high annual measured N₂O emission value of 1.53 kg N ha⁻¹ yr⁻¹ in 2010 for urea at 120 kg N ha⁻¹ was due to deviation from sampling protocol, with the snowpack being cleared from the sampling location resulting in a large N₂O emission peak (Table 3-4). Modelled annual N₂O emissions for dryland and irrigated sites and all N rates (0 – 120 kg N ha⁻¹) ranged between 0.13 – 0.68 kg N ha⁻¹ year⁻¹ (Table 3-5). Modelled N₂O emissions were similar regardless of N source (<0.01 kg N ha⁻¹ year⁻¹ difference), and modelled annual N₂O emissions increased linearly with increasing N fertilizer rates of 0 to 120 kg N ha⁻¹ (Figures 3-4A, 3-5A; Tables 3-3, 3-5). Modelled annual N₂O emissions were 0.04 – 0.16 kg N ha⁻¹ year⁻¹ greater at the dryland site than the irrigated site for all years except 2009, where N₂O emissions were similar (<0.03 kg N ha⁻¹ year⁻¹ difference) regardless of irrigation (Table 3-5).

Daily modelled N₂ fluxes ranged between 0 – 0.12 kg N ha⁻¹ day⁻¹ and corresponded with daily modelled N₂O fluxes, as low O₂ availability resulted in the reduction of N₂O to N₂ when N₂O was used as a terminal electron acceptor (Figures 3-4B, 3-5B). Modelled annual N₂ emissions ranged between 0.14 – 0.51 kg N ha⁻¹ year⁻¹ depending on the year and irrigation and increased with higher N rates from 0 to 120 kg N ha⁻¹ (Tables 3-3, 3-5). As with annual modelled N₂O emissions, annual modelled N₂ emissions were similar (<0.06 kg N ha⁻¹ year⁻¹ difference) regardless of N source (Table 3-5). Modelled annual N₂ emissions were similar (<0.1 kg N ha⁻¹ year⁻¹ difference) for dryland and irrigated sites (Table 3-5).

Daily modelled NH₃-N fluxes ranged between 0 – 0.18 kg N ha⁻¹ day⁻¹, with higher NH₃-N fluxes occurring later in the growing season when SWC was low, and conditions were dry (Figures 3-1A, 3-4C, 3-5C). Modelled annual NH₃-N losses ranged between 2.49 – 7.59 kg N ha⁻¹ year⁻¹ depending on the year and irrigation and increased with higher N rates from 0 to 120 kg N ha⁻¹ (Table 3-5). Modelled NH₃-N losses were similar regardless of N source (<0.07 kg N ha⁻¹ year⁻¹ difference), and ESN only slightly

reduced NH₃-N losses at the dryland site in 2009 at N rates of 30 and 60 kg N ha⁻¹ by 0.14 – 0.15 kg N ha⁻¹ year⁻¹ compared to those with urea (-2.0%) (Table 3-5). Modelled NH₃-N volatilization losses were 0.7 – 3.4 kg N ha⁻¹ year⁻¹ greater at the dryland site than at the irrigated site (Table 3-3). In the drier years of 2008 and 2009 (Table 3-1), modelled NH₃-N losses were 1.6 – 3.4 kg N ha⁻¹ year⁻¹ greater at the dryland site than at the irrigated site, while in the wetter years of 2010 and 2011 (Table 3-1), modelled NH₃-N losses were 0.7 – 1.3 kg N ha⁻¹ year⁻¹ greater at the dryland site than at the irrigated site (Table 3-5).

Daily modelled surface N runoff ranged between 0 – 0.44 kg N ha⁻¹ day⁻¹ (Figures 3-4D, 3-5D). Modelled surface N runoff was low (<3.0 mm) for all years of the study, which resulted in minimal modelled surface N runoff losses of 0 – 0.44 kg N ha⁻¹ year⁻¹ (Table 3-5; Supplementary Figure 3-5). Modelled surface N runoff losses were greater for fertilized (30 – 120 kg N ha⁻¹) than the unfertilized (0 kg N ha⁻¹) treatments but were similar between N rates of 30 – 120 kg N ha⁻¹ (Table 3-5). Different N sources (urea and ESN) did not affect modelled surface N runoff (Tables 3-3, 3-5). In the drier years of 2008 and 2009, less than 0.1 kg N ha⁻¹ year⁻¹ was lost via surface runoff which corresponded with minimal (<1.5 mm) modelled surface runoff (Table 3-5, Supplementary Figure 3-5). In the wetter years of 2010 and 2011, which had greater modelled surface runoff (1.5 – 2.5 mm), modelled surface N runoff losses were greater (0.13 – 0.44 kg N ha⁻¹ year⁻¹) (Table 3-5, Supplementary Figure 3-5). Modelled surface N runoff losses were similar (<0.1 kg N ha⁻¹ year⁻¹ difference) at dryland and irrigated sites (Tables 3-3, 3-5).

Daily modelled subsurface N losses ranged between 0 – 2.3 kg N ha⁻¹ day⁻¹ and were driven by daily modelled discharge events (Figures 3-1B, 3-4E, 3-5E). Modelled subsurface N losses ranged between 0 – 30.2 kg N ha⁻¹ year⁻¹ depending on the year and irrigation and were higher for fertilized than unfertilized treatments (Tables 3-3, 3-5). Modelled subsurface N losses were similar between N rates of 30 – 120 kg N ha⁻¹ (Table 3-5). Different N sources (urea and ESN) did not affect modelled subsurface N losses (Tables 3-3, 3-5). Modelled subsurface N losses were low in the drier years of 2008 and 2009

(0.003 – 4.97 kg N ha⁻¹ yr⁻¹), and higher in the wetter years of 2010 and 2011 (8.74 – 30.2 kg N ha⁻¹ yr⁻¹) (Table 3-5), corresponding with lower modelled daily discharge amounts in the drier years and higher modelled daily discharge amounts in the wetter years (Figure 3-1B). High-modelled discharge in 2010 (200 – 300 mm; Figure 3-1B) resulted in high-modelled subsurface N losses in 2010 and the year following (Figure 3-1B; Table 3-5). Wetter conditions and greater modelled discharge at the irrigated site also resulted in greater modelled subsurface N losses at the irrigated site than at the dryland site for 2008 – 2011 (Figure 3-1B; Tables 3-3, 3-5).

Average combined modelled N losses (N₂O, N₂, NH₃, surface runoff, and subsurface N losses) ranged between 10.8 – 17.2 kg N ha⁻¹ year⁻¹ (Table 3-3). Average modelled N losses increased with increasing N rates (Table 3-3). Average modelled N losses were similar regardless of N source, and ESN had 0.01 – 0.04 kg N ha⁻¹ year⁻¹ greater average modelled N losses than urea, except for N rates of 30 and 60 kg N ha⁻¹ at the dryland site, which was driven by lower volatilization losses with ESN in 2009 (Tables 3, 5). Lower total modelled N losses occurred in the drier years of 2008 and 2009 (5.5 – 9.9 kg N ha⁻¹), and higher total modelled N losses occurred in the wetter year of 2010 and the year following, 2011 (9.77 – 34.6 kg N ha⁻¹) (Table 3-5). In 2008, total modelled N losses were greater at the dryland site than at the irrigated site due to greater modelled NH₃-N and N₂O-N losses (Table 3-5). In 2009, total modelled N losses were similar between sites, with higher modelled NH₃-N losses at the dryland site and higher modelled subsurface N losses at the irrigated site (Table 3-5). In 2010 and 2011, total modelled N losses were greater at the irrigated site than the dryland site due to greater modelled subsurface N losses (Table 3-5).

3.3.3 Area-Based Emission Factors and Yield-Scaled Emissions

Area-based emission factors (EF_{area}) for modelled direct N₂O emissions ranged between 0.16 – 0.37% depending on the year and irrigation and declined with increasing N rates (Table 3-6). Direct

EFarea were similar regardless of urea or ESN, with ESN being 0 – 0.014% greater than urea (Supplementary Table 3-3). Except for 2009, direct EFarea was higher at the dryland site (0.16 – 0.37%) than at the irrigated site (0.17 – 0.28%) (Table 3-6). Area-based emission factors for measured annual N₂O emissions estimated based on linear interpolation (see section 3.2.1) were available at the irrigated site only, and were 0.1 – 1.1%, and the EFarea for modelled direct N₂O emissions were 0.19 – 0.24% (Table 3-4). When considering indirect N₂O emissions, EFarea declined by 0.03 – 0.12% at the irrigated site in 2008, and increased by 0.01 – 0.29% for the other sites and years (Table 3-6). Direct + indirect EFarea ranged between 0.16 – 0.59% and declined with increasing N rates except for the irrigated site in 2008, which increased with increasing N rates (Table 3-6). Direct + indirect EFarea were similar regardless of urea or ESN, with ESN being 0 – 0.017% greater than urea (Supplementary Table 3-3). Direct + indirect EFarea were 0.18 – 0.59% at the dryland site, and 0.16 – 0.50% at the irrigated site (Table 3-6). Direct + indirect EFarea was higher at the dryland site than at the irrigated site in 2008 and 2011, and higher at the irrigated site than at the dryland site in 2009 and 2010 (Table 3-6).

Modelled direct yield scaled N₂O-N emissions ranged between 0.029 – 0.093 g N₂O-N kg⁻¹ Grain Yield DM (Table 3-6). Direct yield scaled emissions for measured annual N₂O emissions estimated based on linear interpolation (see section 3.2.1) were available at the irrigated site only, and were 0.028 – 0.260 g N₂O kg⁻¹ grain yield DM, and for modelled results were 0.035 – 0.084 g N₂O-N kg⁻¹ grain yield DM (Table 3-4). Modelled direct yield scaled emissions were often higher at lower N rates of 0 – 30 kg N ha⁻¹, lower at intermediate rates of 60 – 90 kg N ha⁻¹, and higher at 120 kg N ha⁻¹, although there were some site-years where modelled direct yield scaled emissions increased with N rates between 30 – 120 kg N ha⁻¹ (Table 3-6). Modelled direct yield scaled emissions were similar regardless of urea or ESN, with ESN being 0 – 0.002 g N₂O-N kg⁻¹ Grain yield DM greater than urea (+0 to 3%; Supplementary Table 3-3). Modelled direct yield scaled emissions were 0.01 – 0.03 g N₂O-N kg⁻¹ grain yield DM greater at the dryland site than the irrigated site in 2008 – 2010, and in 2011 modelled yield scaled emissions were

similar regardless of irrigation. When considering indirect N₂O emissions from modelled NH₃-N, surface N, and subsurface N losses, yield-scaled emissions increased by 0.006 – 0.107 g N₂O-N kg⁻¹ grain yield DM, and ranged between 0.044 – 0.155 g N₂O-N kg⁻¹ grain yield DM (Table 3-6). Modelled direct + indirect yield scaled N₂O-N emissions had similar responses to increasing N rates as modelled direct N₂O-N yield scaled emissions (Table 3-6), and were similar regardless of N source (+0 – 0.0024 g N₂O-N kg⁻¹ grain yield DM with ESN compared to urea; Supplementary Table 3-3) (Table 3-6). In the drier years of 2008 and 2009, modelled direct + indirect yield scaled N₂O-N emissions were greater at the dryland site than at the irrigated site due to greater NH₃-N losses. In the wet year of 2010 and the year following, 2011, modelled direct + indirect yield scaled emissions were greater at the irrigated site than at the dryland site due to higher subsurface N losses (Tables 3-5, 3-6).

3.4 Discussion

3.4.1 Effectiveness of ESN in Reducing Nitrogen Losses

Nitrogen release from ESN must better match crop N uptake than does that from urea for ESN to increase crop N uptake, reduce inorganic N accumulation in the soil, and reduce N losses (Nelson et al. 2008; Golden et al. 2011; Soon et al. 2011; Li et al. 2018; Yang et al. 2021). Modelled N release from ESN did not improve synchronization with crop N uptake compared to urea at this cool, semi-arid site in Southern Alberta (see Chapter 2) (Supplementary Figure 3-2). Accordingly, modelled inorganic N accumulation (NO₃-N and NH₄-N), N₂O-N, NH₃-N, surface N and subsurface N losses were similar regardless of N source.

3.4.1.1 Inorganic N Accumulation

Despite a delay in modelled N release from ESN compared to urea, modelled soil nitrate-N and ammonium-N levels were similar regardless of N source (Figures 3-2, 3-3). Differences in modelled N release between urea and ESN were small (<7 kg N ha⁻¹) throughout the growing season, particularly at

lower N rates, and peaked during rapid crop N uptake (Supplementary Figure 3-6; see Chapter 2). Therefore, the greatest difference in the N availability between urea and ESN occurred when inorganic N accumulation was lower due to rapid crop N uptake compared to early and late in the growing season (Figures 3-2, 3-3; Supplementary Figure 3-6). In addition, high levels of inorganic soil N at seeding likely masked the effects of different N sources on N availability (Thilakarathna et al. 2020) (Figures 3-2, 3-3). In a global meta-analysis, Yang et al. (2021) found that controlled-release fertilizers (CRFs) such as ESN did not significantly affect nitrate-N and ammonium-N levels compared to conventional fertilizer N sources such as urea unless the N fertilizer rate was $>150 \text{ kg N ha}^{-1}$. The prolonged delay in modelled N release from ESN due to cool soil temperatures (see Chapter 2) and hence slower modelled crop N uptake resulted in slightly higher post-harvest residual nitrate-N levels compared to urea ($0.5 - 4.9 \text{ kg N ha}^{-1}$ at 0 – 2.0 meters in the soil profile for $30 \text{ to } 120 \text{ kg N ha}^{-1}$), although this only made up 1.1 – 6.8% of applied N fertilizer. In accordance with modelled results, Gagnon et al. (2012) found that ESN had $2 - 9 \text{ kg N ha}^{-1}$ greater nitrate-N than urea ammonium nitrate (UAN) (1.3 – 6.0% of applied N fertilizer) in the top 0.15 meters of the soil profile post-harvest and attributed this to a delay in N availability with ESN. Clément et al. (2021) also found that ESN resulted in slightly higher residual nitrate-N levels of $0.9 - 4.7 \text{ kg N ha}^{-1}$ compared to ESN in a blend with urea (0.5 – 2.35% of applied N fertilizer) in 0 – 0.9 meters in the soil profile post-harvest. Greater modelled residual soil $\text{NO}_3\text{-N}$ with ESN could result in greater post-harvest N losses with ESN compared to that of urea (Gagnon et al. 2012; Clément et al. 2021) (Figures 3-2, 3-3).

3.4.1.2 $\text{N}_2\text{O-N}$, $\text{NH}_3\text{-N}$ and Subsurface N Losses

Accordingly, similar modelled crop N uptake and modelled soil inorganic N levels for ESN or urea N sources resulted in similar modelled $\text{N}_2\text{O-N}$, $\text{NH}_3\text{-N}$, surface N and subsurface N losses for urea and ESN at this semi-arid site in Southern Alberta (Table 3-5). In accordance with modelled results, An et al. (2020) and Thilakarathna et al. (2020) found that a delayed N availability with ESN did not result in a shift in N_2O emission peaks, and found no reduction in cumulative N_2O emissions at semi-arid and semi-

humid sites in Alberta for winter and spring wheat cropping systems. At sites throughout Alberta, Li et al. (2012, 2016) found that in some site-years, the delayed N availability with ESN occasionally shifted the N₂O emission peaks to later in the growing season compared to conventional urea, but this did not result in reduced cumulative N₂O emissions. Furthermore, Li et al. (2012, 2016) found that N₂O emissions were similar regardless of N source for most site-years, with similar N₂O emissions for ESN and urea at 9/9 site years for canola, and 7/9 site years for barley. Across different climatic conditions and soil zones throughout Alberta, Mezbahuddin et al. (2020) found no reduction in N₂O emissions with ESN compared to urea. Under sub-humid conditions in the Northern Canadian prairies, Soon et al. (2011) found that ESN could reduce N₂O emissions up to 1.7x compared to urea, but only when conditions promoted high N₂O production such as above-average temperatures, high soil moisture, and high soil nitrate-N levels. However, under wetter conditions in Southern Manitoba, where growing season precipitation is 100 mm greater than in Northern Alberta, Burton et al. (2008) found that N₂O emissions were similar regardless of ESN or urea N sources. Variability in ESN effectiveness in reducing N₂O losses in the Canadian prairies is likely due to the differences in the timing of N availability with conditions prone to N losses, such as large precipitation events (Burton et al. 2008; Li et al. 2012, 2016). In addition, temperature, and moisture rather than N availability may have a greater influence on N₂O emissions than small differences in N availability from different N sources under the cool and dry conditions of the semi-arid Canadian prairies (Burton et al. 2008; Rochette et al. 2008; Li et al. 2012, 2016; An et al. 2020).

The effectiveness of ESN for reducing modelled NH₃-N losses was inconsistent and minor (Table 3-5). In contrast to model findings, Mezbahuddin et al. (2020) found that ESN reduced NH₃ losses by 2.2 – 8% across different soil and climatic zones in Alberta due to a delayed urea hydrolysis and N release with ESN. However, in a global meta-analysis of wheat cropping systems, Ti et al. (2019) found that reductions in volatilization losses with CRFs such as ESN were highly variable and not significant. The effectiveness of ESN in reducing volatilization losses in cereal cropping systems likely depends on the

timing of N availability with drier conditions which promote volatilization losses, as well as soil chemical and physical properties such as soil pH, CEC, and soil texture, which affect soil buffering capacity and adsorption of NH_4^+ on soil colloids (Cameron et al. 2013; Ti et al. 2019).

Modelled surface and subsurface N losses were similar for urea and ESN, which is in accordance with other literature findings in cool, semi-arid regions (Table 3-5) (John et al. 2017; Mezbahuddin et al. 2020). While there are limited studies on nitrate-N leaching losses in semi-arid dryland agroecosystems (John et al. 2017), other research suggests that ESN may be more effective in reducing N leaching losses under wetter conditions and in coarse-textured soils (Wilson et al. 2010; Gagnon et al. 2012; Li et al. 2018; Clément et al. 2021). However, even under wetter conditions, the effectiveness of ESN in reducing N leaching losses will depend on the timing of N availability coinciding with downward water movement, with ESN increasing nitrate leaching if delayed N availability coincides with greater downward water movement (Omonode et al. 2017; Clément et al. 2021).

3.4.1.3 Factors Influencing ESN Effectiveness: Climatic Conditions, Soil Properties, and Management Practices

The effectiveness of ESN in reducing N losses may be limited or inconsistent in the semi-arid Canadian prairies due to the cool, dry conditions (Burton et al. 2008; Li et al. 2012, 2016; John et al. 2017; Mezbahuddin et al. 2020; An et al. 2020; Thilakarathna et al. 2020) (see section 3.4.1.2) (Figures 3-4, 3-5; Table 3-5), but under warmer and wetter conditions, PCUs such as ESN have been found to be more effective at reducing N losses (Nelson et al. 2008; Gagnon et al. 2012; Drury et al. 2012; Li et al. 2018; Zhang et al. 2019; Yang et al. 2021). ESN must improve the synchronization between available N and crop N demand to reduce N losses. Otherwise, reductions in N losses may be a result of a prolonged delay in N release, which may continue after the growing season and be subject to further N losses rather than improved crop N uptake (Thapa et al. 2016; Li et al. 2018). Li et al. (2018) found that PCU fertilizers such as ESN were only effective at increasing yields and NUE in cropping systems with a mean

annual temperature (MAT) of 10 – 20 °C, and an annual precipitation of 800 – 1200 mm, which is higher than the MAT of 5.8 °C and an annual precipitation of 365 mm at this cool, semi-arid site (Table 3-1).

Under warmer and wetter conditions, urea would hydrolyze more rapidly, and a delay in N release from ESN compared to urea could improve the synchronization between N supply and crop N demand, reduce inorganic N accumulation in the soil, and thereby reduce N losses (Nelson et al. 2008; Golden et al. 2011; Soon et al. 2011; Li et al. 2018; Yang et al. 2021). For instance, in corn cropping systems where N fertilizer application occurs at temperatures > 10 °C (Cahill et al. 2010b; Gagnon et al. 2012), a global meta-analysis for corn agroecosystems found that PCU fertilizers increased yields by 5.3% and reduced N₂O-N, NH₃-N, and N leaching losses by 24%, 39%, and 27%, respectively (Zhang et al. 2019). In addition to climatic conditions, other factors such as soil properties (SOC, texture, soil pH) and management practices (N rate, N placement, tillage regime) have been found to influence the efficacy of PCU fertilizers such as ESN (Drury et al. 2012; Nelson et al. 2014; Thapa et al. 2016; Feng et al. 2016; Li et al. 2018; Zhang et al. 2019; Yang et al. 2021). The effectiveness of PCU fertilizers has been found to be greater when SOC is low (<10-15 g kg⁻¹) (Li et al. 2018; Zhang et al. 2019), soil texture is coarse (Thapa et al. 2016; Li et al. 2018; Yang et al. 2021), and N rates are >150 kg N ha⁻¹ in global meta-analyses (Zhang et al. 2019; Yang et al. 2021). In global meta-analyses, Li et al. (2018) reported that soils with a pH >8 could reduce the effectiveness of PCU, and Feng et al (2016) found that subsurface banded fertilizer application of PCU did not increase yields or reduce N₂O emissions. Application of PCU in no-tillage cropping systems has also been found to be less effective at increasing yields and reducing N₂O emissions than conventional tillage (Drury et al. 2012; Nelson et al. 2014; Thapa et al. 2016; Feng et al. 2016). The soil in this modelling experiment had high SOC (>20 g kg⁻¹), a moderately fine soil texture (clay loam), and a pH>8 (Table 3-2). In addition, the experiment was under a no-tillage regime, N rates were applied at ≤120 kg N ha⁻¹, and fertilizer was subsurface banded, which may have also reduced the effectiveness of ESN according to the above-mentioned studies. Therefore, climatic conditions, soil

properties, and management factors should be considered when deciding on the use of PCU fertilizers such as ESN as an N management practice aiming to increase yields, NUE and reduce N losses (Cahill et al. 2010a; Feng et al. 2016; Li et al. 2018).

3.4.2 Nitrogen Losses and Nitrogen Rate

3.4.2.1 N₂O-N Emissions

Modelled daily N₂O fluxes were low (0 – 0.057 kg N ha⁻¹ day⁻¹) and coincided with rises in soil temperature and precipitation and irrigation events (Figures 3-1A, 3-1D, 3-4A, 3-5A). In this cool, semi-arid region (Table 3-1), N₂O fluxes have been found to be constrained by temperature and moisture, rather than N availability, resulting in low daily N₂O fluxes (≤ 0.04 kg N ha⁻¹ day⁻¹) (Li et al. 2012, 2016; An et al. 2020) (Figures 3-1A, 3-1D, 3-4A, 3-5A). Initial daily modelled N₂O fluxes occurred early in the growing season after N application and spring thaw, as rising soil temperatures and high SWC increased denitrification rates (Nyborg et al. 1997; Burton et al. 2008; Li et al. 2012; An et al. 2020; Thilakarathna et al. 2020). Peaks in modelled N₂O fluxes also occurred later in the growing season in July and August with further increases in soil temperature combined with large precipitation and irrigation events (Figures 3-1A, 3-1D, 3-4A, 3-5A) (Stanford et al. 1975; Grant et al. 2006; Metivier et al. 2009; Li et al. 2012; An et al. 2020). At the irrigated site, increased water availability increased crop N uptake, reducing inorganic N substrate for denitrification and offsetting the effects of increased SWC (Figures 3-1A, 3-1D, 3-5A, Table 3-5) (Djaman et al. 2013; Maharjan et al. 2014; Thilakarathna et al. 2020). Under saturated conditions such as after major rainfall events, the rate of denitrification increases as nitrate is used as a terminal electron acceptor instead of O₂ and is reduced to N₂O (Figures 3-4A, 3-5A). When anaerobic conditions persist and the demand for electron acceptors is not met by N₂O, N₂O may be reduced to N₂ (Figures 3-4B, 3-5B) (Grant et al. 2006; Metivier et al. 2009; Cameron et al. 2013; Mezbahuddin et al. 2020). Soil temperature is also a major control on the production of N₂O, as increases in temperature increase microbial activity and O₂ demand, which increases the rate of denitrification (Stanford et al. 1975; Grant

et al. 2006; Metivier et al. 2009; Cameron et al. 2013). Metivier et al. (2009) found N₂O production to increase fourfold with a 6 °C temperature rise, and Stanford et al. (1975) found that N₂O production doubled with every 10 °C degrees Celsius rise between 15 to 35 °C.

Annual modelled direct N₂O emissions of 0.13 – 0.68 kg N ha⁻¹ year⁻¹ for N rates of 0 – 120 kg N ha⁻¹ (Table 3-5) fell within the range of annual N₂O emissions reported by other studies in cool, semi-arid Southern Alberta (Rochette et al. 2008; Li et al. 2012; An et al. 2020). Li et al. (2012) reported annual cumulative N₂O emissions of 0.46 – 0.56 kg N ha⁻¹ year⁻¹ for canola at N rates of 30 – 97 kg N ha⁻¹ in Lethbridge, Alberta. An et al. (2020) found annual N₂O emissions for winter wheat production were 0.21 – 0.95 kg N ha⁻¹ year⁻¹ at N rates of 146 – 176 kg N ha⁻¹. From 155 site years in the brown and dark brown soil zones in the semi-arid Western Canadian prairies, Rochette et al. (2008) found that N₂O emissions were <1 kg N ha⁻¹ year⁻¹. Modelled results and previous literature findings of low annual N₂O emissions in this cool, semi-arid region highlight the importance of regional-specific GHG emissions accounting. However, although N₂O emissions in this cool, semi-arid region are low, the high global warming potential of N₂O (298 times that of CO₂) means that even low N₂O emissions will have a large contribution to GHG emissions (Forster et al. 2007; Venterea et al. 2012).

Increasing N rates resulted in a linear increase in modelled annual N₂O emissions (Table 3-5), which is a trend reported by field studies in semi-arid regions (Rochette et al. 2008; Halvorson et al. 2014) as well as other studies (Gagnon et al. 2011; Zhang et al. 2019). In contrast, other studies have reported that N₂O emissions increased non-linearly or exponentially with N rate as N availability exceeded crop N demand (Grant et al. 2006; Zebarth et al. 2008; Kim et al. 2013). In this semi-arid region, temperature and precipitation are the primary controls on N₂O emissions rather than N availability (Burton et al. 2008; Rochette et al. 2008; Li et al. 2012, 2016; An et al. 2020), which may explain the linear relationship between N rate and annual N₂O emissions. In addition, the increased productivity from higher N rates resulted in reduced SWC due to increased transpiration (Figure 3-1A),

which may offset increases in N₂O emissions from increased N availability with higher N fertilizer application rates (Kaiser et al. 1998; Grant et al. 2006). The linear relationship between N₂O emissions and N fertilizer rate highlights the importance of optimal N rates, as N₂O emissions increase with N fertilizer rate (Table 3-5) while yield gains diminish as crop N demand is met (see Chapter 2).

3.4.2.2 NH₃-N Losses

Modelled NH₃-N losses of 2.5 – 7.6 kg N ha⁻¹ (Table 3-5) were higher than ammonia volatilization losses of 3.0 – 4.5 kg N ha⁻¹ estimated by Yang et al. (2023) using the Canadian Agricultural Budget model and higher than the estimated 2.5 kg N ha⁻¹ estimated by Sheppard et al. (2010) using a model based on land area and regression equations with coefficients for N fertilizer type, soil pH, and CEC. A soil pH of 8.15 (Table 3-2) likely resulted in higher modelled NH₃-N emissions compared to the above-mentioned studies, as a pH >7.3 has been found to increase volatilization losses by as much as 39% (Bouwman et al. 2002). Volatilization emissions estimated by Sheppard et al. (2010) from a land area with a pH > 7.3 represented only 8.9% of soil areas in Canada, likely resulting in the lower NH₃-N loss estimates compared to modelled results. In addition, a CEC of <26 cmol kg⁻¹ (Table 3-2) in this modelling experiment likely also contributed to greater NH₃-N losses, as Bouwman et al. (2002) found 40% higher NH₃-N losses when CEC was <32 cmol kg⁻¹ due to reduced retention of ammonium ions on soil colloids (Cameron et al. 2013). While modelled NH₃-N losses rose with fertilization, NH₃-N losses levelled off at N application rates >30 kg N ha⁻¹. Ammonium levels were similar between N rates of 30 – 120 kg N ha⁻¹ (Table 3-3; Supplementary Figure 3-1), which likely resulted in similar NH₃-N losses between N fertilizer rates of 30 – 120 kg N ha⁻¹ as NH₃-N losses increase with higher ammonium concentrations (Cameron et al. 2013). In addition, in a global meta-analysis of corn agroecosystems, Zhang et al. (2019) found that NH₃ emissions did not increase linearly with N rate, unlike other forms of N losses such as denitrification and leaching. Rapid nitrification of ammonium may also lead to reduced N rate effects on ammonia volatilization losses (Cameron et al. 2013). Daily modelled NH₃-N losses coincided with dry periods

(Figures 3-1A, 3-1D, 3-4C, 3-5C) and were lower at the irrigated site compared to the dryland site (Table 3-5), highlighting the importance of $\text{NH}_3\text{-N}$ volatilization losses in this semi-arid region, particularly under rainfed conditions. Ammonia losses will not only have negative impacts on human and environmental health due to decreased air quality and increased N loading to terrestrial and aquatic ecosystems, but ammonia losses may also result in indirect N_2O losses as NH_3 is deposited offsite and later reemitted as N_2O (Sheppard et al. 2010; Cameron et al. 2013). Accordingly, quantifying all forms of N losses, including NH_3 volatilization losses, is important when examining the effects of different N management practices and irrigation on agroecosystems.

3.4.2.3 Deep Soil Nitrate-N and Subsurface N Losses

Modelled downwards nitrate-N movement in the soil profile and subsurface N losses occurred in wetter years (e.g. 2010) at this semi-arid site and were driven by above-average precipitation and large modelled discharge events (Figures 3-1B, 3-1D, 3-2, 3-3, Table 3-5). Subsurface N losses, and deep soil nitrate-N below the rooting zone may be considered a leaching loss as N is beyond the zone of maximum barley root N uptake (~1 meter) (Campbell et al. 2006; Fan et al. 2016; He et al. 2016; Chantigny et al. 2019; Yang et al. 2023). Repeated N fertilizer applications in the model spin-up before the experimental years (see section 3.2.2) resulted in high levels of deep modelled soil nitrate-N below 0.9 meters of 52 – 113 kg N ha^{-1} prior to seeding (Figures 3-2, 3-3). Modelled post-harvest deep soil nitrate-N of 49 – 127 kg N ha^{-1} in 0.9 – 2.0 meters of the soil profile (Figures 3-2, 3-3) was similar to the range of 96 – 152 kg N ha^{-1} in 0.9 – 2.1 meters of the soil profile reported by Campbell et al. (2006) in a continuous wheat cropping system at a semi-arid site in the Canadian prairies.

In the drier years of 2008 and 2009 at the dryland site, modelled soil nitrate-N did not increase below 0.9 meters in the soil profile due to a lack of downwards nitrate-N movement, and subsurface N losses were minimal (0 – 1.85 $\text{kg N ha}^{-1} \text{ yr}^{-1}$) (Figure 3-2, Table 3-5). In a continuous wheat cropping system in the semi-arid Canadian prairies where N was applied at a rate of 30 kg N ha^{-1} , Campbell et al.

(2006) estimated nitrate-N movement below 1.2 meters from the applied N fertilizer by comparing the fertilized treatment with an unfertilized control. Over a period of 37 years, Campbell et al. (2006) found that 47 kg N ha^{-1} ($\sim 1.3 \text{ kg N ha}^{-1} \text{ year}^{-1}$) moved below 1.2 meters compared to the unfertilized treatment. However, in this modelling experiment, the unfertilized treatment frequently (2009 – 2011; Figure 3-2) had higher modelled deep soil residual nitrate-N due to greater mineralization of soil humus, lower crop N uptake and higher SWC from reduced transpiration (see Chapter 2), indicating that differences in feedback mechanisms may not allow for accurate estimations of N leaching when comparing fertilized and unfertilized treatments. In accordance with this, Campbell et al. (2006) found that the unfertilized treatment in a fallow-containing wheat cropping system had higher N leaching than the fertilized treatment due to greater mineralization and lower crop N uptake. He et al. (2016) modelled N leaching as soil nitrate-N below 1.2 meters in the soil profile at a semi-arid site in the Canadian prairies using the Decision Support System for Agrotechnology Transfer (DSSAT) model, and found nitrate-N leaching losses were low ($< 7 \text{ kg N ha}^{-1} \text{ year}^{-1}$) when precipitation was at or below the average annual precipitation of 350 mm. Yang et al. (2023) estimated N leaching below 1.0 meters in the soil profile using an N balance equation and modelled discharge events and found that in the semi-arid Canadian prairies, N leaching was $0 - 4 \text{ kg N ha}^{-1} \text{ year}^{-1}$ due to dry conditions and low residual nitrate-N levels. However, these N leaching estimates did not account for extreme precipitation events (Yang et al. 2023), which was what drove the large, modelled discharge events and subsequent subsurface N losses in the wetter years of this modelling experiment (Figures 3-1B, 3-4E, 3-5E). In wetter years (2010, 2011), when annual precipitation was 121 – 154% higher than the climate normal (Table 3-1), modelled nitrate-N below 0.9 meters increased $5 - 14 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (Figure 3-2), and subsurface N losses were $6 - 17 \text{ kg N ha}^{-1} \text{ year}^{-1}$ at the dryland site (Table 3-5) (Total: $17 - 28 \text{ kg N ha}^{-1} \text{ year}^{-1}$ of downwards $\text{NO}_3\text{-N}$ beyond 0.9 meters + subsurface N losses). Likewise, in wetter years where annual precipitation was 443 – 525 mm (127 – 150% greater than average annual precipitation), He et al. (2016) modelled nitrate leaching below 1.2

meters to be 25 – 140 kg N ha⁻¹ year⁻¹. At a site in semi-arid Montana (average annual precipitation of 390 mm), John et al. (2017) estimated nitrate-N leached below 1.0 meters based on an N balance method which accounted for inputs, outputs, and changes in soil N stocks and found N leaching losses to be 18 – 69 kg N ha⁻¹ year⁻¹ in a wheat cropping system. While estimated N leaching was in part high due to a prior fallow rotation, which increased soil inorganic N prior to seeding of spring wheat, growing season precipitation was also 121 – 225% greater than the long-term average, which also contributed to the high N leaching rates (John et al. 2017).

While N leaching losses may be minimal in drier years (Table 3-5) in cool semi-arid agroecosystems, high levels of soil nitrate-N combined with wetter conditions may increase the risk for N leaching losses (Campbell et al. 2006; He et al. 2016; John et al. 2017). Over time, repeated N fertilizer applications may result in the accumulation of deep soil nitrate-N (Figures 3-2, 3-3), which is beyond the zone of root N uptake and is therefore at risk for N leaching and groundwater contamination (Campbell et al. 2006; Cameron et al. 2013; He et al. 2016; Yang et al. 2023). Quantifying deep soil nitrate-N below 0.9 meters using models such as *ecosys* that account for large precipitation and drainage events that drive downward nitrate-N movement would help assess the risk for nitrate-N groundwater contamination in different regions and under variable climatic conditions. Incorporating crops with deeper root systems that can uptake deep soil nitrate-N such as alfalfa (1.8 meters; Fan et al. (2016)) into crop rotations would help reduce deep soil nitrate N, minimizing N leaching losses and indirect N₂O emissions (Mathers et al. 1975; Snyder et al. 2009; Grant et al. 2020).

3.4.3 Nitrogen Losses at Dryland vs Irrigated Sites

Irrigation affected the type and magnitude of modelled N losses (Figures 3-4, 3-5; Tables 3-3, 3-5). Irrigated sites are at a greater risk for leaching and denitrification losses compared to dryland sites due to the wetter conditions (Maharjan et al. 2014; Liang et al. 2020; Guo et al. 2022) (Figure 3-1A).

Irrigation reduced modelled volatilization losses but increased N leaching losses (deep soil residual nitrate-N below 0.9 meters + subsurface N losses) compared to the dryland site, particularly in wetter years (2010, 2011) (Figures 3-2, 3-3, 3-4, 3-5; Table 3-5). Greater moisture inputs (precipitation + irrigation) drove larger modelled discharge events, resulting in greater modelled downward nitrate-N movement and subsurface N losses at the irrigated site (Figures 3-1B, 3-5E; Table 3-5). Guo et al. (2022) and Maharjan et al. (2014) also found greater N leaching with greater irrigation amounts, and in a modelling experiment using the DSSAT model, He et al. (2016) found increasing N leaching losses below 1.2 meters with greater moisture inputs.

Compared to the dryland site, the irrigated site had lower annual N₂O emissions in all years except 2009, in which N₂O emissions were similar for the dryland and irrigated site (Table 3-5). This was due to increased crop N uptake in 2008 and 2009 which offset the effects of increased SWC ((Djaman et al. 2013; Maharjan et al. 2014) (see chapter 2), as well as an increased complete reduction of N₂O to N₂ in 2009 (Kuang et al. 2019) (Figures 3-4, 3-5; Table 3-5). In 2010 and 2011, lower N₂O losses at the irrigated site were likely due to a trade-off with increased subsurface N losses (Omonode et al. 2017; Kuang et al. 2019; Clément et al. 2021) (Table 3-5). David et al. (2018) found that despite higher N fertilizer rates (+37 to + 56 kg N ha⁻¹) at irrigated sites and higher soil moisture, N₂O emissions were not substantially higher at irrigated than dryland sites in the semi-arid Canadian prairies. In addition, David et al. (2018) found that the proportion of N fertilizer lost as N₂O was lower at the irrigated sites than the dryland sites, which is similar to modelled results in which area-based direct N₂O emission factors were lower at irrigated than dryland sites (Table 3-6). However, this study did not measure other forms of N losses, such as N leaching (David et al. 2018). Nitrogen availability coinciding with deep water percolation may increase N leaching losses instead of N₂O emissions (Omonode et al. 2017; Clément et al. 2021), resulting in a trade-off between different types of N losses depending on the environmental conditions and irrigation quantity and timing. Maharjan et al. (2014) found that irrigation significantly

increased N leaching but did not increase N₂O emissions compared to a dryland site. In a soil column experiment, Kuang et al. (2019) found that N₂O surface emissions were lower at a higher SWC than at a lower SWC due to greater downwards nitrate-N movement, reduced gas diffusivity in the soil profile, and increased reduction of N₂O to N₂. Therefore, while in 2010 and 2011 N₂O losses were lower at the irrigated site, increased subsurface N losses resulted in overall higher N losses, and higher direct + indirect yield scaled emissions than at the dryland site in these years (Table 3-6). This highlights the importance of quantifying all forms of N losses to determine the full impact of irrigation management in water-limited semi-arid agroecosystems on N losses and GHG emissions accounting.

3.4.4 Area-Based Emission Factors and Yield-Scaled Emissions for Direct and Indirect N₂O-N Emissions

Modelled area-based direct EFs were 0.16 – 0.37% (Table 3-6), which was within the range of EFs reported in the literature in this semi-arid region. In Southern Alberta, An et al. (2020) reported EFs of 0.013 – 0.356% for winter wheat production, and Chai et al. (2020) reported an average EF of 0.23% for irrigated wheat and canola production. In Lethbridge, Alberta, Li et al. (2012) reported an EF of 0.37% for canola production. Rochette et al. (2018) reported an EF of 0.16% in the brown and dark brown soil zones of the Canadian Prairies, and Thilakarathna et al. (2020) reported an EF of 0.31% for spring wheat production in semi-humid central Alberta. Liang et al. (2020) developed an empirical model to estimate EFs as a function of growing season precipitation, and according to this method, EFs in this experiment would range between 0.19 – 0.41%, which closely agrees with modelled EFs (Figure 3-1D, Table 3-1).

Area-based emission factors from modelled results and previously reported EFs are lower than the 2019 IPCC default EF of 1%, highlighting the importance of regional EFs to account for the effects of different climatic conditions, soil properties, and management practices on N₂O emissions (Rochette et al. 2018; Hergoualc’h et al. 2019; Liang et al. 2020; Thilakarathna et al. 2020). On average, when including indirect N₂O emissions from volatilization and leaching in modelled EFs, modelled EFs increased by 0.06% (+24%)

(Table 3-6), indicating the potential to reduce N₂O emissions via indirect N₂O losses, as well as the importance of considering indirect N₂O emission losses when assessing total N₂O emission losses (Venterea et al. 2012).

Modelled yield-scaled emissions of 0.029 – 0.093 g N₂O-N kg⁻¹ grain yield DM (Table 3-6) were low and fell within the range of yield-scaled emissions reported by other studies in semi-arid Southern Alberta. In Lethbridge, Alberta, An et al. (2020) reported yield-scaled emissions of 0.046 – 0.238 g N₂O-N kg⁻¹ grain yield DM for winter wheat production and Li et al. (2012, 2016) reported yield-scaled emissions intensities of 0.07 – 0.20 g N₂O-N kg⁻¹ grain yield DM for barley and canola production. For irrigated wheat and canola production, Chai et al. (2020) reported yield-scaled emissions of 0.001 – 0.1 g N₂O-N kg⁻¹ grain yield DM. As N rates increased, both N₂O emissions and crop yields increased due to higher N availability for crop N uptake and N₂O production (Table 3-3) (Thilakarathna et al. 2020). To account for this, yield-scaled emissions consider N₂O emission losses relative to crop productivity (Van Groenigen et al. 2010). Modelled yield scaled emissions were often higher at low N rates of 0 and 30 kg N ha⁻¹ due to lower yields, and higher at 120 kg N ha⁻¹ (Table 3-6) as N availability exceeded crop N uptake and yield gains diminished (Table 3-3; see Chapter 2 for yield response to N rates). Unfertilized treatments often had similar or higher modelled yield-scaled emissions than fertilized treatments (Table 3-6). This was likely because unfertilized treatments had lower yields and reduced transpiration resulting in higher SWC (Figure 3-1A), which likely increased N₂O production relative to the fertilized treatments, which had greater crop N uptake, higher yields and lower SWC (Kaiser et al. 1998, Grant et al. 2006). Similarly, Van Groenigen et al. (2010) found that yield-scaled emissions were lowest at intermediate N rates due to greater crop productivity rather than at lower N rates. Accordingly, yield-scaled emissions should be considered in N fertilizer management so that trade-offs between N rates, yields and N₂O losses may be assessed, and reductions in N₂O emissions at one site are not offset by higher yield-scaled emissions and N₂O losses at another (Venterea et al. 2011).

3.4.5 Soil N Stocks: SON and Residual Nitrate-N

Nitrogen fertilizer application reduced the depletion of modelled SON, thereby contributing to the maintenance of long-term soil fertility, but increasing N fertilizer rates increased modelled residual nitrate-N levels, which are subject to N losses after the growing season (Chantigny et al. 2019; Mahal et al. 2019; Grant et al. 2020; Yang et al. 2023). Increasing N fertilizer rates increased modelled SON by decreasing net mineralization of modelled soil humus (Supplementary Figure 3-4) with increased allocation of microbial decomposition products to humus from increased microbial growth driven by increased litterfall (Supplementary Figure 3-3). In accordance with these model findings, Mahal et al. (2019) found that N fertilization reduced the mineralization of soil organic matter, thereby contributing to the maintenance of soil fertility in a long-term field experiment. Additionally, in a long-term modelling experiment, Grant et al. (2020) found that N fertilization increased SON and soil organic carbon stocks compared to an unfertilized treatment that was consistent with field measurements due to increased net primary production and hence litterfall with fertilizer inputs. Of the applied N fertilizer, 20 – 50% contributed to the maintenance of modelled SON, with the relative proportion of N fertilizer contribution to SON declining with increasing N rates (Table 3-3). A substantial portion of the applied N fertilizer being incorporated into SON agrees with the 30% of applied urea fertilizer retained in SOM determined in an incubation experiment by Daly and Hernandez-Ramirez (2020).

Of the applied N fertilizer, 0 – 40% was retained as residual nitrate-N, with modelled residual nitrate-N increasing non-linearly with N rate as N availability exceeded crop N demand (Table 3-3). He et al. (2016) modelled soil mineral N levels using the DSSAT model at a semi-arid site in the Canadian prairies and found that soil mineral N increased exponentially with N rates of 0 – 90 kg N ha⁻¹. At N rates of 90 – 120 kg N ha⁻¹ for urea, modelled residual nitrate-N increased 6 – 27 kg N ha⁻¹ relative to initial NO₃-N levels on average for 2008 – 2011, while at N rates <90 kg N ha⁻¹ modelled residual nitrate-N declined relative to initial NO₃-N levels due to higher modelled N uptake efficiency (see Chapter 2) (Table

3-3). Similarly, using the Canadian Agricultural budget model, Yang et al. (2023) found that at N rates of 83 – 135 kg N ha⁻¹, residual nitrate-N values were 13 – 40 kg N ha⁻¹ in the Canadian prairies. Despite modelled soil nitrate-N being lower than the nitrate-N limit listed in the Agricultural Operations Practices Act (AOPA), in wetter years (e.g. 2010), modelled downwards nitrate-N movement resulted in greater deep modelled soil nitrate-N accumulation and subsurface N losses (see section 3.4.2.3) (Figures 3-2, 3-3, Table 3-5) (Alberta Agriculture and Rural Development 2008). Non-linear increases in residual nitrate-N levels with increasing N fertilizer rates highlight the importance of proper N fertilizer applications to reduce residual nitrate-N losses which increases the risk of water contamination (Yang et al. 2023) and is at risk for overwinter N leaching and denitrification losses (Chantigny et al. 2019). Even in the dry, cold soils of the semi-arid Canadian prairies, overwinter N losses have been found to be 60 – 75% from residual nitrate-N left in the soil after harvest (Chantigny et al. 2019). Accordingly, proper nitrogen fertilizer management must balance the maintenance of long-term soil fertility by sustaining SON stocks while also minimizing residual nitrate-N with optimum N-rate applications (Snyder et al. 2009).

3.5 Conclusion

A comprehensive nitrogen budget in semi-arid Southern Alberta was developed using the process-based ecosystem model *ecosys* to assess the effects of N source, N rate, irrigated vs dryland, and interannual climatic variability on the fate of N in the agroecosystem. Results from this modelling experiment indicate that optimal N fertilizer application rates rather than N source (urea vs ESN) should be a priority for effective N fertilizer management. Under the cool, dry conditions of the semi-arid Canadian prairies, ESN did not increase crop N uptake or reduce N losses compared to conventional urea fertilizer. Cold soil temperatures slowed N release from ESN such that there was no improved synchronization between N availability and crop N uptake, which did not reduce inorganic N accumulation in the soil profile and did not reduce N losses. Increasing N rates reduced the depletion of SON, but increased N₂O-N, NH₃-N, and subsurface N losses, and increased residual nitrate-N levels non-

linearly. Therefore, proper N fertilizer application must balance sustaining long-term soil fertility with N losses and residual nitrate-N, which may be subject to post-harvest N losses. Interannual climatic variability and irrigation influenced the type and magnitude of N losses, with larger volatilization losses in drier years and at dryland sites, and larger subsurface N losses in wetter years and at irrigated sites. Large increases in area-based emission factors from the inclusion of indirect N₂O emissions estimated from volatilization and subsurface N losses highlight the potential to reduce N₂O emissions via indirect N₂O losses. High residual nitrate-N deep in the soil profile also indicates the potential to reduce potential N leaching and indirect N₂O losses by incorporating crops with deeper rooting systems which can access deep soil nitrate-N into crop rotations, and the importance of optimal N fertilizer rates to reduce residual nitrate-N levels. Due to the variability in climate, soils, and cropping systems throughout Canada, N management practices will need to be fine-tuned for different regions and environmental conditions. This modelling study demonstrated that *ecosys* could be an effective tool to assess the impacts of different N management practices, irrigation, and interannual climatic variability on soil N stocks and N leaching, volatilization, and denitrification losses and could be used to inform effective N fertilizer management strategies for policymakers and producers.

3.6 References

- ACIS 2021. Alberta Climate Information Service. [Online] Available: <https://agriculture.alberta.ca/acis/> [2021 Oct. 1].
- Agriculture and Agri-Food Canada 2022. Discussion Document: Reducing emissions arising from the application of fertilizer in Canada's agriculture sector - agriculture.canada.ca. [Online] Available: <https://agriculture.canada.ca/en/about-our-department/transparency-and-corporate-reporting/public-opinion-research-and-consultations/share-ideas-fertilizer-emissions-reduction-target/discussion-document-reducing-emissions-arising-application-fertilizer-canadas-agriculture-sector> [2022 Sep. 22].
- Alberta Agriculture and Rural Development 2008. 2008 Reference Guide Agricultural Operation Practices Act. [Online] Available: <https://open.alberta.ca/publications/4221828#summary> [2023 Oct. 9].
- An, H., Owens, J., Stoeckli, J., Hao, X., Beres, B., and Li, Y. 2020. Nitrous oxide emissions following split fertilizer application on winter wheat grown on Mollisols of Southern Alberta, Canada. *Geoderma Regional* **21**. Elsevier B.V. doi:10.1016/j.geodrs.2020.e00272.
- Bouwman, A.F., Boumans, L.J.M., and Batjes, N.H. 2002. Estimation of global NH₃ volatilization loss from synthetic fertilizers and animal manure applied to arable lands and grasslands. *Global Biogeochem Cycles* **16**. American Geophysical Union. doi:10.1029/2000gb001389.
- Burton, D.L., Li, X., and Grant, C.A. 2008. Influence of fertilizer nitrogen source and management practice on N₂O emissions from two Black Chernozemic soils. *Can J Soil Sci* **88**: 219–227. doi:10.4141/CJSS06020.
- Cahill, S., Osmond, D., and Israel, D. 2010a. Nitrogen release from coated urea fertilizers in different soils. *Commun Soil Sci Plant Anal* **41**: 1245–1256. doi:10.1080/00103621003721437.
- Cahill, S., Osmond, D., Weisz, R., and Heiniger, R. 2010b. Evaluation of alternative nitrogen fertilizers for corn and winter wheat production. *Agron J* **102**: 1226–1236. doi:10.2134/agronj2010.0095.
- Cameron, K.C., Di, H.J., and Moir, J.L. 2013. Nitrogen losses from the soil/plant system: A review. *Annals of Applied Biology* **162**: 145–173. doi:10.1111/aab.12014.
- Campbell, C.A., Selles, F., Zentner, R.P., De Jong, R., Lemke, R., and Hamel, C. 2006. Nitrate leaching in the semiarid prairie : Effect of cropping frequency, crop type, and fertilizer after 37 years. *Can J Soil Sci* **86**: 701–710. doi:10.4141/S05-008.
- Cassman, K.G., Dobermann, A., and Walters, D.T. 2002. Agroecosystems, Nitrogen-use Efficiency and Nitrogen management. *Amibio* **31**: 132–139. doi:10.1579/0044-7447-31.2.132.
- Chai, L.L., Hernandez-Ramirez, G., Dyck, M., Pauly, D., Kryzanowski, L., Middleton, A., Powers, L.A., Lohstraeter, G., and Werk, D. 2020. Can fertigation reduce nitrous oxide emissions from wheat and canola fields? *Science of the Total Environment* **745**. Elsevier B.V. doi:10.1016/j.scitotenv.2020.141014.
- Chantigny, M.H., Bittman, S., Larney, F.J., Lapen, D., Hunt, D.E., Goyer, C., and Angers, D.A. 2019. A multi-region study reveals high overwinter loss of fall-applied reactive nitrogen in cold and frozen soils. *Can J Soil Sci* **99**: 126–135. Agricultural Institute of Canada. doi:10.1139/cjss-2018-0151.
- Chen, J., Lü, S., Zhang, Z., Zhao, X., Li, X., Ning, P., and Liu, M. 2018. Environmentally friendly fertilizers: A review of materials used and their effects on the environment. *Science of the Total Environment* **613–614**: 829–839. Elsevier B.V. doi:10.1016/j.scitotenv.2017.09.186.

- Clément, C.C., Cambouris, A.N., Ziadi, N., Zebarth, B.J., and Karam, A. 2021. Potato yield response and seasonal nitrate leaching as influenced by nitrogen management. *Agronomy* **11**. MDPI. doi:10.3390/agronomy11102055.
- Daly, E.J., and Hernandez-Ramirez, G. 2020. Sources and priming of soil N₂O and CO₂ production: Nitrogen and simulated exudate additions. *Soil Biol Biochem* **149**: 107942. Elsevier Ltd. doi:10.1016/j.soilbio.2020.107942.
- David, C., Lemke, R., Helgason, W., and Farrell, R.E. 2018. Current inventory approach overestimates the effect of irrigated crop management on soil-derived greenhouse gas emissions in the semi-arid Canadian Prairies. *Agric Water Manag* **208**: 19–32. Elsevier. doi:10.1016/j.agwat.2018.06.006.
- Djaman, K., Irmak, S., Martin, D.L., Ferguson, R.B., and Bernards, M.L. 2013. Plant nutrient uptake and soil nutrient dynamics under full and limited irrigation and rainfed maize production. *Agron J* **105**: 527–538. doi:10.2134/agronj2012.0269.
- Drury, C.F., Reynolds, W.D., Yang, X.M., McLaughlin, N.B., Welacky, T.W., Calder, W., and Grant, C.A. 2012. Nitrogen Source, Application Time, and Tillage Effects on Soil Nitrous Oxide Emissions and Corn Grain Yields. *Soil Science Society of America Journal* **76**: 1268–1279. Wiley. doi:10.2136/sssaj2011.0249.
- Environment and Climate Change Canada 2022. National Inventory Report 1990–2022: Greenhouse Gas Sources and Sinks in Canada.
- Fan, J., McConkey, B., Wang, H., and Janzen, H. 2016. Root distribution by depth for temperate agricultural crops. *Field Crops Res* **189**: 68–74. Elsevier B.V. doi:10.1016/j.fcr.2016.02.013.
- Feng, J., Li, F., Deng, A., Feng, X., Fang, F., and Zhang, W. 2016. Integrated assessment of the impact of enhanced-efficiency nitrogen fertilizer on N₂O emission and crop yield. *Agric Ecosyst Environ* **231**: 218–228. Elsevier B.V. doi:10.1016/j.agee.2016.06.038.
- Forster, P., Ramaswamy, P.A., Berntsen, T., R, B., Fahey, D.W., and J, H. 2007. Changes in Atmospheric Constituents and in Radiative Forcing. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*.
- Gagnon, B., Ziadi, N., and Grant, C. 2012. Urea fertilizer forms affect grain corn yield and nitrogen use efficiency. *Can J Soil Sci* **92**: 341–351. doi:10.4141/cjss2011-074.
- Gagnon, B., Ziadi, N., Rochette, P., Chantigny, M.H., and Angers, D.A. 2011. Fertilizer Source Influenced Nitrous Oxide Emissions from a Clay Soil under Corn. *Soil Science Society of America Journal* **75**: 595–604. Wiley. doi:10.2136/sssaj2010.0212.
- Golden, B., Slaton, N., Norman, R., Gbur, E., and Wilson, C. 2011. Nitrogen release from environmentally smart nitrogen fertilizer as influenced by soil series, temperature, moisture, and incubation method. *Commun Soil Sci Plant Anal* **42**: 1809–1824. doi:10.1080/00103624.2011.587568.
- Grant, C., and Wu, R. 2008. Enhanced-Efficiency Fertilizers for Use on the Canadian Prairies. *Crop Management* **7**: 1–15. American Society of Agronomy. doi:10.1094/cm-2008-0730-01-rv.
- Grant, C.A., Wu, R., Selles, F., Harker, K.N., Clayton, G.W., Bittman, S., Zebarth, B.J., and Lupwayi, N.Z. 2012. Crop yield and nitrogen concentration with controlled release urea and split applications of nitrogen as compared to non-coated urea applied at seeding. *Field Crops Res* **127**: 170–180. doi:10.1016/j.fcr.2011.11.002.
- Grant, R. 2001. A Review of the Canadian Ecosystem Model - ecosys. Pages 173–263 *in* M. Shaffer, L. Ma, and S. Hansen, eds. *Modeling Carbon and Nitrogen Dynamics for Soil Management*. CRC Press, Boca Raton, Florida.

- Grant, R.F., Dyck, M., and Puurveen, D. 2020. Nitrogen and phosphorus control carbon sequestration in agricultural ecosystems: Modelling carbon, nitrogen, and phosphorus balances at the breton plots with ecosys under historical and future climates¹. *Can J Soil Sci* **100**: 408–429. Agricultural Institute of Canada. doi:10.1139/cjss-2019-0132.
- Grant, R.F., Juma, N.G., Robertson, J.A., Izaurrealde, R.C., and McGill, W.B. 2001. Long-Term Changes in Soil Carbon under Different Fertilizer, Manure, and Rotation. *Soil Science Society of America Journal* **65**: 205–214. Wiley. doi:10.2136/sssaj2001.651205x.
- Grant, R.F., Pattey, E., Goddard, T.W., Kryzanowski, L.M., and Puurveen, H. 2006. Modeling the Effects of Fertilizer Application Rate on Nitrous Oxide Emissions. *Soil Science Society of America Journal* **70**: 235–248. Wiley. doi:10.2136/sssaj2005.0104.
- Van Groenigen, J.W., Velthof, G.L., Oenema, O., Van Groenigen, K.J., and Van Kessel, C. 2010. Towards an agronomic assessment of N₂O emissions: a case study for arable crops. *Eur J Soil Sci* **61**: 903–913. doi:10.1111/j.1365-2389.2009.01217.x.
- Guo, J., Fan, J., Xiang, Y., Zhang, F., Yan, S., Zhang, X., Zheng, J., Li, Y., Tang, Z., and Li, Z. 2022. Coupling effects of irrigation amount and nitrogen fertilizer type on grain yield, water productivity and nitrogen use efficiency of drip-irrigated maize. *Agric Water Manag* **261**. Elsevier B.V. doi:10.1016/j.agwat.2021.107389.
- Halvorson, A.D., Snyder, C.S., Blaylock, A.D., and Del Grosso, S.J. 2014. Enhanced-efficiency nitrogen fertilizers: Potential role in nitrous oxide emission mitigation. *Agron J* **106**: 715–722. doi:10.2134/agronj2013.0081.
- Hao, X., Chang, C., Carefoot, J.M., Janzen, H.H., and Ellert, B.H. 2001. Nitrous oxide emissions from an irrigated soil as affected by fertilizer and straw management. *Nutr Cycl Agroecosyst* **60**: 1–8. doi:10.1023/A:1012603732435.
- He, W., Yang, J.Y., Zhou, W., Drury, C.F., Yang, X.M., Reynolds, W.D., Wang, H., He, P., and Li, Z.T. 2016. Sensitivity analysis of crop yields, soil water contents and nitrogen leaching to precipitation, management practices and soil hydraulic properties in semi-arid and humid regions of Canada using the DSSAT model. *Nutr Cycl Agroecosyst* **106**: 201–215. Springer Netherlands. doi:10.1007/s10705-016-9800-3.
- Hergoualc’h, K., Akiyama, H., Bernoux, M., Chirinda, N., del Prado, A., Kasimir, A., Douglas MacDonald, J., Michael Ogle, S., Regina, K., van der Weerden, T.J., Liang, C., and Noble, A. 2019. Chapter 11: N₂O Emissions from Managed Soils, and CO₂ Emissions from Lime and Urea Application.
- John, A.A., Jones, C.A., Ewing, S.A., Sigler, W.A., Bekkerman, A., and Miller, P.R. 2017. Fallow replacement and alternative nitrogen management for reducing nitrate leaching in a semiarid region. *Nutr Cycl Agroecosyst* **108**: 279–296. Springer Netherlands. doi:10.1007/s10705-017-9855-9.
- Kaiser, E.-A., Kohrs, K., Kücke, M., Schnug, E., Heinemeyer, O., and Munch, J.C. 1998. Nitrous oxide release from arable soil: Importance of N-fertilization, crops and temporal variation. *Soil Biol Biochem* **30**: 1553–1563. doi:10.1016/S0038-0717(98)00036-4.
- Karimi, R., Pogue, S.J., Kröbel, R., Beauchemin, K.A., Schwinghamer, T., and Henry Janzen, H. 2020. An updated nitrogen budget for Canadian agroecosystems. *Agric Ecosyst Environ* **304**. Elsevier B.V. doi:10.1016/j.agee.2020.107046.
- Kim, D.G., Hernandez-Ramirez, G., and Giltrap, D. 2013. Linear and nonlinear dependency of direct nitrous oxide emissions on fertilizer nitrogen input: A meta-analysis. *Agric Ecosyst Environ* **168**: 53–65. doi:10.1016/j.agee.2012.02.021.

- Kryzanowski, L., McKenzie, R., Middleton, A., Sprout, C., Henriquez, B., and O'Donovan, J. 2009. Enabling Adoption of Environmentally Smart Nitrogen (ESN) Technology to Maximize Economic Returns and Environmental Benefits in Alberta Progress Report.
- Li, C., Hao, X., Blackshaw, R.E., Clayton, G.W., O'Donovan, J.T., and Harker, K.N. 2016. Nitrous Oxide Emissions in Response to ESN and Urea Application in a No-Till Barley Cropping System. *Commun Soil Sci Plant Anal* **47**: 692–705. Taylor & Francis. doi:10.1080/00103624.2016.1146745.
- Li, C., Hao, X., Blackshaw, R.E., O'Donovan, J.T., Harker, K.N., and Clayton, G.W. 2012. Nitrous oxide emissions in response to ESN and urea, herbicide management and canola cultivar in a no-till cropping system. *Soil Tillage Res* **118**: 97–106. Elsevier B.V. doi:10.1016/j.still.2011.10.017.
- Li, T., Zhang, W., Yin, J., Chadwick, D., Norse, D., Lu, Y., Liu, X., Chen, X., Zhang, F., Powlson, D., and Dou, Z. 2018. Enhanced-efficiency fertilizers are not a panacea for resolving the nitrogen problem. *Glob Chang Biol* **24**: e511–e521. Blackwell Publishing Ltd. doi:10.1111/gcb.13918.
- Liang, C., MacDonald, D., Thiagarajan, A., Flemming, C., Cerkowniak, D., and Desjardins, R. 2020. Developing a country specific method for estimating nitrous oxide emissions from agricultural soils in Canada. *Nutr Cycl Agroecosyst* **117**: 145–167. Springer. doi:10.1007/s10705-020-10058-w.
- Mahal, N.K., Osterholz, W.R., Miguez, F.E., Poffenbarger, H.J., Sawyer, J.E., Olk, D.C., Archontoulis, S. V., and Castellano, M.J. 2019. Nitrogen Fertilizer Suppresses Mineralization of Soil Organic Matter in Maize Agroecosystems. *Front Ecol Evol* **7**. Frontiers Media S.A. doi:10.3389/fevo.2019.00059.
- Maharjan, B., Venterea, R.T., and Rosen, C. 2014. Fertilizer and irrigation management effects on nitrous oxide emissions and nitrate leaching. *Agron J* **106**: 703–714. doi:10.2134/agronj2013.0179.
- Malhi, S.S., Grant, C.A., Johnston, A.M., and Gill, K.S. 2001. Nitrogen fertilization management for no-till cereal production in the Canadian Great Plains: a review. *Soil Tillage Res* **60**: 101–122. doi:10.1016/S0167-1987(01)00176-3.
- Malhi, S.S., Soon, Y.K., Grant, C.A., Lemke, R., Lupwayi, N., and Lemke, C.A. 2010. Influence of controlled-release urea on seed yield and N concentration, and N use efficiency of small grain crops grown on Dark Gray Luvisols. *Can J Soil Sci* **90**: 363–372. doi:10.4141/CJSS09102.
- Mathers, A.C., Stewart, B.A., and Blair, B. 1975. Nitrate-nitrogen Removal from Soil Profiles by Alfalfa. *J Environ Qual* **4**: 403–405. Wiley. doi:10.2134/jeq1975.00472425000400030026x.
- Metivier, K.A., Pattey, E., and Grant, R.F. 2009. Using the ecosys mathematical model to simulate temporal variability of nitrous oxide emissions from a fertilized agricultural soil. *Soil Biol Biochem* **41**: 2370–2386. Elsevier Ltd. doi:10.1016/j.soilbio.2009.03.007.
- Mezbahuddin, S., Spiess, D., Hildebrand, D., Kryzanowski, L., Itenfisu, D., Goddard, T., Iqbal, J., and Grant, R. 2020. Assessing Effects of Agronomic Nitrogen Management on Crop Nitrogen Use and Nitrogen Losses in the Western Canadian Prairies. *Front Sustain Food Syst* **4**: 1–21. doi:10.3389/fsufs.2020.512292.
- Nelson, K.A., Motavalli, P.P., and Dudenhoefter, C.J. 2014. Cropping System Affects Polymer-Coated Urea Release and Corn Yield Response in Claypan Soils. *J Agron Crop Sci* **200**: 54–65. doi:10.1111/jac.12040.
- Nelson, K.A., Scharf, P.C., Bundy, L.G., and Tracy, P. 2008. Agricultural Management of Enhanced-Efficiency Fertilizers in the North-Central United States. *Crop Management* **7**: 1–12. doi:10.1094/cm-2008-0730-03-rv.
- Nyborg, M., Laidlaw, J.W., Solberg, E.D., and Malhi, S.S. 1997. Denitrification and nitrous oxide emissions from a Black Chernozemic soil during spring thaw in Alberta.

- Omonode, R.A., Halvorson, A.D., Gagnon, B., and Vyn, T.J. 2017. Achieving lower nitrogen balance and higher nitrogen recovery efficiency reduces nitrous oxide emissions in North America's maize cropping systems. *Front Plant Sci* **8**. Frontiers Media S.A. doi:10.3389/fpls.2017.01080.
- Puntel, L.A., Sawyer, J.E., Barker, D.W., Dietzel, R., Poffenbarger, H., Castellano, M.J., Moore, K.J., Thorburn, P., and Archontoulis, S. V. 2016. Modeling long-term corn yield response to nitrogen rate and crop rotation. *Front Plant Sci* **7**. Frontiers Research Foundation. doi:10.3389/fpls.2016.01630.
- Ransom, C.J., Jolley, V.D., Blair, T.A., Sutton, L.E., and Hopkins, B.G. 2020. Nitrogen release rates from slow- And controlled-release fertilizers influenced by placement and temperature. *PLoS One* **15**: 1–21. doi:10.1371/journal.pone.0234544.
- Rochette, P., Liang, C., Pelster, D., Bergeron, O., Lemke, R., Kroebel, R., MacDonald, D., Yan, W., and Flemming, C. 2018. Soil nitrous oxide emissions from agricultural soils in Canada: Exploring relationships with soil, crop and climatic variables. *Agric Ecosyst Environ* **254**: 69–81. Elsevier B.V. doi:10.1016/j.agee.2017.10.021.
- Rochette, P., Worth, D.E., Lemke, R.L., McConkey, B.G., Pennock, D.J., Wagner-Riddle, C., and Desjardins, R.L. 2008. Estimation of N₂O emissions from agricultural soils in Canada. I. Development of a country-specific methodology. *Can J Soil Sci* **88**: 641–654. doi:10.4141/CJSS07025.
- Sainju, U.M. 2017. Determination of nitrogen balance in agroecosystems. *MethodsX* **4**: 199–208. Elsevier B.V. doi:10.1016/j.mex.2017.06.001.
- Saxton, K.E., and Rawls, W.J. 2006. Soil Water Characteristic Estimates by Texture and Organic Matter for Hydrologic Solutions. *Soil Science Society of America Journal* **70**: 1569–1578. Wiley. doi:10.2136/sssaj2005.0117.
- Setiyono, T.D., Yang, H., Walters, D.T., Dobermann, A., Ferguson, R.B., Roberts, D.F., Lyon, D.J., Clay, D.E., and Cassman, K.G. 2011. Maize-N: A decision tool for nitrogen management in maize. *Agron J* **103**: 1276–1283. doi:10.2134/agronj2011.0053.
- Sheppard, S.C., Bittman, S., and Bruulsema, T.W. 2010. Monthly ammonia emissions from fertilizers in 12 Canadian Ecoregions. *Can J Soil Sci* **90**: 113–127. doi:10.4141/CJSS09006.
- Snyder, C.S., Bruulsema, T.W., Jensen, T.L., and Fixen, P.E. 2009. Review of greenhouse gas emissions from crop production systems and fertilizer management effects. *Agric Ecosyst Environ* **133**: 247–266. San Jose. doi:10.1016/j.agee.2009.04.021.
- Soon, Y.K., Malhi, S.S., Lemke, R.L., Lupwayi, N.Z., and Grant, C.A. 2011. Effect of polymer-coated urea and tillage on the dynamics of available N and nitrous oxide emission from Gray Luvisols. *Nutr Cycl Agroecosyst* **90**: 267–279. doi:10.1007/s10705-011-9428-2.
- Stanford, G., Dzienia, S., and Vander Pol, R.A. 1975. Effect of Temperature on Denitrification Rate in Soils. *Soil Science Society of America Journal* **39**: 867–870. Wiley. doi:10.2136/sssaj1975.03615995003900050024x.
- Statistics Canada 2022. September 29. 2016 Census of Agriculture. [Online] Available: <https://www.statcan.gc.ca/en/ca2016> [2022 Nov. 12].
- Steffen, W., Richardson, K., Rockström, J., Cornell, S.E., Fetzer, I., Bennett, E.M., Biggs, R., Carpenter, S.R., De Vries, W., De Wit, C.A., Folke, C., Gerten, D., Heinke, J., Mace, G.M., Persson, L.M., Ramanathan, V., Reyers, B., and Sörlin, S. 2015. Planetary boundaries: Guiding human development on a changing planet. *Science (1979)* **347**. American Association for the Advancement of Science. doi:10.1126/science.1259855.
- Stewart, W.M., Dibb, D.W., Johnston, A.E., and Smyth, T.J. 2005. The contribution of commercial fertilizer nutrients to food production. *Agron J* **97**: 1–6. American Society of Agronomy. doi:10.2134/agronj2005.0001.

- Thapa, R., Chatterjee, A., Awale, R., McGranahan, D.A., and Daigh, A. 2016. Effect of Enhanced Efficiency Fertilizers on Nitrous Oxide Emissions and Crop Yields: A Meta-analysis. *Soil Science Society of America Journal* **80**: 1121–1134. doi:10.2136/sssaj2016.06.0179.
- Thilakarathna, S.K., Hernandez-Ramirez, G., Puurveen, D., Kryzanowski, L., Lohstraeter, G., Powers, L.A., Quan, N., and Tenuta, M. 2020. Nitrous oxide emissions and nitrogen use efficiency in wheat: Nitrogen fertilization timing and formulation, soil nitrogen, and weather effects. *Soil Science Society of America Journal* **84**: 1910–1927. John Wiley and Sons Inc. doi:10.1002/saj2.20145.
- Ti, C., Xia, L., Chang, S.X., and Yan, X. 2019. Potential for mitigating global agricultural ammonia emission: A meta-analysis. *Environmental Pollution* **245**: 141–148. Elsevier Ltd. doi:10.1016/j.envpol.2018.10.124.
- Udvardi, M., Below, F.E., Castellano, M.J., Eagle, A.J., Giller, K.E., Ladha, J.K., Liu, X., Maaz, T.M.C., Nova-Franco, B., Raghuram, N., Robertson, G.P., Roy, S., Saha, M., Schmidt, S., Tegeder, M., York, L.M., and Peters, J.W. 2021. May 31. A Research Road Map for Responsible Use of Agricultural Nitrogen. *Frontiers Media S.A.* doi:10.3389/fsufs.2021.660155.
- United Nations Environment Programme 2014. *UNEP Year Book 2014 Emerging Issues in our Global Environment*. [Online] Available: <https://www.unep.org/resources/year-books> [2022 Jan. 9].
- Venterea, R.T., Halvorson, A.D., Kitchen, N., Liebig, M.A., Cavigelli, M.A., Grosso, S.J. Del, Motavalli, P.P., Nelson, K.A., Spokas, K.A., Singh, B.P., Stewart, C.E., Ranaivoson, A., Stroock, J., and Collins, H. 2012. Challenges and opportunities for mitigating nitrous oxide emissions from fertilized cropping systems. *Front Ecol Environ* **10**: 562–570. doi:10.1890/120062.
- Venterea, R.T., Maharjan, B., and Dolan, M.S. 2011. Fertilizer Source and Tillage Effects on Yield-Scaled Nitrous Oxide Emissions in a Corn Cropping System. *J Environ Qual* **40**: 1521–1531. Wiley. doi:10.2134/jeq2011.0039.
- Wilson, M.L., Rosen, C.J., and Moncrief, J.F. 2010. Effects of Polymer-coated Urea on Nitrate Leaching and Nitrogen Uptake by Potato. *J Environ Qual* **39**: 492–499. doi:10.2134/jeq2009.0265.
- Yang, J.Y., Drury, C.F., Jiang, R., Yang, X.M., Worth, D.E., Bittman, S., Grant, B.B., Smith, W.N., and Reid, K. 2023. Simulating nitrogen balance in Canadian agricultural soils from 1981 to 2016. *J Environ Manage* **341**: 118015. doi:10.1016/j.jenvman.2023.118015.
- Yang, M., Zhu, X., Bai, Y., Sun, D., Zou, H., Fang, Y., and Zhang, Y. 2021. Coated controlled-release urea creates a win-win scenario for producing more staple grains and resolving N loss dilemma worldwide. *J Clean Prod* **288**. Elsevier Ltd. doi:10.1016/j.jclepro.2020.125660.
- Zebarth, B.J., Drury, C.F., Tremblay, N., and Cambouris, A.N. 2009. Opportunities for improved fertilizer nitrogen management in production of arable crops in eastern Canada: A review. *Can J Soil Sci* **89**: 113–132. doi:10.4141/CJSS07102.
- Zebarth, B.J., Rochette, P., and Burton, D.L. 2008. N₂O emissions from spring barley production as influenced by fertilizer nitrogen rate. *Can J Soil Sci* **88**: 197–205. doi:10.4141/CJSS06006.
- Zhang, W., Liang, Z., He, X., Wang, X., Shi, X., Zou, C., and Chen, X. 2019. The effects of controlled release urea on maize productivity and reactive nitrogen losses: A meta-analysis. *Environmental Pollution* **246**: 559–565. Elsevier Ltd. doi:10.1016/j.envpol.2018.12.059.

3.7 Tables

Table 3-1. Monthly mean air temperature (°C) for the growing season (May – September), mean annual temperature (°C)(MAT) for 2008 – 2011, monthly total precipitation (mm) for the growing season (May – September) and total annual precipitation (mm) for 2008 – 2011 at Lethbridge, Alberta compared to the 30-year climate normal (1971 – 2000) (ACIS 2021). Monthly irrigation amounts (mm) for the growing season (May – September), and total growing season irrigation + precipitation for 2008 – 2011 at the irrigated site in Lethbridge, Alberta (Kryzanowski et al. 2009).

<u>Mean Air Temperature (°C)</u>						<u>Total Precipitation (mm)</u>						<u>Total Irrigation (Irrigated Site Only)</u>				
Month(s)	2008	2009	2010	2011	30 Year Climate Normal (1971-2000)	Month(s)	2008	2009	2010	2011	30 Year Climate Normal (1971 - 2000)	Month(s)	2008	2009	2010	2011
May	11.4	10.9	8.1	9.8	11.4	May	70.9	29.0	114.8	87.6	48.3	May	-	24.0	-	-
June	14.4	14.0	14.3	13.9	15.6	June	88.3	57.1	127.8	76.4	53.0	June	47.5	40.4	-	-
July	17.0	16.8	16.9	17.7	18.2	July	84.7	42.0	43.6	42.0	37.2	July	89.4	143.9	63	36.4
August	16.6	15.9	15.5	17.5	17.7	August	28.6	81.2	65.8	33.9	47.4	August	45.3	-	-	40.6
September	11.5	15.4	10.5	15.1	12.3	September	60.4	6.4	41.2	11.3	38.3	September	-	-	-	-
May - September	14.2	14.6	13.1	14.8	15.0	May - September	332.9	215.7	393.2	251.2	224.2	May - September	182.2	208.3	63	77
Mean Annual Air Temperature	5.4	5.0	5.2	5.3	5.8	Total Annual Precipitation	419	341.5	560.6	440.4	365	Total Growing Season Irrigation + Precipitation	515.1	424	456.2	328.2

Table 3-2. Model inputs for the soil properties at Lethbridge, Alberta obtained from field and laboratory measurements (Kryzanowski et al. 2009). *Estimated from Saxton and Rawls (2006).

Depth (m)	0.01	0.05	0.10	0.15	0.30	0.45	0.60	0.90	1.20	2.00
Bulk Density (Mg m ⁻³)	1.4	1.4	1.4	1.41	1.42	1.42	1.49	1.49	1.5	1.5
Field Capacity (m ³ m ⁻³)*	0.293	0.293	0.293	0.288	0.29	0.29	0.282	0.282	0.27	0.27
Wilting Point (m ³ m ⁻³)*	0.157	0.157	0.157	0.155	0.159	0.159	0.156	0.156	0.13	0.13
Saturated Hydraulic Conductivity (mm hr ⁻¹)*	16.65	16.65	16.65	13.83	9.78	9.78	8.99	8.99	5.4	5.4
Sand Content (kg kg ⁻¹)	456	456	456	450	442	442	452	452	410	410
Silt Content (kg kg ⁻¹)	318	318	318	320	310	310	302	302	370	370
Clay Content (kg kg ⁻¹)	226	226	226	230	248	248	246	246	220	220
pH	8.15	8.15	8.15	8.08	7.93	7.93	7.95	7.95	7.5	7.5
Cation Exchange Capacity (CEC) (cmol kg ⁻¹)	25.5	25.5	25.5	24.4	24.4	24.1	23	23	11	11
Anion Exchange Capacity (AEC) (cmol kg ⁻¹)	3	3	3	3	3	3	3	3	3	3
Organic Carbon (g kg ⁻¹)	21.5	21.5	21.5	17.3	12.4	12.4	9.4	9.4	0.7	0
Organic Nitrogen (g Mg ⁻¹)	1933	1933	1933	1557	1115	1115	850	850	70	0
Organic Phosphorus (g Mg ⁻¹)	213	213	213	171	123	123	93	93	7	0
NO ₃ -N (g Mg ⁻¹)	8.25	8.25	8.25	6.5	1.75	1.75	4.25	4.25	0	0
NH ₄ -N (g Mg ⁻¹)	3.6	3.6	3.6	2.53	2.08	2.08	2.9	2.9	0	0
Exchangeable PO ₄ -P (g Mg ⁻¹)	35.25	35.25	35.25	17.5	5.75	5.75	5.5	5.5	2	2
K (g Mg ⁻¹)	460.5	460.5	460.5	373.75	340	340	248	248	3.9	3.9
SO ₄ -S (g Mg ⁻¹)	18.75	18.75	18.75	62.75	200	200	200	200	48	48

Table 3-3. Average N budgets (kg N ha⁻¹ year⁻¹) from modelled outputs over a 4-year period (2008 – 2011) for N rates (0, 30, 60, 90, and 120 kg N ha⁻¹), and N sources (Control (0 kg N ha⁻¹), Urea, ESN), at dryland and irrigated sites in Lethbridge, Alberta. The change in N stocks is the gain (positive) or loss (negative) at the year's end compared to the year's beginning. Modelled gaseous and aqueous N₂O and N₂ gases within the soil profile were not included in the stock changes, likely resulting in negative N budget balances.

Year	2008 - 2011																							
	Site	Dryland								Irrigated														
Nitrogen Source		Control				ESN				Urea				Control				ESN				Urea		
Nitrogen Rate	0	30	60	90	120	30	60	90	120	0	30	60	90	120	30	60	90	120						
Change in Stocks																								
Change in SON	-70.68	-59.09	-53.05	-48.68	-46.41	-58.30	-51.09	-46.94	-44.50	-69.03	-55.22	-47.20	-41.32	-38.56	-54.12	-45.67	-39.14	-36.23						
Change NO ₃ ⁻	-11.51	-21.44	-9.16	9.08	30.59	-22.83	-11.64	5.96	27.00	-9.74	-23.25	-15.49	-0.74	19.26	-24.39	-17.47	-3.70	15.37						
Change NH ₄ ⁺	22.15	25.32	26.39	27.24	27.67	25.84	26.87	27.63	28.10	21.50	22.89	23.02	23.15	23.28	23.13	23.36	23.60	23.83						
Fluxes In (Negative)																								
N ₂ fixation	-0.23	-0.19	-0.19	-0.19	-0.19	-0.21	-0.20	-0.19	-0.19	-0.27	-0.28	-0.27	-0.27	-0.27	-0.29	-0.27	-0.28	-0.27						
N in Seed	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30	-3.30						
N from Deposition	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43	-2.43						
Fertilizer N	0.00	-30.00	-60.00	-90.00	-120.00	-30.00	-60.00	-90.00	-120.00	0.00	-30.00	-60.00	-90.00	-120.00	-30.00	-60.00	-90.00	-120.00						
Fluxes Out (Positive)																								
Subsurface Flux	5.43	7.40	7.37	7.36	7.36	7.39	7.36	7.35	7.35	10.02	12.76	12.59	12.57	12.56	12.73	12.56	12.55	12.54						
Surface Flux	0.16	0.17	0.17	0.18	0.17	0.17	0.17	0.17	0.17	0.14	0.15	0.14	0.14	0.15	0.15	0.14	0.14	0.14						
N ₂ O Flux	0.21	0.31	0.37	0.43	0.48	0.31	0.37	0.42	0.48	0.18	0.25	0.31	0.36	0.41	0.25	0.30	0.35	0.40						
NH ₃ Flux	4.79	5.61	5.88	6.10	6.18	5.66	5.93	6.08	6.18	3.25	3.57	3.65	3.72	3.75	3.57	3.65	3.72	3.76						
N ₂ Flux	0.22	0.27	0.28	0.28	0.29	0.27	0.27	0.27	0.28	0.21	0.27	0.29	0.30	0.30	0.27	0.29	0.30	0.30						
Removal in Grain N	55.04	77.23	87.36	92.93	96.82	77.30	87.40	94.14	98.46	49.31	74.48	88.60	97.71	104.66	74.30	88.75	98.09	105.71						
Total	-0.13	-0.13	-0.31	-1.00	-2.76	-0.12	-0.28	-0.82	-2.38	-0.16	-0.11	-0.08	-0.09	-0.18	-0.11	-0.08	-0.08	-0.17						

*SON = soil organic nitrogen

Table 3-4. Measured annual N₂O emissions based on linear interpolation (Kryzanowski et al. 2009) (standard deviations presented in brackets), and modelled annual N₂O-N emissions (kg N ha⁻¹), measured and modelled area-based emission factors (% kg N₂O-N kg⁻¹ N Fertilizer), and measured and modelled yield-based emission intensities (g N₂O-N kg⁻¹ Grain Yield Dry Matter (DM)) for N rates (0, 60, and 120 kg N ha⁻¹), and N sources (Control (0 kg N ha⁻¹), Urea, ESN), at the irrigated site in Lethbridge, Alberta for 2008 – 2011.

Year	N Amount (kg N ha ⁻¹)	N Source	Measured Annual N ₂ O-N Emissions (kg N ha ⁻¹)	Modelled Annual N ₂ O-N Emissions (kg N ha ⁻¹)	Measured EF Area (% kg N ₂ O-N kg ⁻¹ N Fertilizer)	Modelled EF Area (% kg N ₂ O-N kg ⁻¹ N Fertilizer)	Measured Yield Based Emissions Intensity (g N ₂ O-N kg ⁻¹ Grain Yield DM)	Modelled Yield Based Emissions Intensity (g N ₂ O-N kg ⁻¹ Grain Yield DM)
2008	0	Control	0.17 (0.03)	0.26	–	–	0.036	0.084
	60	ESN	0.34 (0.03)	0.40	0.29	0.24	0.054	0.062
	60	Urea	0.23 (0.03)	0.40	0.10	0.23	0.036	0.062
	120	ESN	0.41 (0.03)	0.51	0.20	0.22	0.056	0.071
	120	Urea	0.26 (0.03)	0.51	0.08	0.21	0.038	0.071
2009	0	Control	0.18 (0.03)	0.15	–	–	0.035	0.037
	60	ESN	0.33 (0.03)	0.27	0.26	0.21	0.053	0.036
	60	Urea	0.32 (0.03)	0.27	0.24	0.20	0.049	0.035
	120	ESN	0.57 (0.03)	0.36	0.33	0.18	0.080	0.045
	120	Urea	0.58 (0.05)	0.36	0.34	0.17	0.086	0.044
2010	0	Control	0.19 (0.09)	0.13	–	–	0.043	0.047
	60	ESN	0.25 (0.09)	0.25	0.1	0.20	0.047	0.049
	60	Urea	0.41 (0.03)	0.24	0.4	0.20	0.080	0.048
	120	ESN	0.4 (0.09)	0.35	0.2	0.18	0.064	0.058
	120	Urea	1.53 (0.1)	0.34	1.1	0.18	0.260	0.057
2011	0	Control	0.09 (0.01)	0.17	–	–	0.028	0.050
	60	ESN	0.14 (0.01)	0.31	0.09	0.22	0.031	0.056
	60	Urea	0.21 (0.02)	0.30	0.21	0.22	0.049	0.055
	120	ESN	0.29 (0.02)	0.40	0.17	0.19	0.050	0.065
	120	Urea	0.36 (0.04)	0.40	0.23	0.19	0.065	0.064

Table 3-5. Annual modelled subsurface N, surface N, N₂O-N, NH₃-N, and N₂ losses (kg N ha⁻¹ year⁻¹) for N rates (0, 30, 60, 90, and 120 kg N ha⁻¹), and N sources (Control (0 kg N ha⁻¹), Urea, ESN), at dryland and irrigated sites for 2008 – 2011 in Lethbridge, Alberta.

N Source	Dryland Site								Irrigated Site									
	Control	ESN				Urea				Control	ESN				Urea			
N Rate (kg N ha ⁻¹)	0	30	60	90	120	30	60	90	120	0	30	60	90	120	30	60	90	120
<i>Subsurface N Flux (kg N ha⁻¹ year⁻¹)</i>																		
2008	0.003	0.003	0.004	0.004	0.004	0.004	0.004	0.004	0.004	4.94	1.38	0.895	0.889	0.886	1.373	0.899	0.892	0.890
2009	1.83	1.85	1.85	1.85	1.85	1.85	1.85	1.85	1.85	4.06	4.98	4.98	4.97	4.97	4.99	4.98	4.98	4.97
2010	14.0	16.8	16.7	16.7	16.7	16.7	16.7	16.6	16.6	22.3	30.2	30.1	30.1	30.0	30.1	30.0	30.0	30.0
2011	5.89	11.0	10.9	10.9	10.9	11.0	10.9	10.9	10.9	8.74	14.5	14.4	14.4	14.4	14.4	14.4	14.3	14.3
<i>Surface N Flux (kg N ha⁻¹ year⁻¹)</i>																		
2008	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2009	0	0	0	0	0	0	0	0	0	0.073	0.060	0.053	0.051	0.050	0.059	0.052	0.049	0.048
2010	0.203	0.249	0.252	0.264	0.256	0.252	0.251	0.254	0.258	0.133	0.179	0.179	0.182	0.204	0.187	0.176	0.180	0.180
2011	0.439	0.439	0.439	0.439	0.439	0.439	0.439	0.439	0.439	0.344	0.344	0.344	0.344	0.344	0.344	0.344	0.344	0.344
<i>N₂O-N Flux (kg N ha⁻¹ year⁻¹)</i>																		
2008	0.350	0.456	0.525	0.596	0.675	0.454	0.522	0.593	0.669	0.256	0.338	0.399	0.461	0.515	0.340	0.397	0.457	0.513
2009	0.139	0.207	0.252	0.295	0.333	0.204	0.248	0.291	0.330	0.148	0.229	0.274	0.315	0.362	0.226	0.270	0.311	0.356
2010	0.204	0.312	0.368	0.428	0.483	0.312	0.364	0.425	0.479	0.125	0.191	0.248	0.302	0.345	0.187	0.243	0.299	0.342
2011	0.163	0.277	0.335	0.384	0.437	0.275	0.332	0.381	0.431	0.173	0.250	0.307	0.354	0.398	0.249	0.304	0.351	0.395
<i>NH₃-N Flux (kg N ha⁻¹ year⁻¹)</i>																		
2008	6.10	6.57	6.70	7.03	7.17	6.59	6.71	7.02	7.13	3.40	3.72	3.75	3.78	3.79	3.72	3.74	3.77	3.80
2009	5.16	6.79	7.37	7.57	7.53	6.92	7.51	7.55	7.59	3.58	3.97	4.07	4.14	4.17	3.98	4.09	4.14	4.16
2010	4.78	5.20	5.24	5.36	5.47	5.20	5.25	5.35	5.47	3.53	3.70	3.75	3.84	3.86	3.70	3.76	3.85	3.89
2011	3.13	3.86	4.21	4.43	4.53	3.93	4.26	4.40	4.54	2.49	2.88	3.04	3.14	3.18	2.89	3.02	3.12	3.21
<i>N₂ Flux (kg N ha⁻¹ year⁻¹)</i>																		
2008	0.413	0.472	0.498	0.503	0.513	0.475	0.479	0.487	0.500	0.360	0.421	0.442	0.466	0.474	0.423	0.440	0.461	0.472
2009	0.168	0.167	0.163	0.164	0.167	0.165	0.161	0.162	0.165	0.174	0.228	0.244	0.253	0.256	0.229	0.244	0.250	0.256
2010	0.163	0.245	0.245	0.250	0.258	0.245	0.244	0.248	0.257	0.136	0.200	0.224	0.240	0.235	0.195	0.220	0.233	0.234
2011	0.140	0.200	0.200	0.203	0.206	0.200	0.199	0.200	0.204	0.187	0.246	0.241	0.244	0.250	0.245	0.238	0.243	0.246

Table 3-6. Modelled N₂O emissions, Area-based emission factors, and yield scaled emissions for direct and direct + indirect N₂O emissions for urea at N rates of 0, 30, 60, 90 and 120 kg N ha⁻¹ at dryland and irrigated sites for 2008 – 2011 at Lethbridge, Alberta. (Results for ESN presented in Supplementary Table 3-3).

Year	Site	N Rate (kg N ha ⁻¹)	Direct N ₂ O emissions (kg N ha ⁻¹ yr ⁻¹)	Area Based Emission Factor (Direct N ₂ O emissions) (% kg N ₂ O-N kg ⁻¹ N Fertilizer)	Yield Scaled N ₂ O emissions (Direct N ₂ O emissions) (g N ₂ O-N kg ⁻¹ Grain Yield DM)	Direct + Indirect N ₂ O emissions (kg N ha ⁻¹ yr ⁻¹)	Area Based Emission Factor (Direct and Indirect N ₂ O emissions) (% kg N ₂ O-N kg ⁻¹ N Fertilizer)	Yield Scaled N ₂ O emissions (Direct and Indirect N ₂ O emissions) (g N ₂ O-N kg ⁻¹ Grain Yield DM)
2008	Dryland	0	0.35	–	0.085	0.41	–	0.100
		30	0.45	0.35	0.083	0.52	0.36	0.095
		60	0.52	0.29	0.082	0.59	0.30	0.093
		90	0.59	0.27	0.086	0.66	0.28	0.097
		120	0.67	0.27	0.093	0.74	0.27	0.103
	Irrigated	0	0.26	–	0.084	0.34	–	0.112
		30	0.34	0.28	0.064	0.39	0.16	0.074
		60	0.40	0.23	0.062	0.44	0.17	0.069
		90	0.46	0.22	0.062	0.50	0.18	0.069
		120	0.51	0.21	0.071	0.56	0.18	0.078
2009	Dryland	0	0.14	–	0.029	0.21	–	0.044
		30	0.20	0.22	0.032	0.29	0.28	0.047
		60	0.25	0.18	0.037	0.34	0.22	0.052
		90	0.29	0.17	0.044	0.39	0.20	0.059
		120	0.33	0.16	0.050	0.43	0.18	0.065
	Irrigated	0	0.15	–	0.037	0.23	–	0.057
		30	0.23	0.26	0.034	0.32	0.31	0.049
		60	0.27	0.20	0.035	0.37	0.23	0.048
		90	0.31	0.18	0.039	0.41	0.20	0.051
		120	0.36	0.17	0.044	0.45	0.19	0.057
2010	Dryland	0	0.20	–	0.067	0.41	–	0.135
		30	0.31	0.36	0.072	0.55	0.48	0.127
		60	0.36	0.27	0.068	0.60	0.33	0.113
		90	0.42	0.25	0.072	0.66	0.29	0.112
		120	0.48	0.23	0.077	0.72	0.26	0.115
	Irrigated	0	0.13	–	0.047	0.41	–	0.155
		30	0.19	0.21	0.047	0.56	0.50	0.140
		60	0.24	0.20	0.048	0.61	0.34	0.122
		90	0.30	0.19	0.053	0.67	0.29	0.118
		120	0.34	0.18	0.057	0.71	0.25	0.119
2011	Dryland	0	0.16	–	0.056	0.26	–	0.091
		30	0.28	0.37	0.052	0.44	0.59	0.083
		60	0.33	0.28	0.056	0.50	0.39	0.084
		90	0.38	0.24	0.060	0.55	0.32	0.087
		120	0.43	0.22	0.066	0.60	0.28	0.093
	Irrigated	0	0.17	–	0.050	0.30	–	0.086
		30	0.25	0.25	0.053	0.44	0.47	0.094
		60	0.30	0.22	0.055	0.50	0.33	0.090
		90	0.35	0.20	0.059	0.54	0.27	0.091
		120	0.40	0.19	0.064	0.59	0.24	0.095

3.8 Figures

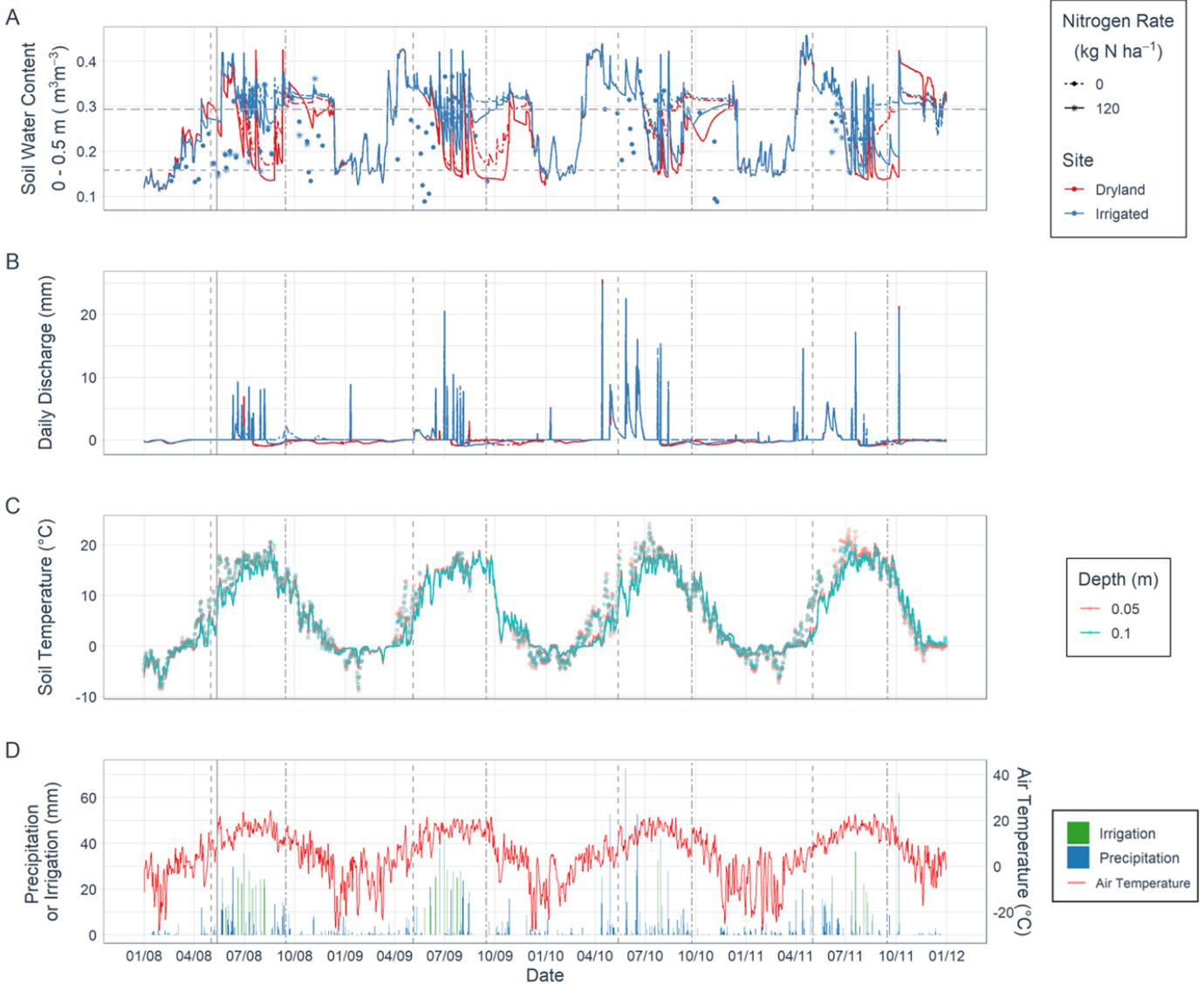


Figure 3-1. A) Modelled (lines) and measured (points) volumetric soil water content ($\text{m}^3 \text{m}^{-3}$) (SWC) for dryland (red) and irrigated (blue) sites at N fertilizer application rates of 0 kg N ha^{-1} (two dashed line, circle symbol) and 120 kg N ha^{-1} (solid line, star symbol) for 2008 – 2011 in Lethbridge, AB. Measured SWC was only available for the irrigated site. The field capacity ($0.293 \text{ m}^3 \text{m}^{-3}$) and wilting point ($0.157 \text{ m}^3 \text{m}^{-3}$) are represented by long dashed and short dashed horizontal lines, respectively. **B)** Modelled daily discharge (mm) for dryland (red) and irrigated (blue) sites at N fertilizer application rates of 0 kg N ha^{-1} (two dashed line) and 120 kg N ha^{-1} (solid line) for 2008 – 2011 in Lethbridge, AB. **C)** Modelled (lines) and measured (points) soil temperature ($^{\circ}\text{C}$) at 0.05 (orange) and 0.1 (green) meters for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. **D)** Daily average air temperature ($^{\circ}\text{C}$) (red line), daily total precipitation (mm) (blue bars), or total daily irrigation (mm) (green bars) for 2008 – 2011 in Lethbridge, Alberta. For all panels, vertical dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). The solid vertical line is the seeding/fertilizer application date for the irrigated site in 2008. Daily average air temperature and total precipitation data were obtained from ACIS (2021) and measured soil moisture, soil temperature, and irrigation data from Kryzanowski et al. (2009).

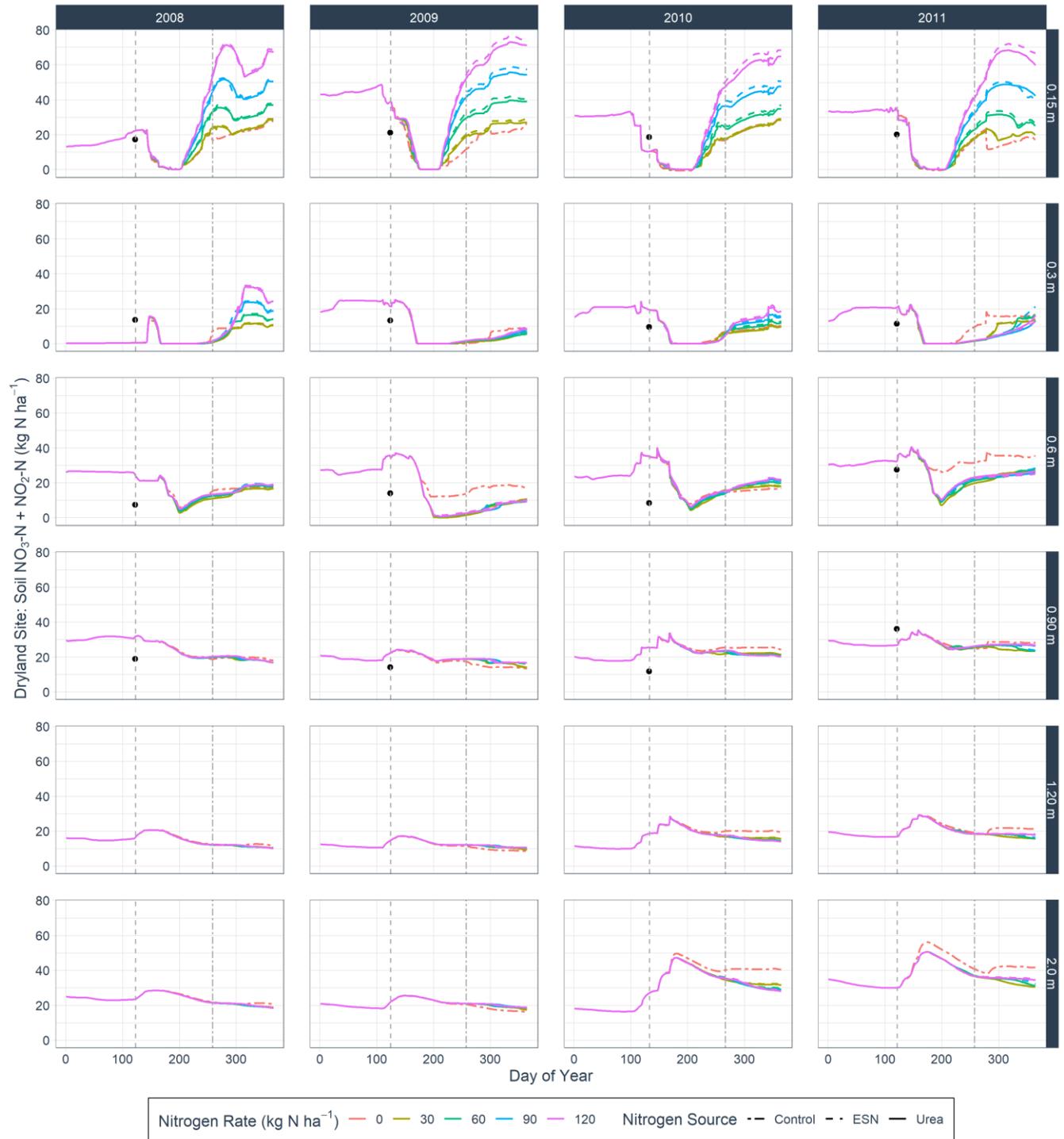


Figure 3-2. Modelled (lines) and measured (points) soil nitrate + nitrite N (kg N ha^{-1}) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at the dryland site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). Measured soil nitrate is obtained from a field experiment by Kryzanowski et al. (2009).

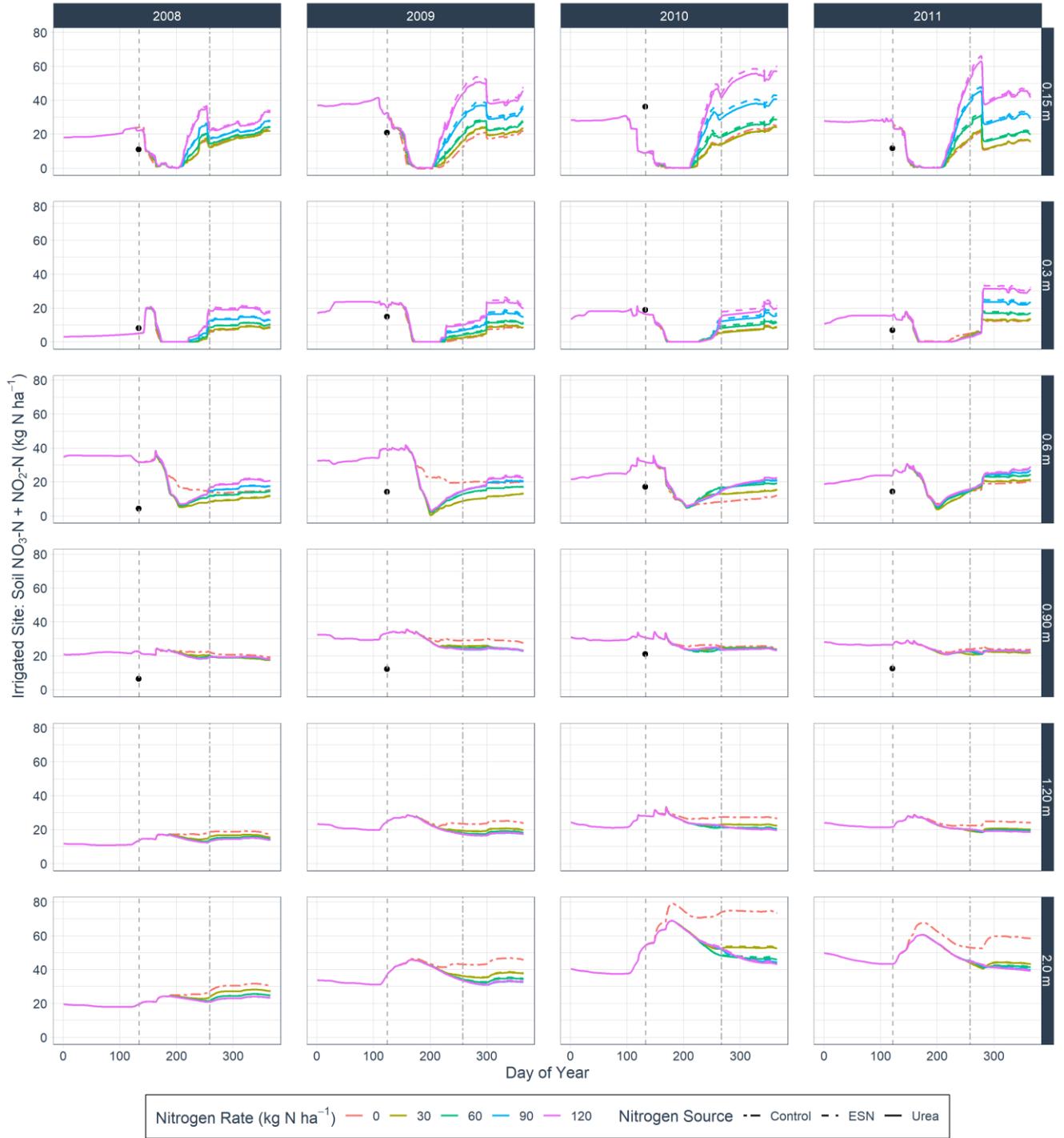


Figure 3-3. Modelled (lines) and measured (points) soil nitrate + nitrite N (kg N ha^{-1}) at different depths in the soil profile (0 – 2.0 meters) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines). Measured soil nitrate is obtained from a field experiment by Kryzanowski et al. (2009).



Figure 3-4. Daily modelled **A)** nitrous oxide-N (N_2O -N) flux, **B)** nitrogen gas (N_2) flux, **C)** ammonium-N (NH_3 -N) flux, **D)** Surface N flux, and **E)** Subsurface N flux ($kg\ N\ ha^{-1}\ d^{-1}$) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) $kg\ N\ ha^{-1}$ for 2008 – 2011 at the dryland site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines).

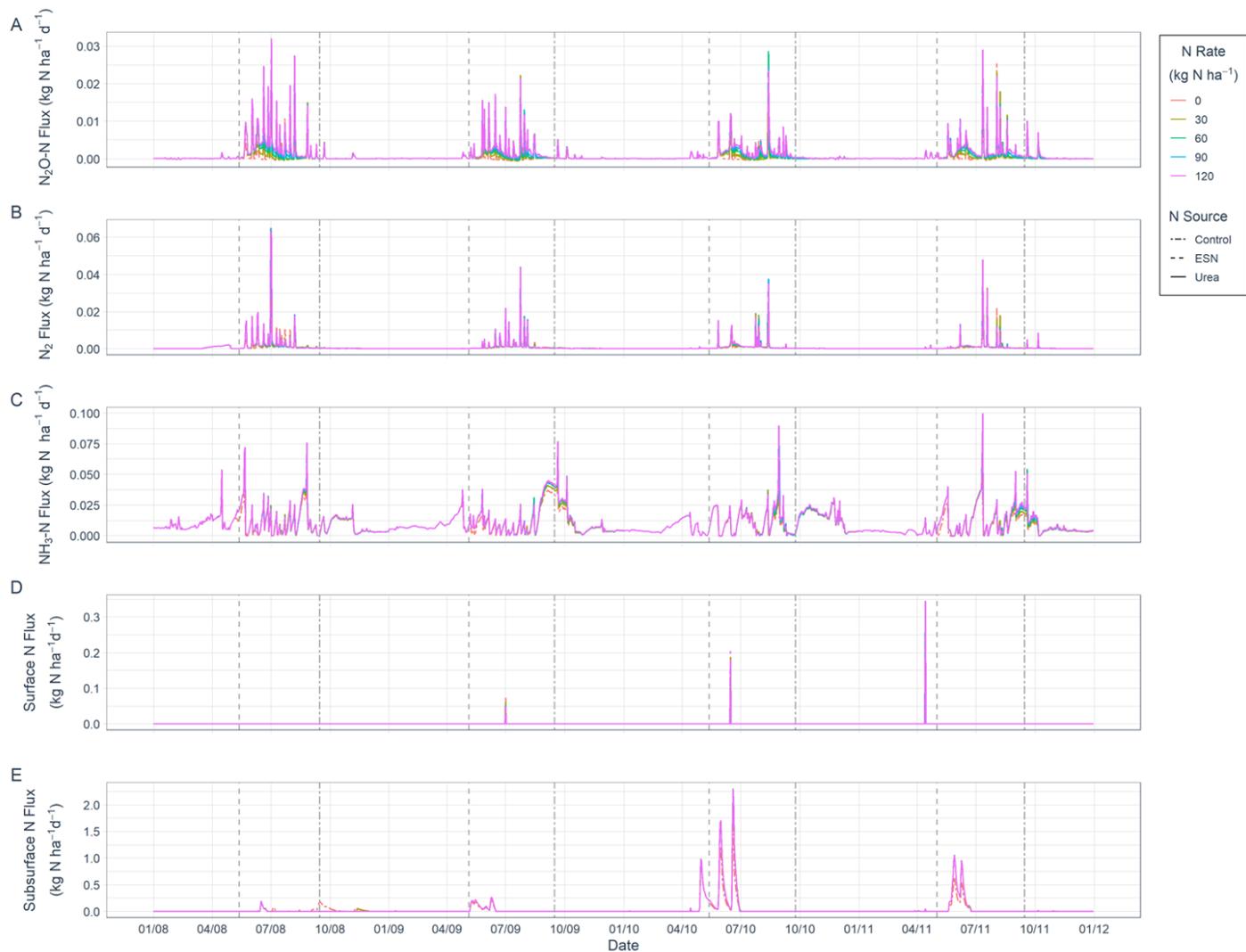


Figure 3-5. Daily modelled **A)** nitrous oxide-N ($\text{N}_2\text{O-N}$) flux, **B)** nitrogen gas (N_2) flux, **C)** ammonium-N ($\text{NH}_3\text{-N}$) flux, **D)** Surface N flux, and **E)** Subsurface N flux ($\text{kg N ha}^{-1} \text{d}^{-1}$) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at the irrigated site in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines).

3.9 Appendix

Supplementary Tables

Supplementary Table 3-1. Irrigation schedule (mm) and total irrigation (mm) for 2008 – 2011 at the irrigated site in Lethbridge, Alberta (Kryzanowski et al. 2009).

Year	Month/Day	DOY	Irrigation (mm)	Total Irrigation (mm)
2008	June 20	172	25	182.2
	June 27	179	22.5	
	July 10	192	25	
	July 15	197	19.5	
	July 18	200	20.5	
	July 31	213	24.4	
	Aug. 7	220	24.5	
Aug. 8	221	20.8		
2009	May 26	146	12	208.3
	May 29	150	12	
	June 5	156	15.4	
	June 15	166	25	
	July 1	182	41.3	
	July 6	187	25	
	July 17	198	27.6	
	July 24	205	25	
July 30	211	25		
2010	July 24	205	32.6	63
	July 29	210	30.4	
2011	July 19	200	36.4	77
	Aug. 3	215	22.2	
	Aug. 8	220	18.4	

Supplementary Table 3-2. Modelled and measured soil ammonium-N (NH₄-N), soil nitrate-N (NO₃-N), and total inorganic N (NH₄-N + NO₃-N) (kg N ha⁻¹) in 0 – 0.15, 0.15 – 0.30, 0.30 – 0.60, and 0.60 – 0.90 meters in the soil profile after spin up but prior to seeding/fertilizer application in 2008 – 2011 at Dryland and Irrigated sites in Lethbridge, Alberta. Measured soil N is obtained from a field experiment by Kryzanowski et al. (2009).

Year	Site	Depth in Soil Profile (m)	Measured Soil NH ₄ -N (kg N ha ⁻¹)	Modelled Soil NH ₄ -N (kg N ha ⁻¹)	Measured Soil NO ₃ -N (kg N ha ⁻¹)	Modelled Soil NO ₃ -N (kg N ha ⁻¹)	Measured Total Inorganic N (NO ₃ -N + NH ₄ -N) (kg N ha ⁻¹)	Modelled Total Inorganic N (NH ₄ -N + NO ₃ -N) (kg N ha ⁻¹)
2008	Dryland	0-0.15	7.6	6.8	17	22.2	24.9	29.0
		0.15-0.30	5.3	2.2	14	0.5	19.1	2.7
		0.30-0.60	8.9	3.8	7	24.1	16.3	27.9
		0.60-0.90	13.0	1.0	19	31.7	32.0	32.7
	Irrigated	0-0.15	7.1	5.0	11	24.0	18.1	29.0
		0.15-0.30	5.6	0.9	8	5.0	13.8	5.9
		0.30-0.60	7.9	1.7	4	31.7	12.1	33.4
		0.60-0.90	12.6	1.0	6	22.3	19.0	23.3
2009	Dryland	0-0.15	5.0	6.1	21	38.8	26.3	44.9
		0.15-0.30	4.4	1.1	13	21.4	17.8	22.5
		0.30-0.60	6.7	1.6	14	34.7	20.8	36.3
		0.60-0.90	12.1	0.9	14	22.5	26.3	23.4
	Irrigated	0-0.15	4.4	5.3	21	32.5	25.4	37.8
		0.15-0.30	3.7	1.3	15	20.2	18.6	21.5
		0.30-0.60	6.2	1.8	14	38.7	20.3	40.5
		0.60-0.90	8.8	0.9	12	33.4	20.9	34.3
2010	Dryland	0-0.15	4.7	6.7	19	10.3	23.2	17.1
		0.15-0.30	5.6	1.4	10	19.5	15.3	20.9
		0.30-0.60	9.5	2.3	9	35.0	18.0	37.3
		0.60-0.90	14.0	1.1	12	25.4	25.8	26.5
	Irrigated	0-0.15	3.7	5.6	36	8.9	40.0	14.5
		0.15-0.30	2.8	1.5	19	16.4	21.7	17.9
		0.30-0.60	4.5	2.2	17	31.6	21.7	33.9
		0.60-0.90	7.1	1.1	21	30.7	28.1	31.7
2011	Dryland	0-0.15	4.0	4.0	20	33.8	24.2	37.8
		0.15-0.30	3.3	1.3	11	20.7	14.7	22.1
		0.30-0.60	4.8	1.9	28	32.8	32.5	34.7
		0.60-0.90	7.4	0.9	36	26.7	43.6	27.6
	Irrigated	0-0.15	3.4	3.4	12	27.0	15.1	30.4
		0.15-0.30	3.5	1.3	7	15.8	10.4	17.0
		0.30-0.60	6.2	1.9	14	24.4	20.6	26.4
		0.60-0.90	7.9	0.9	12	26.6	20.4	27.4

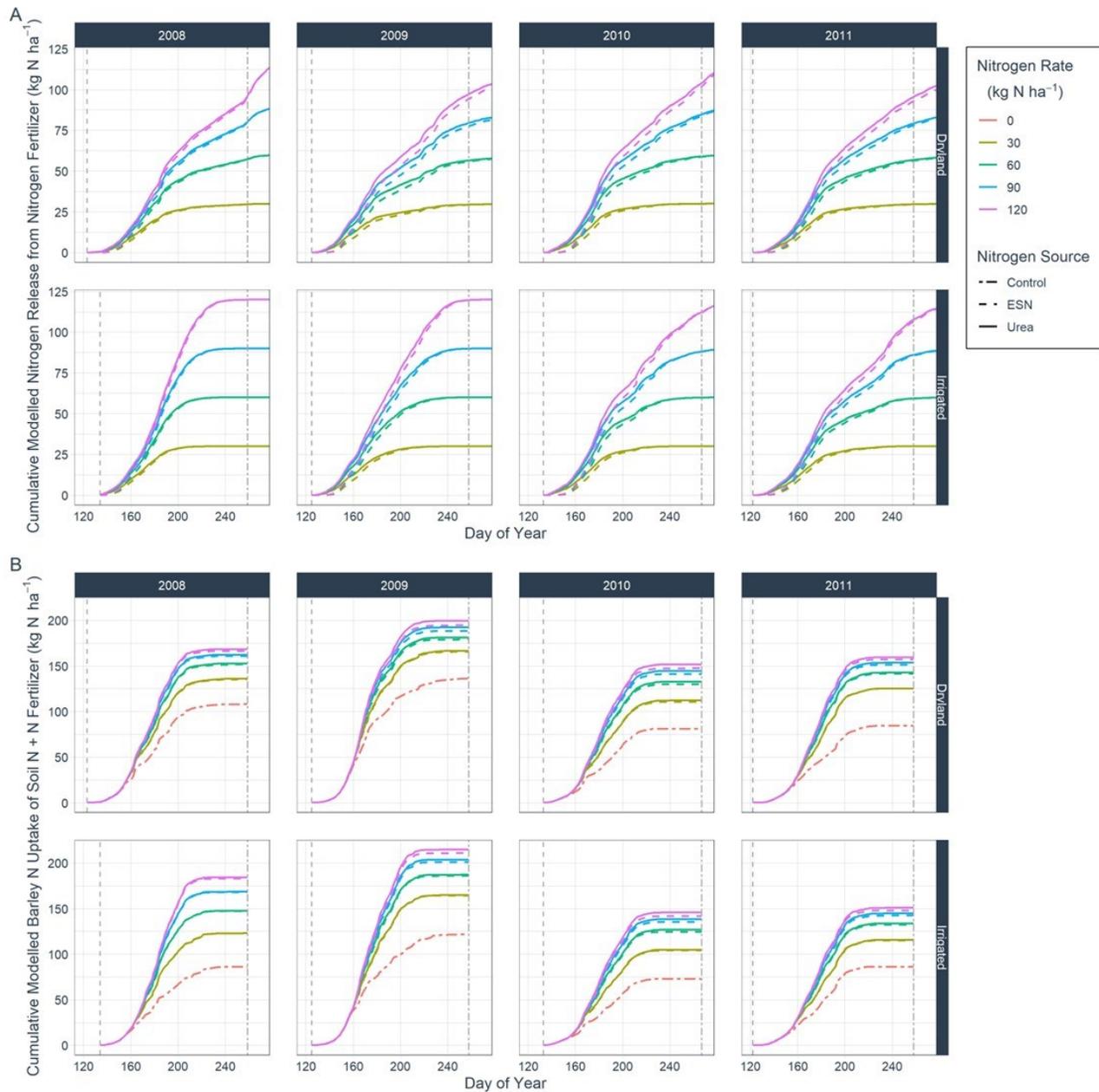
Supplementary Table 3-3. Modelled N₂O emissions, Area-based emission factors, and yield scaled emissions for direct and direct + indirect N₂O emissions for ESN at N rates of 0, 30, 60, 90 and 120 kg N ha⁻¹ at dryland and irrigated sites for 2008 – 2011 at Lethbridge, Alberta. (Results for urea presented in Table 3-6).

Year	Site	N Rate (kg N ha ⁻¹)	Direct N ₂ O emissions (kg N ha ⁻¹ yr ⁻¹)	Area Based Emission Factor (Direct N ₂ O emissions) (% kg N ₂ O-N kg ⁻¹ N Fertilizer)	Yield Scaled N ₂ O emissions (Direct N ₂ O emissions) (g N ₂ O-N kg ⁻¹ Grain Yield DM)	Direct + Indirect N ₂ O emissions (kg N ha ⁻¹ yr ⁻¹)	Area Based Emission Factor (Direct and Indirect N ₂ O emissions) (% kg N ₂ O-N kg ⁻¹ N Fertilizer)	Yield Scaled N ₂ O emissions (Direct and Indirect N ₂ O emissions) (g N ₂ O-N kg ⁻¹ Grain Yield DM)
2008	Dryland	0	0.35	-	0.0848	0.41	-	0.100
		30	0.46	0.36	0.0838	0.52	0.37	0.096
		60	0.53	0.29	0.0829	0.59	0.30	0.093
		90	0.60	0.27	0.0871	0.67	0.28	0.097
		120	0.68	0.27	0.0947	0.75	0.28	0.105
	Irrigated	0	0.26	-	0.0836	0.34	-	0.112
		30	0.34	0.27	0.0635	0.39	0.15	0.073
		60	0.40	0.24	0.0624	0.45	0.17	0.070
		90	0.46	0.23	0.0627	0.51	0.18	0.069
		120	0.51	0.22	0.0710	0.56	0.18	0.078
2009	Dryland	0	0.14	-	0.0287	0.21	-	0.044
		30	0.21	0.23	0.0330	0.30	0.28	0.047
		60	0.25	0.19	0.0380	0.35	0.23	0.052
		90	0.29	0.17	0.0447	0.39	0.20	0.059
		120	0.33	0.16	0.0505	0.43	0.18	0.065
	Irrigated	0	0.15	-	0.0366	0.23	-	0.057
		30	0.23	0.27	0.0344	0.32	0.32	0.049
		60	0.27	0.21	0.0356	0.37	0.23	0.048
		90	0.31	0.19	0.0385	0.41	0.20	0.050
		120	0.36	0.18	0.0446	0.46	0.19	0.057
2010	Dryland	0	0.20	-	0.0672	0.41	-	0.135
		30	0.31	0.36	0.0716	0.55	0.48	0.127
		60	0.37	0.27	0.0692	0.61	0.33	0.114
		90	0.43	0.25	0.0730	0.67	0.29	0.114
		120	0.48	0.23	0.0785	0.72	0.26	0.118
	Irrigated	0	0.13	-	0.0475	0.41	-	0.155
		30	0.19	0.22	0.0473	0.56	0.51	0.139
		60	0.25	0.20	0.0491	0.62	0.35	0.123
		90	0.30	0.20	0.0540	0.67	0.29	0.120
		120	0.35	0.18	0.0582	0.72	0.26	0.121
2011	Dryland	0	0.16	-	0.0562	0.26	-	0.091
		30	0.28	0.38	0.0523	0.44	0.59	0.083
		60	0.34	0.29	0.0568	0.50	0.40	0.085
		90	0.38	0.25	0.0617	0.55	0.32	0.089
		120	0.44	0.23	0.0684	0.61	0.29	0.095
	Irrigated	0	0.17	-	0.0500	0.30	-	0.086
		30	0.25	0.26	0.0533	0.44	0.48	0.094
		60	0.31	0.22	0.0559	0.50	0.34	0.091
		90	0.35	0.20	0.0598	0.55	0.28	0.092
		120	0.40	0.19	0.0646	0.59	0.24	0.096

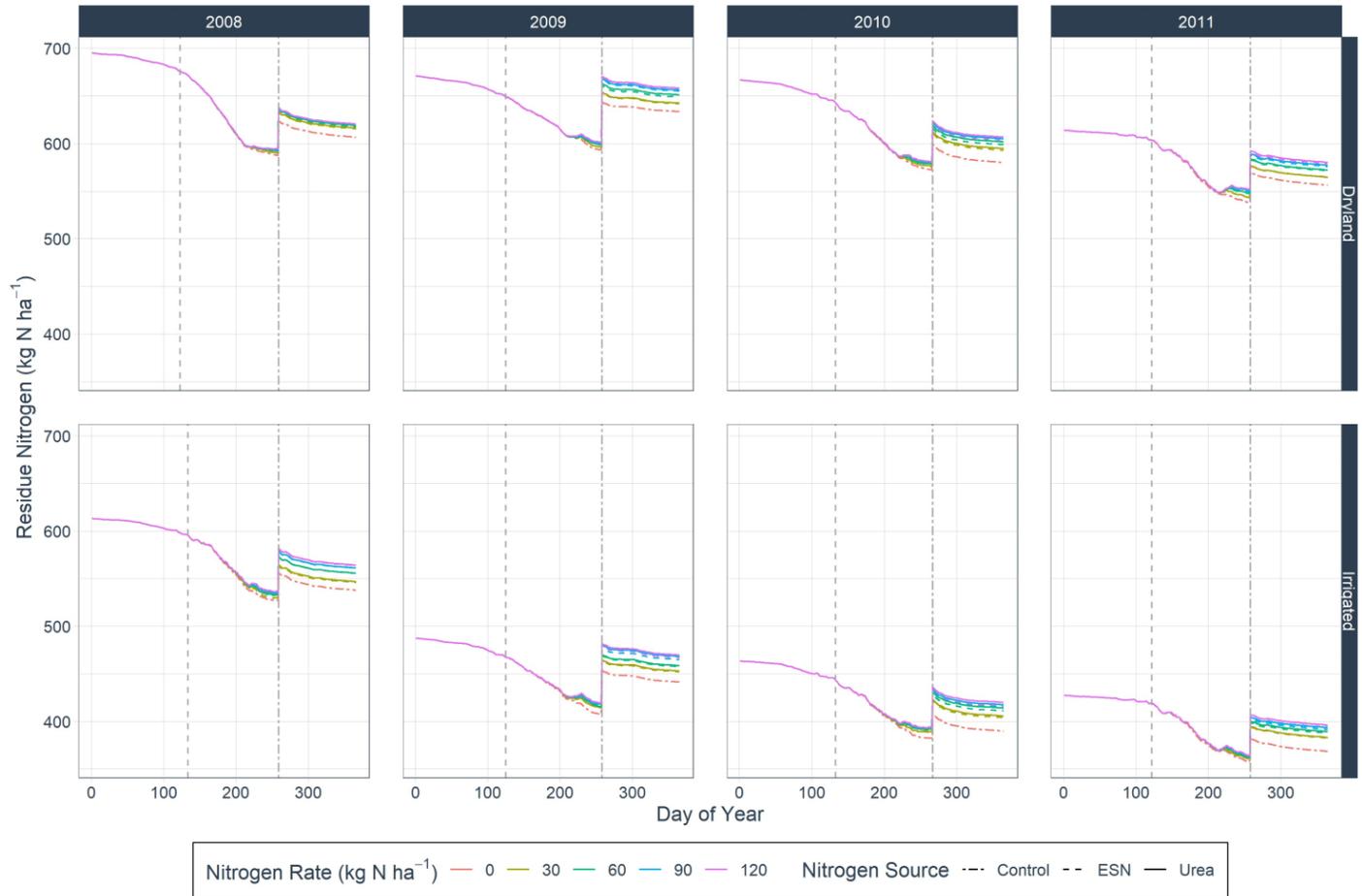
Supplementary Figures



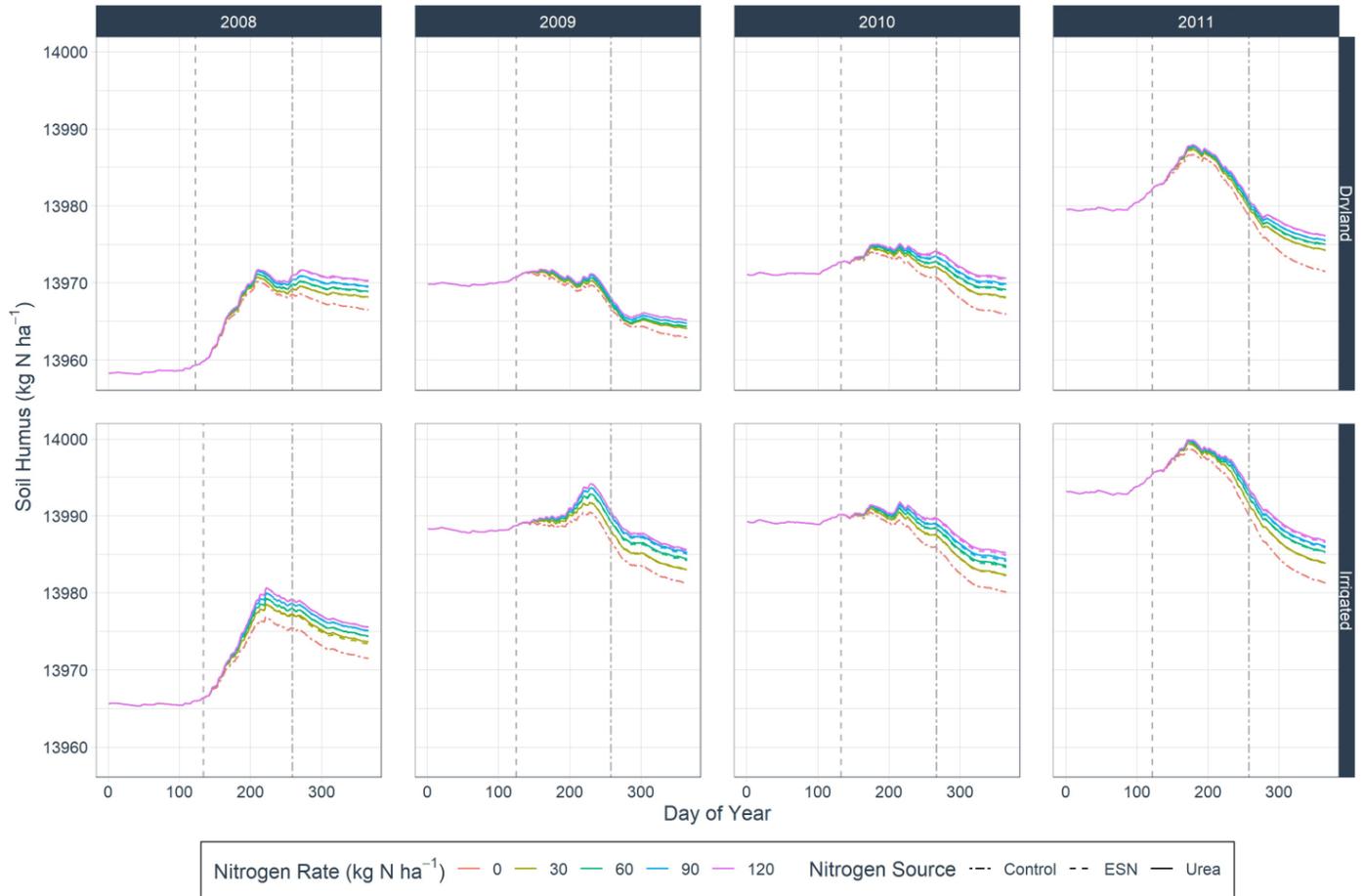
Supplementary Figure 3-1. Cumulative ammonium ($\text{NH}_4\text{-N}$) plus ammonia nitrogen ($\text{NH}_3\text{-N}$) (kg N ha^{-1}) in the soil profile for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008-2011 at dryland and irrigated sites in Lethbridge, Alberta.



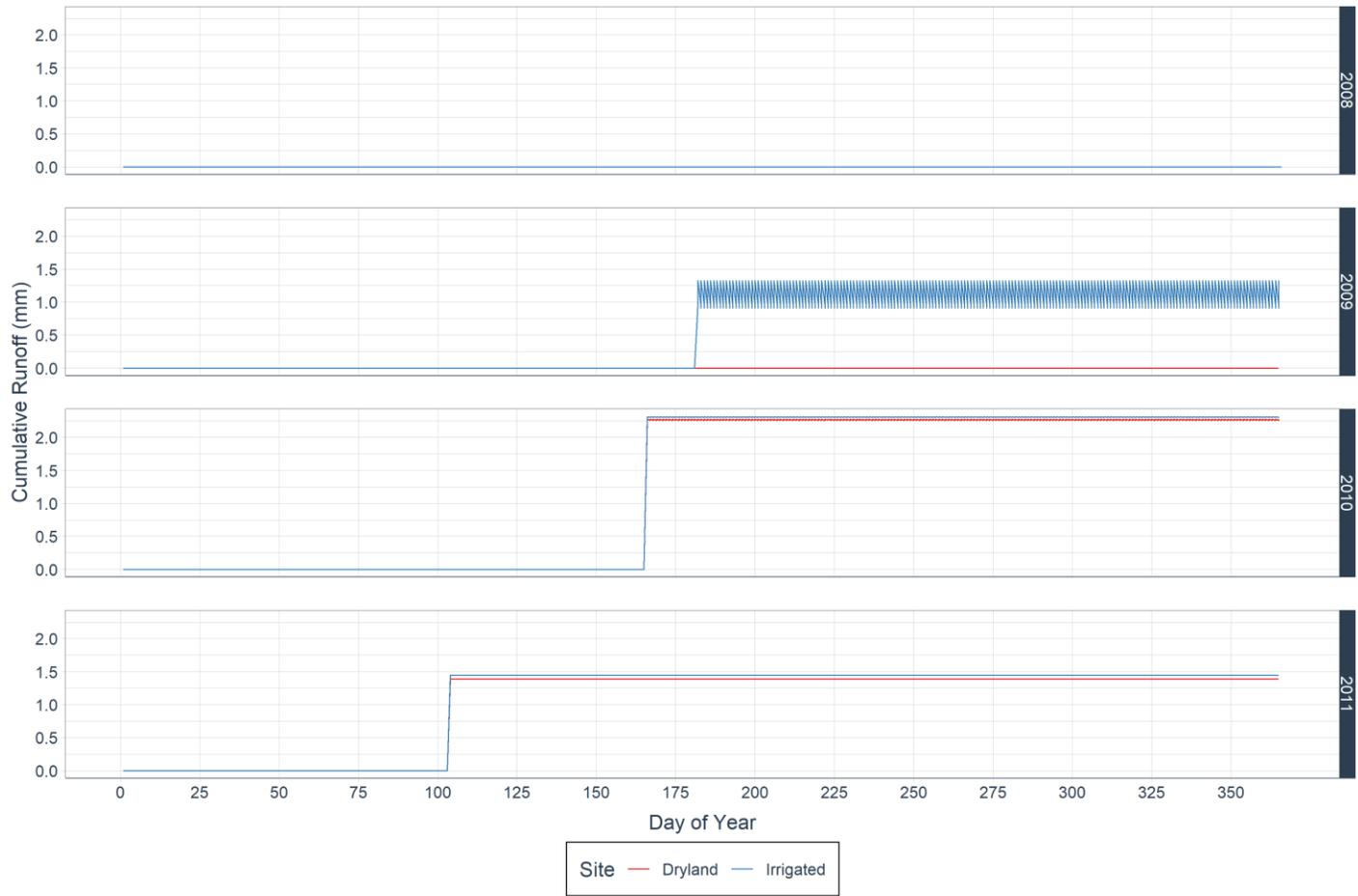
Supplementary Figure 3-2. A) Modelled cumulative nitrogen release (kg N ha^{-1}) and **B)** Modelled barley N uptake of soil N + N fertilizer (kg N ha^{-1}) over the growing season for control (no N fertilizer applied, two-dashed line), urea (solid line) and Environmentally Smart Nitrogen (ESN) (dashed line) N sources at 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for Dryland and Irrigated Sites for 2008 – 2011 in Lethbridge, Alberta. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines).



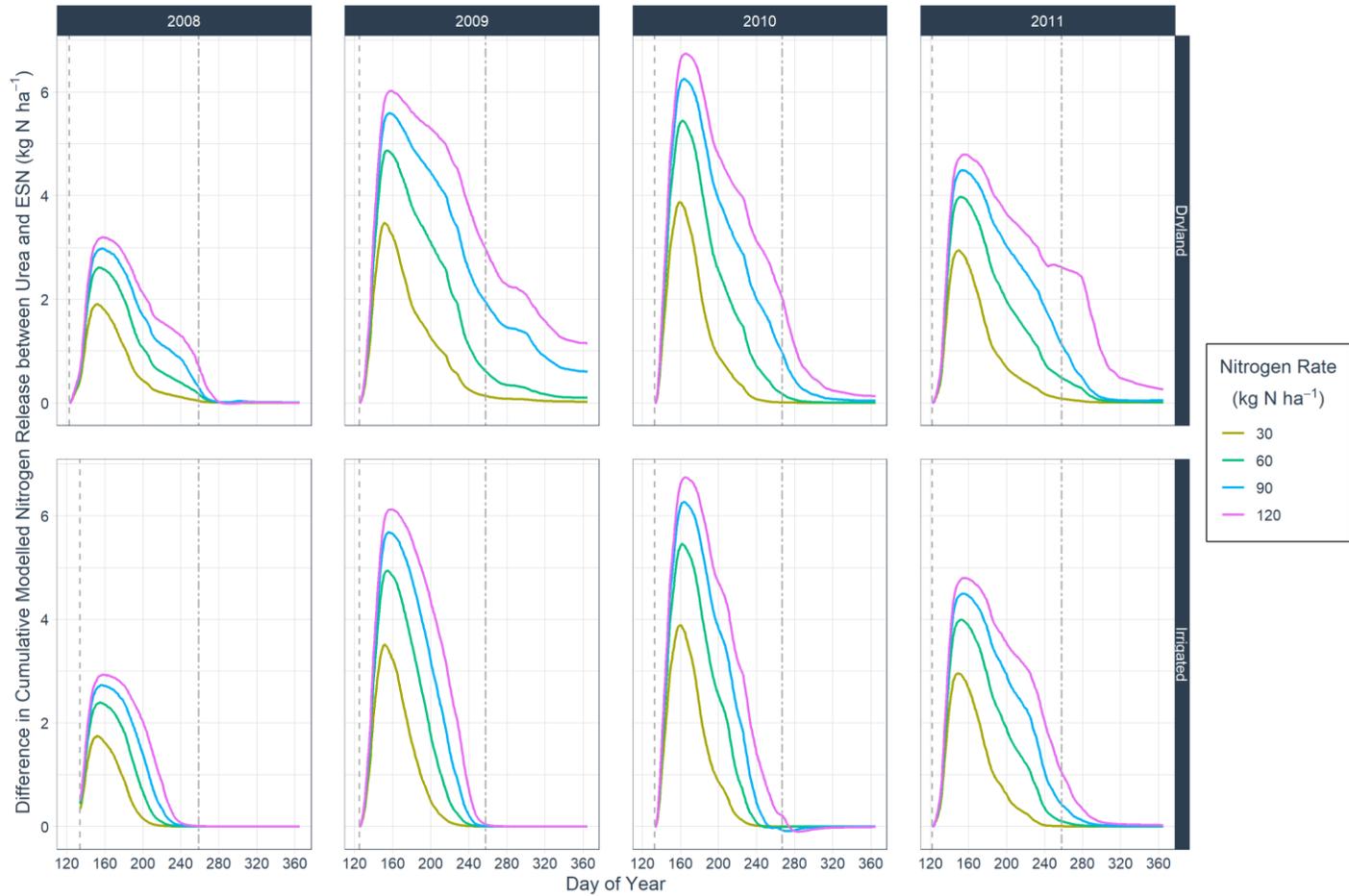
Supplemental Figure 3-3. Residue nitrogen (kg N ha⁻¹) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha⁻¹ for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta. Residue nitrogen declines with mineralization and rises after harvest as crop residues are left behind on the soil surface.



Supplemental Figure 3-4. Soil humus (kg N ha^{-1}) for control (no N fertilizer applied) (two dashed line), ESN (dashed line), and urea (solid line) at rates of 0 (red), 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for 2008 – 2011 at dryland and irrigated sites in Lethbridge, Alberta. Soil humus rises with immobilization and declines with mineralization.



Supplementary Figure 3-5. Cumulative modelled surface runoff (mm) for 2008 – 2011 at dryland (red) and irrigated (blue) sites in Lethbridge, Alberta.



Supplementary Figure 3-6. The difference in cumulative modelled nitrogen release between urea and Environmentally Smart Nitrogen (ESN) at 30 (yellow), 60 (green), 90 (blue), and 120 (pink) kg N ha^{-1} for Dryland and Irrigated Sites for 2008 – 2011 in Lethbridge, Alberta. Positive results indicate ESN has a lower N release than that of urea, while negative results indicate that N release from ESN is greater than that of urea. Vertical dark grey dashed lines indicate seeding/fertilizer application dates (dashed lines), or harvest dates (two-dashed lines).

4.0 Conclusion

Low crop nitrogen use efficiency (NUE) of applied nitrogen (N) fertilizer results in reduced economic returns on N fertilizer investments for producers and increased N losses, which negatively impact human and environmental health (Cassman et al. 2002). Nitrous oxide (N₂O) emissions from N fertilizer are of particular concern as N₂O is a potent greenhouse gas (GHG) with a global warming potential 298 times that of CO₂ (Forster et al. 2007). The Government of Canada established the Fertilizer Emissions Reduction Target to address climate change issues, which aims to reduce fertilizer GHG emissions by 30% below 2020 levels by 2030 (Agriculture and Agri-Food Canada 2022). Effective N fertilizer management that matches N supply with crop N demand (e.g., the 4 R's) may allow for reduced N losses while maintaining or increasing yields. To identify effective N fertilizer management practices, a comprehensive N budget was developed using the process-based model *ecosys* to assess the effects of N rate (0 – 120 kg N ha⁻¹), N source (Urea vs ESN), irrigation vs dryland, and interannual climatic variability (2008 – 2011) on modelled crop yields, grain N, fertilizer NUE, N losses, and soil N stocks at a cool, semi-arid site in Southern Alberta. Compared to conventional urea fertilizer, modelled N release from ESN did not better match N availability with crop N demand and did not improve modelled yields or fertilizer NUE or reduce modelled N losses. Nitrogen rate had a greater impact on the N budget than the N source, indicating the importance of optimal N rate applications in effective N fertilizer management. Increasing N rates increased modelled yields at N rates of 30 – 90 kg N ha⁻¹, but above 90 kg N ha⁻¹, yield gains were minimal (<3%) (Figure 4-1) (38 – 127 kg N ha⁻¹ yr⁻¹ modelled grain N harvest removals), with fertilizer NUE (27 – 111%) declining with increasing N rates. Modelled soil organic N stocks declined 18 to 90 kg N ha⁻¹ yr⁻¹ with greater declines at lower N rates. In contrast, modelled N₂O emissions increased linearly with increasing N rates (Figure 4-1). Reducing N fertilizer rate applications from the maximum N rate in this study (120 kg N ha⁻¹) to economically optimum N rates (71 kg N ha⁻¹ at dryland site, 79 kg N ha⁻¹ at the irrigated site at a 7.4 fertilizer-to-grain price ratio; Figure 4-1) would result in N₂O emissions

reductions of 18 – 22%, with only minimal yield reductions of 2.7 – 3.6% (Figure 4-1). Lowering N rates to ≤ 30 kg N ha⁻¹ often resulted in higher yield scaled emissions than N rates of 60 – 90 kg N ha⁻¹ due to substantially lower modelled yields relative to modelled N₂O emissions production. Further N₂O emissions reductions may be achieved by reducing indirect N₂O emission losses from NH₃ volatilization (2.5 – 7.6 kg N ha⁻¹ yr⁻¹) and subsurface N (0 – 30.2 kg N ha⁻¹ yr⁻¹) losses, and reducing residual nitrate-N levels (0 – 51 kg N ha⁻¹ yr⁻¹) which are at risk for post-harvest N losses. Irrigation and interannual climatic variability affected the magnitude of modelled N₂O, NH₃ and subsurface N losses. Overall, modelled N₂O emissions were slightly higher at the dryland site (0.14 – 0.68 kg N ha⁻¹ yr⁻¹) than the irrigated site (0.13 – 0.51 kg N ha⁻¹ yr⁻¹) (Figure 4-1) due to higher modelled crop N uptake and fertilizer NUE at the irrigated site in dry years (e.g., 2008, 2009) (46 – 127 kg N ha⁻¹ modelled grain N harvest removals at the irrigated site vs 60 – 106 kg N ha⁻¹ at the dryland site; 52 – 107% fertilizer NUE at the irrigated site vs 25 – 61% at the dryland site) and greater subsurface N losses at the irrigated site in the wet year and the year following (e.g., 2010, 2011). The dryland site had higher modelled volatilization losses (3.1 – 7.6 kg N ha⁻¹ yr⁻¹) than the irrigated site (2.5 – 4.2 kg N ha⁻¹ yr⁻¹), particularly in dry years (e.g., 2008, 2009) which increased direct and indirect N₂O emission factors by 3 – 21%. However, repeated N fertilizer applications in the years leading up to the experimental treatments (1998 – 2007) resulted in the accumulation of modelled soil nitrate-N below the zone of root N uptake (49 – 127 kg N ha⁻¹ below 0.9 meters). This accumulated nitrate-N was subject to subsurface N losses in wet years (e.g., 2010) and at the irrigated site (4 – 30.2 kg N ha⁻¹ yr⁻¹; vs <2 kg N ha⁻¹ yr⁻¹ in dry years at the dryland site), which increased direct and indirect N₂O emission factors by 5 – 57%. Nitrogen fertilizer rate applications > 90 kg N ha⁻¹ greatly increased modelled residual nitrate-N (15 – 51 kg N ha⁻¹) compared to lower N rates, which was subject to downward nitrate-N movement beyond the crop rooting depth and N leaching. Therefore, optimizing N rate applications would reduce direct and indirect N₂O losses, and reduce the risk of N losses from residual nitrate-N. Fertilizer NUE and N losses varied substantially with N rates, interannual

climatic variability and irrigation at one site in the semi-arid Canadian prairies, indicating the importance of site-specific N management practices in developing effective N management practices to increase fertilizer NUE and reduce N losses. The results from this thesis could provide a methodology for developing effective N management strategies which balance agronomic benefits and environmental impacts for policymakers and producers.

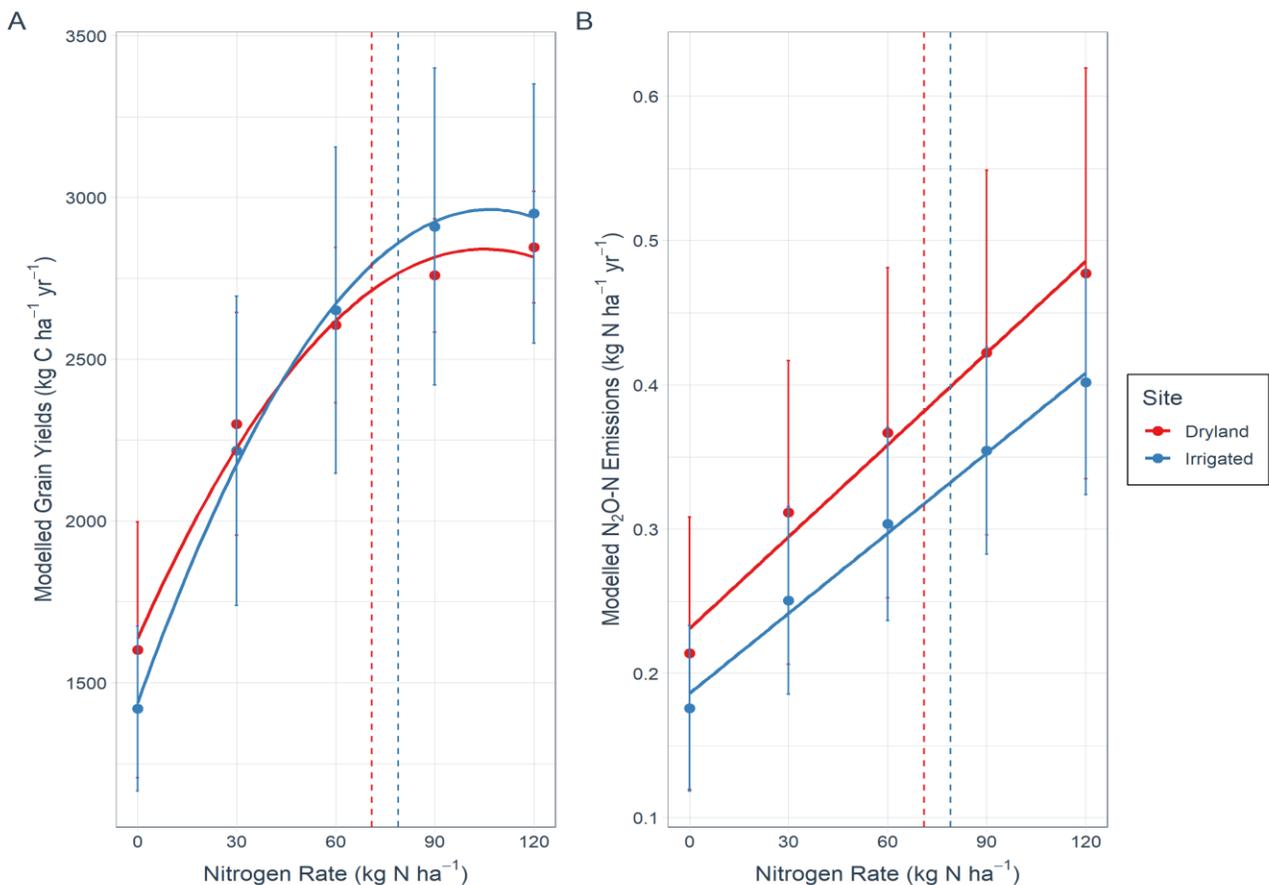


Figure 4-1. A) Mean modelled barley grain yields (kg C ha⁻¹ yr⁻¹) and **B)** Mean modelled N₂O-N emissions (kg N ha⁻¹ yr⁻¹) response to increasing N rates (0 – 120 kg N ha⁻¹) for urea fertilizer at dryland (red) and irrigated (blue) sites in Lethbridge, Alberta for 2008 – 2011. Error bars represent the standard deviation of mean-modelled barley grain yields or mean-modelled N₂O-N emissions due to yearly variability (2008 – 2011). Vertical dashed lines indicate the economic optimum N rate (EONR) based on a 7.4 fertilizer-to-grain price ratio for dryland (red; 71 kg N ha⁻¹) and irrigated (blue; 79 kg N ha⁻¹) sites for 2008 – 2011. Quadratic regression results for modelled grain yields: Dryland: $y = -0.11x^2 + 23x + 1636$; $R^2 = 0.74$; $p < 0.001$. Irrigated: $y = -0.13x^2 + 29x + 1437$; $R^2 = 0.69$; $p < 0.001$. Linear regression results for modelled N₂O-N emissions: Dryland: $y = 0.002x + 0.23$; $R^2 = 0.44$; $p = 0.002$. Irrigated: $y = 0.002x + 0.19$; $R^2 = 0.64$; $p < 0.001$.

References

- ACIS 2021. Alberta Climate Information Service. [Online] Available: <https://agriculture.alberta.ca/acis/> [2021 Oct. 1].
- Agehara, S., and Warncke, D.D. 2005. Soil Moisture and Temperature Effects on Nitrogen Release from Organic Nitrogen Sources. *Soil Science Society of America Journal* **69**: 1844–1855. doi:10.2136/sssaj2004.0361.
- Agriculture and Agri-Food Canada 2022. Discussion Document: Reducing emissions arising from the application of fertilizer in Canada's agriculture sector - agriculture.canada.ca. [Online] Available: <https://agriculture.canada.ca/en/about-our-department/transparency-and-corporate-reporting/public-opinion-research-and-consultations/share-ideas-fertilizer-emissions-reduction-target/discussion-document-reducing-emissions-arising-application-fertilizer-canadas-agriculture-sector> [2022 Sep. 22].
- Alberta Agriculture and Rural Development 2008. 2008 Reference Guide Agricultural Operation Practices Act. [Online] Available: <https://open.alberta.ca/publications/4221828#summary> [2023 Oct. 9].
- An, H., Owens, J., Stoeckli, J., Hao, X., Beres, B., and Li, Y. 2020. Nitrous oxide emissions following split fertilizer application on winter wheat grown on Mollisols of Southern Alberta, Canada. *Geoderma Regional* **21**. Elsevier B.V. doi:10.1016/j.geodrs.2020.e00272.
- Basso, B., Shuai, G., Zhang, J., and Robertson, G.P. 2019. Yield stability analysis reveals sources of large-scale nitrogen loss from the US Midwest. *Sci Rep* **9**. Nature Publishing Group. doi:10.1038/s41598-019-42271-1.
- Blackshaw, R.E., Hao, X., Brandt, R.N., Clayton, G.W., Harker, K.N., O'Donovan, J.T., Johnson, E.N., and Vera, C.L. 2011a. Canola response to ESN and urea in a four-year no-till cropping system. *Agron J* **103**: 92–99. doi:10.2134/agronj2010.0299.
- Blackshaw, R.E., Hao, X., Harker, K.N., O'Donovan, J.T., Johnson, E.N., and Vera, C.L. 2011b. Barley productivity response to polymer-coated urea in a no-till production system. *Agron J* **103**: 1100–1105. doi:10.2134/agronj2010.0494.
- Blenkinsop, P.G., and Dale, J.E. 1974. The Effects of Nitrate Supply and Grain Reserves on Fraction I Protein Level in the First Leaf of Barley. *J Exp Bot* **25**: 913–926. doi:10.1093/jxb/25.5.913.
- Bouwman, A.F., Boumans, L.J.M., and Batjes, N.H. 2002. Estimation of global NH₃ volatilization loss from synthetic fertilizers and animal manure applied to arable lands and grasslands. *Global Biogeochem Cycles* **16**. American Geophysical Union. doi:10.1029/2000gb001389.
- Burns, I.G. 1980. Influence of the Spatial Distribution of Nitrate on the Uptake of N by Plants: A Review and a Model for Rooting Depth. *Journal of Soil Science* **31**: 155–173. doi:10.1111/j.1365-2389.1980.tb02073.x.
- Burton, D.L., Li, X., and Grant, C.A. 2008. Influence of fertilizer nitrogen source and management practice on N₂O emissions from two Black Chernozemic soils. *Can J Soil Sci* **88**: 219–227. doi:10.4141/CJSS06020.
- Cahill, S., Osmond, D., and Israel, D. 2010a. Nitrogen release from coated urea fertilizers in different soils. *Commun Soil Sci Plant Anal* **41**: 1245–1256. doi:10.1080/00103621003721437.
- Cahill, S., Osmond, D., Weisz, R., and Heiniger, R. 2010b. Evaluation of alternative nitrogen fertilizers for corn and winter wheat production. *Agron J* **102**: 1226–1236. doi:10.2134/agronj2010.0095.
- Cameron, K.C., Di, H.J., and Moir, J.L. 2013. Nitrogen losses from the soil/plant system: A review. *Annals of Applied Biology* **162**: 145–173. doi:10.1111/aab.12014.

- Campbell, C.A., Selles, F., Zentner, R.P., De Jong, R., Lemke, R., and Hamel, C. 2006. Nitrate leaching in the semiarid prairie : Effect of cropping frequency, crop type, and fertilizer after 37 years. *Can J Soil Sci* **86**: 701–710. doi:10.4141/S05-008.
- Cassman, K.G., Dobermann, A., and Walters, D.T. 2002. Agroecosystems, Nitrogen-use Efficiency and Nitrogen management. *Amibio* **31**: 132–139. doi:10.1579/0044-7447-31.2.132.
- Chai, L.L., Hernandez-Ramirez, G., Dyck, M., Pauly, D., Kryzanowski, L., Middleton, A., Powers, L.A., Lohstraeter, G., and Werk, D. 2020. Can fertigation reduce nitrous oxide emissions from wheat and canola fields? *Science of the Total Environment* **745**. Elsevier B.V. doi:10.1016/j.scitotenv.2020.141014.
- Chantigny, M.H., Bittman, S., Larney, F.J., Lapen, D., Hunt, D.E., Goyer, C., and Angers, D.A. 2019. A multi-region study reveals high overwinter loss of fall-applied reactive nitrogen in cold and frozen soils. *Can J Soil Sci* **99**: 126–135. Agricultural Institute of Canada. doi:10.1139/cjss-2018-0151.
- Chen, J., Lü, S., Zhang, Z., Zhao, X., Li, X., Ning, P., and Liu, M. 2018. Environmentally friendly fertilizers: A review of materials used and their effects on the environment. *Science of the Total Environment* **613–614**: 829–839. Elsevier B.V. doi:10.1016/j.scitotenv.2017.09.186.
- Clément, C.C., Cambouris, A.N., Ziadi, N., Zebarth, B.J., and Karam, A. 2021. Potato yield response and seasonal nitrate leaching as influenced by nitrogen management. *Agronomy* **11**. MDPI. doi:10.3390/agronomy11102055.
- Congreves, K.A., Otchere, O., Ferland, D., Farzadfar, S., Williams, S., and Arcand, M.M. 2021. Nitrogen Use Efficiency Definitions of Today and Tomorrow. *Front Plant Sci* **12**. Frontiers Media S.A. doi:10.3389/fpls.2021.637108.
- Daly, E.J., and Hernandez-Ramirez, G. 2020. Sources and priming of soil N₂O and CO₂ production: Nitrogen and simulated exudate additions. *Soil Biol Biochem* **149**: 107942. Elsevier Ltd. doi:10.1016/j.soilbio.2020.107942.
- David, C., Lemke, R., Helgason, W., and Farrell, R.E. 2018. Current inventory approach overestimates the effect of irrigated crop management on soil-derived greenhouse gas emissions in the semi-arid Canadian Prairies. *Agric Water Manag* **208**: 19–32. Elsevier. doi:10.1016/j.agwat.2018.06.006.
- Djaman, K., Irmak, S., Martin, D.L., Ferguson, R.B., and Bernards, M.L. 2013. Plant nutrient uptake and soil nutrient dynamics under full and limited irrigation and rainfed maize production. *Agron J* **105**: 527–538. doi:10.2134/agronj2012.0269.
- Drury, C.F., Reynolds, W.D., Yang, X.M., McLaughlin, N.B., Welacky, T.W., Calder, W., and Grant, C.A. 2012. Nitrogen Source, Application Time, and Tillage Effects on Soil Nitrous Oxide Emissions and Corn Grain Yields. *Soil Science Society of America Journal* **76**: 1268–1279. Wiley. doi:10.2136/sssaj2011.0249.
- Du, C.W., Zhou, J.M., and Shaviv, A. 2006. Release characteristics of nutrients from polymer-coated compound controlled release fertilizers. *J Polym Environ* **14**: 223–230. doi:10.1007/s10924-006-0025-4.
- Environment and Climate Change Canada 2022. National Inventory Report 1990-2022: Greenhouse Gas Sources and Sinks in Canada.
- Fan, J., McConkey, B., Wang, H., and Janzen, H. 2016. Root distribution by depth for temperate agricultural crops. *Field Crops Res* **189**: 68–74. Elsevier B.V. doi:10.1016/j.fcr.2016.02.013.
- Feng, J., Li, F., Deng, A., Feng, X., Fang, F., and Zhang, W. 2016. Integrated assessment of the impact of enhanced-efficiency nitrogen fertilizer on N₂O emission and crop yield. *Agric Ecosyst Environ* **231**: 218–228. Elsevier B.V. doi:10.1016/j.agee.2016.06.038.

- Forster, P., Ramaswamy, P.A., Bernsten, T., R, B., Fahey, D.W., and J, H. 2007. Changes in Atmospheric Constituents and in Radiative Forcing. *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.*
- Gagnon, B., Ziadi, N., and Grant, C. 2012. Urea fertilizer forms affect grain corn yield and nitrogen use efficiency. *Can J Soil Sci* **92**: 341–351. doi:10.4141/cjss2011-074.
- Gagnon, B., Ziadi, N., Rochette, P., Chantigny, M.H., and Angers, D.A. 2011. Fertilizer Source Influenced Nitrous Oxide Emissions from a Clay Soil under Corn. *Soil Science Society of America Journal* **75**: 595–604. Wiley. doi:10.2136/sssaj2010.0212.
- Golden, B., Slaton, N., Norman, R., Gbur, E., and Wilson, C. 2011. Nitrogen release from environmentally smart nitrogen fertilizer as influenced by soil series, temperature, moisture, and incubation method. *Commun Soil Sci Plant Anal* **42**: 1809–1824. doi:10.1080/00103624.2011.587568.
- Grant, C., and Wu, R. 2008. Enhanced-Efficiency Fertilizers for Use on the Canadian Prairies. *Crop Management* **7**: 1–15. American Society of Agronomy. doi:10.1094/cm-2008-0730-01-rv.
- Grant, C.A., Wu, R., Selles, F., Harker, K.N., Clayton, G.W., Bittman, S., Zebarth, B.J., and Lupwayi, N.Z. 2012. Crop yield and nitrogen concentration with controlled release urea and split applications of nitrogen as compared to non-coated urea applied at seeding. *Field Crops Res* **127**: 170–180. doi:10.1016/j.fcr.2011.11.002.
- Grant, R. 2001. A Review of the Canadian Ecosystem Model - ecosys. Pages 173–263 in M. Shaffer, L. Ma, and S. Hansen, eds. *Modeling Carbon and Nitrogen Dynamics for Soil Management*. CRC Press, Boca Raton, Florida.
- Grant, R.F., Dyck, M., and Puurveen, D. 2020. Nitrogen and phosphorus control carbon sequestration in agricultural ecosystems: Modelling carbon, nitrogen, and phosphorus balances at the breton plots with ecosys under historical and future climates. *Can J Soil Sci* **100**: 408–429. Agricultural Institute of Canada. doi:10.1139/cjss-2019-0132.
- Grant, R.F., Juma, N.G., Robertson, J.A., Izaurralde, R.C., and McGill, W.B. 2001. Long-Term Changes in Soil Carbon under Different Fertilizer, Manure, and Rotation. *Soil Science Society of America Journal* **65**: 205–214. Wiley. doi:10.2136/sssaj2001.651205x.
- Grant, R.F., and Pattey, E. 2003. Modelling variability in N₂O emissions from fertilized agricultural fields. *Soil Biol Biochem* **35**: 225–243. doi:10.1016/S0038-0717(02)00256-0.
- Grant, R.F., Pattey, E., Goddard, T.W., Kryzanowski, L.M., and Puurveen, H. 2006. Modeling the Effects of Fertilizer Application Rate on Nitrous Oxide Emissions. *Soil Science Society of America Journal* **70**: 235–248. Wiley. doi:10.2136/sssaj2005.0104.
- Van Groenigen, J.W., Velthof, G.L., Oenema, O., Van Groenigen, K.J., and Van Kessel, C. 2010. Towards an agronomic assessment of N₂O emissions: a case study for arable crops. *Eur J Soil Sci* **61**: 903–913. doi:10.1111/j.1365-2389.2009.01217.x.
- Guo, J., Fan, J., Xiang, Y., Zhang, F., Yan, S., Zhang, X., Zheng, J., Li, Y., Tang, Z., and Li, Z. 2022. Coupling effects of irrigation amount and nitrogen fertilizer type on grain yield, water productivity and nitrogen use efficiency of drip-irrigated maize. *Agric Water Manag* **261**. Elsevier B.V. doi:10.1016/j.agwat.2021.107389.
- Halvorson, A.D., Snyder, C.S., Blaylock, A.D., and Del Grosso, S.J. 2014. Enhanced-efficiency nitrogen fertilizers: Potential role in nitrous oxide emission mitigation. *Agron J* **106**: 715–722. doi:10.2134/agronj2013.0081.

- Hao, X., Chang, C., Carefoot, J.M., Janzen, H.H., and Ellert, B.H. 2001. Nitrous oxide emissions from an irrigated soil as affected by fertilizer and straw management. *Nutr Cycl Agroecosyst* **60**: 1–8. doi:10.1023/A:1012603732435.
- He, W., Yang, J.Y., Zhou, W., Drury, C.F., Yang, X.M., Reynolds, W.D., Wang, H., He, P., and Li, Z.T. 2016. Sensitivity analysis of crop yields, soil water contents and nitrogen leaching to precipitation, management practices and soil hydraulic properties in semi-arid and humid regions of Canada using the DSSAT model. *Nutr Cycl Agroecosyst* **106**: 201–215. Springer Netherlands. doi:10.1007/s10705-016-9800-3.
- Hergoualc'h, K., Akiyama, H., Bernoux, M., Chirinda, N., del Prado, A., Kasimir, A., Douglas MacDonald, J., Michael Ogle, S., Regina, K., van der Weerden, T.J., Liang, C., and Noble, A. 2019. Chapter 11: N₂O Emissions from Managed Soils, and CO₂ Emissions from Lime and Urea Application.
- John, A.A., Jones, C.A., Ewing, S.A., Sigler, W.A., Bekkerman, A., and Miller, P.R. 2017. Fallow replacement and alternative nitrogen management for reducing nitrate leaching in a semiarid region. *Nutr Cycl Agroecosyst* **108**: 279–296. Springer Netherlands. doi:10.1007/s10705-017-9855-9.
- Jones, D.B. 1941. Factors for Converting Percentages of Nitrogen in Foods and Feeds into Percentages of Proteins. Washington, DC.
- Kaiser, E.-A., Kohrs, K., Kücke, M., Schnug, E., Heinemeyer, O., and Munch, J.C. 1998. Nitrous oxide release from arable soil: Importance of N-fertilization, crops and temporal variation. *Soil Biol Biochem* **30**: 1553–1563. doi:10.1016/S0038-0717(98)00036-4.
- Karimi, R., Pogue, S.J., Kröbel, R., Beauchemin, K.A., Schwinghamer, T., and Henry Janzen, H. 2020. An updated nitrogen budget for Canadian agroecosystems. *Agric Ecosyst Environ* **304**. Elsevier B.V. doi:10.1016/j.agee.2020.107046.
- Khakbazan, M., Grant, C.A., Finlay, G., Wu, R., Malhi, S.S., Selles, F., Clayton, G.W., Lupwayi, N.Z., Soon, Y.K., and Harker, K.N. 2013. An economic study of controlled release urea and split applications of nitrogen as compared with non-coated urea under conventional and reduced tillage management. *Canadian Journal of Plant Science* **93**: 523–534. doi:10.4141/CJPS2012-107.
- Kim, D.G., Hernandez-Ramirez, G., and Giltrap, D. 2013. Linear and nonlinear dependency of direct nitrous oxide emissions on fertilizer nitrogen input: A meta-analysis. *Agric Ecosyst Environ* **168**: 53–65. doi:10.1016/j.agee.2012.02.021.
- Korol, M. 2004. Fertilizer and pesticide management, Canada. Statistics Canada, Agriculture Division.
- Kryzanowski, L., Mckenzie, R., Middleton, A., Sprout, C., Henriquez, B., and O'Donovan, J. 2009. Enabling Adoption of Environmentally Smart Nitrogen (ESN) Technology to Maximize Economic Returns and Environmental Benefits in Alberta Progress Report.
- Lassaletta, L., Billen, G., Garnier, J., Bouwman, L., Velazquez, E., Mueller, N.D., and Gerber, J.S. 2016. Nitrogen use in the global food system: Past trends and future trajectories of agronomic performance, pollution, trade, and dietary demand. *Environmental Research Letters* **11**. Institute of Physics Publishing. doi:10.1088/1748-9326/11/9/095007.
- Li, C., Hao, X., Blackshaw, R.E., Clayton, G.W., O'Donovan, J.T., and Harker, K.N. 2016. Nitrous Oxide Emissions in Response to ESN and Urea Application in a No-Till Barley Cropping System. *Commun Soil Sci Plant Anal* **47**: 692–705. Taylor & Francis. doi:10.1080/00103624.2016.1146745.

- Li, C., Hao, X., Blackshaw, R.E., O'Donovan, J.T., Harker, K.N., and Clayton, G.W. 2012. Nitrous oxide emissions in response to ESN and urea, herbicide management and canola cultivar in a no-till cropping system. *Soil Tillage Res* **118**: 97–106. Elsevier B.V. doi:10.1016/j.still.2011.10.017.
- Li, T., Zhang, W., Yin, J., Chadwick, D., Norse, D., Lu, Y., Liu, X., Chen, X., Zhang, F., Powlson, D., and Dou, Z. 2018. Enhanced-efficiency fertilizers are not a panacea for resolving the nitrogen problem. *Glob Chang Biol* **24**: e511–e521. Blackwell Publishing Ltd. doi:10.1111/gcb.13918.
- Liang, C., MacDonald, D., Thiagarajan, A., Flemming, C., Cerkowniak, D., and Desjardins, R. 2020. Developing a country specific method for estimating nitrous oxide emissions from agricultural soils in Canada. *Nutr Cycl Agroecosyst* **117**: 145–167. Springer. doi:10.1007/s10705-020-10058-w.
- Mahal, N.K., Osterholz, W.R., Miguez, F.E., Poffenbarger, H.J., Sawyer, J.E., Olk, D.C., Archontoulis, S. V., and Castellano, M.J. 2019. Nitrogen Fertilizer Suppresses Mineralization of Soil Organic Matter in Maize Agroecosystems. *Front Ecol Evol* **7**. Frontiers Media S.A. doi:10.3389/fevo.2019.00059.
- Maharjan, B., Venterea, R.T., and Rosen, C. 2014. Fertilizer and irrigation management effects on nitrous oxide emissions and nitrate leaching. *Agron J* **106**: 703–714. doi:10.2134/agronj2013.0179.
- Malhi, S.S., Grant, C.A., Johnston, A.M., and Gill, K.S. 2001. Nitrogen fertilization management for no-till cereal production in the Canadian Great Plains: a review. *Soil Tillage Res* **60**: 101–122. doi:10.1016/S0167-1987(01)00176-3.
- Malhi, S.S., Soon, Y.K., Grant, C.A., Lemke, R., and Lupwayi, N. 2010. Influence of controlled-release urea on seed yield and N concentration, and N use efficiency of small grain crops grown on Dark Gray Luvisols. *Can J Soil Sci* **90**: 363–372. doi:10.4141/CJSS09102.
- Mathers, A.C., Stewart, B.A., and Blair, B. 1975. Nitrate-nitrogen Removal from Soil Profiles by Alfalfa. *J Environ Qual* **4**: 403–405. Wiley. doi:10.2134/jeq1975.00472425000400030026x.
- McKenzie, R.H., Middleton, A.B., DeMulder, J., and Bremer, E. 2004a. Fertilizer response of barley silage in southern and central Alberta. *Can J Soil Sci* **84**: 133–147. doi:10.4141/S03-042.
- McKenzie, R.H., Middleton, A.B., Hall, L., Demulder, J., Bremer, E., and Bremer, J. 2004b. Fertilizer response of barley grain in south and central Alberta. *Can J Soil Sci*: 513–523.
- McKenzie, R.H., Middleton, A.B., Piffner, P.G., and Bremer, E. 2010. Evaluation of polymer-coated urea and urease inhibitor for winter wheat in Southern Alberta. *Agron J* **102**: 1210–1216. doi:10.2134/agronj2009.0194.
- Metivier, K.A., Pattey, E., and Grant, R.F. 2009. Using the ecosys mathematical model to simulate temporal variability of nitrous oxide emissions from a fertilized agricultural soil. *Soil Biol Biochem* **41**: 2370–2386. Elsevier Ltd. doi:10.1016/j.soilbio.2009.03.007.
- Metodieva, M., and Demirevska-Kepova, K. 1992. Rubisco Quantitation in Leaves of Different Barley Varieties by Enzyme-Linked Immunosorbent Assay. *J Exp Bot* **43**: 155–158. doi:10.1093/jxb/43.2.155.
- Mezbahuddin, S., Spiess, D., Hildebrand, D., Kryzanowski, L., Itenfisu, D., Goddard, T., Iqbal, J., and Grant, R. 2020. Assessing Effects of Agronomic Nitrogen Management on Crop Nitrogen Use and Nitrogen Losses in the Western Canadian Prairies. *Front Sustain Food Syst* **4**: 1–21. doi:10.3389/fsufs.2020.512292.
- Millar, N., Robertson, G.P., Grace, P.R., Gehl, R.J., and Hoben, J.P. 2010. Nitrogen fertilizer management for nitrous oxide (N₂O) mitigation in intensive corn (Maize) production: an emissions reduction protocol for US Midwest agriculture. *Mitig Adapt Strateg Glob Chang* **15**: 185–204. doi:10.1007/s11027-010-9212-7.

- Nelson, K.A., Motavalli, P.P., and Dudenhoeffer, C.J. 2014. Cropping System Affects Polymer-Coated Urea Release and Corn Yield Response in Claypan Soils. *J Agron Crop Sci* **200**: 54–65. doi:10.1111/jac.12040.
- Nelson, K.A., Scharf, P.C., Bundy, L.G., and Tracy, P. 2008. Agricultural Management of Enhanced-Efficiency Fertilizers in the North-Central United States. *Crop Management* **7**: 1–12. doi:10.1094/cm-2008-0730-03-rv.
- Nyborg, M., Laidlaw, J.W., Solberg, E.D., and Malhi, S.S. 1997. Denitrification and nitrous oxide emissions from a Black Chernozemic soil during spring thaw in Alberta.
- Nyborg, M., and Malhi, S.S. 1986. Comparison of Fall and Spring Application of Nitrogen Fertilizers in Northern and Central Alberta. *Can J Soil Sci* **66**: 225–236. doi:10.4141/cjss86-025.
- O'Donovan, J.T., Anbessa, Y., Grant, C.A., Macleod, A.L., Edney, M.J., Izydorczyk, M.S., Turkington, T.K., Juskiw, P.E., Lafond, G.P., May, W.E., Harker, K.N., Johnson, E.N., Beres, B.L., McAllister, T.A., Smith, E.G., and Chapman, W. 2015. Relative responses of new malting barley cultivars to increasing nitrogen rates in western Canada. *Canadian Journal of Plant Science* **95**: 831–839. Agricultural Institute of Canada. doi:10.4141/cjps-2014-415.
- Omonode, R.A., Halvorson, A.D., Gagnon, B., and Vyn, T.J. 2017. Achieving lower nitrogen balance and higher nitrogen recovery efficiency reduces nitrous oxide emissions in North America's maize cropping systems. *Front Plant Sci* **8**. Frontiers Media S.A. doi:10.3389/fpls.2017.01080.
- Pancheva, T. v., and Popova, L.P. 1998. Effect of salicylic acid on the synthesis of ribulose-1,5-bisphosphate carboxylase/oxygenase in barley leaves. *J Plant Physiol* **152**: 381–386. doi:10.1016/S0176-1617(98)80251-4.
- Puntel, L.A., Sawyer, J.E., Barker, D.W., Dietzel, R., Poffenbarger, H., Castellano, M.J., Moore, K.J., Thorburn, P., and Archontoulis, S. V. 2016. Modeling long-term corn yield response to nitrogen rate and crop rotation. *Front Plant Sci* **7**. Frontiers Research Foundation. doi:10.3389/fpls.2016.01630.
- Ransom, C.J., Jolley, V.D., Blair, T.A., Sutton, L.E., and Hopkins, B.G. 2020. Nitrogen release rates from slow- And controlled-release fertilizers influenced by placement and temperature. *PLoS One* **15**: 1–21. doi:10.1371/journal.pone.0234544.
- Rasmussen, I.S., Dresbøll, D.B., and Thorup-Kristensen, K. 2015. Winter wheat cultivars and nitrogen (N) fertilization—Effects on root growth, N uptake efficiency and N use efficiency. *European Journal of Agronomy* **68**: 38–49. Elsevier B.V. doi:10.1016/j.eja.2015.04.003.
- Reussi Calvo, N.I., Carciochi, W.D., Prystupa, P., Queirolo, I., and Sainz Rozas, H.R. 2022. Economic optimum nitrogen rate analysis for feed and malting barley. *Crop Sci* **62**: 1997–2010. John Wiley and Sons Inc. doi:10.1002/csc2.20808.
- Rochette, P., Liang, C., Pelster, D., Bergeron, O., Lemke, R., Kroebel, R., MacDonald, D., Yan, W., and Flemming, C. 2018. Soil nitrous oxide emissions from agricultural soils in Canada: Exploring relationships with soil, crop and climatic variables. *Agric Ecosyst Environ* **254**: 69–81. Elsevier B.V. doi:10.1016/j.agee.2017.10.021.
- Rochette, P., Worth, D.E., Lemke, R.L., McConkey, B.G., Pennock, D.J., Wagner-Riddle, C., and Desjardins, R.J. 2008. Estimation of N₂O emissions from agricultural soils in Canada. I. Development of a country-specific methodology. *Can J Soil Sci* **88**: 641–654. doi:10.4141/CJSS07025.
- Sainju, U.M. 2017. Determination of nitrogen balance in agroecosystems. *MethodsX* **4**: 199–208. Elsevier B.V. doi:10.1016/j.mex.2017.06.001.
- Saxton, K.E., and Rawls, W.J. 2006. Soil Water Characteristic Estimates by Texture and Organic Matter for Hydrologic Solutions. *Soil Science Society of America Journal* **70**: 1569–1578. Wiley. doi:10.2136/sssaj2005.0117.

- Setiyono, T.D., Yang, H., Walters, D.T., Dobermann, A., Ferguson, R.B., Roberts, D.F., Lyon, D.J., Clay, D.E., and Cassman, K.G. 2011. Maize-N: A decision tool for nitrogen management in maize. *Agron J* **103**: 1276–1283. doi:10.2134/agronj2011.0053.
- Shaviv, A., Raban, S., and Zaidel, E. 2003. Modeling controlled nutrient release from polymer coated fertilizers: Diffusion release from single granules. *Environ Sci Technol* **37**: 2251–2256. doi:10.1021/es011462v.
- Sheppard, S.C., Bittman, S., and Bruulsema, T.W. 2010. Monthly ammonia emissions from fertilizers in 12 Canadian Ecoregions. *Can J Soil Sci* **90**: 113–127. doi:10.4141/CJSS09006.
- Simova-Stoilova, L., Stoyanova, Z., and Demirevska-Kepova, K. 2001. Ontogenic Changes in Leaf Pigments, Total Soluble Protein and Rubisco in Two Barley Varieties in Relation to Yield. *Bulgarian Journal of Plant Physiology* **27**: 15–24.
- Smith, E.G., Clayton, G.W., O'Donovan, J.T., Turkington, T.K., Harker, K.N., Henderson, W.J., McKenzie, R.H., Juskiw, P.E., Lafond, G.P., May, W.E., Grant, C.A., Brandt, S., Johnson, E.N., and Edney, M.J. 2012. Net return risk for malting barley production in Western Canada as influenced by production strategies. *Agron J* **104**: 1374–1382. American Society of Agronomy. doi:10.2134/agronj2011.0416.
- Snyder, C.S., Bruulsema, T.W., Jensen, T.L., and Fixen, P.E. 2009. Review of greenhouse gas emissions from crop production systems and fertilizer management effects. *Agric Ecosyst Environ* **133**: 247–266. San Jose. doi:10.1016/j.agee.2009.04.021.
- Sogbedji, J.M., van Es, H.M., Klausner, S.D., Bouldin, D.R., and Cox, W.J. 2001. Spatial and temporal processes affecting nitrogen availability at the landscape scale. *Soil Tillage Res* **58**: 233–244. doi:10.1016/S0167-1987(00)00171-9.
- Soon, Y.K., Malhi, S.S., Lemke, R.L., Lupwayi, N.Z., and Grant, C.A. 2011. Effect of polymer-coated urea and tillage on the dynamics of available N and nitrous oxide emission from Gray Luvisols. *Nutr Cycl Agroecosyst* **90**: 267–279. doi:10.1007/s10705-011-9428-2.
- Stanford, G., Dzienia, S., and Vander Pol, R.A. 1975. Effect of Temperature on Denitrification Rate in Soils. *Soil Science Society of America Journal* **39**: 867–870. Wiley. doi:10.2136/sssaj1975.03615995003900050024x.
- Statistics Canada 2022. September 29. 2016 Census of Agriculture. [Online] Available: <https://www.statcan.gc.ca/en/ca2016> [2022 Nov. 12].
- Statistics Canada 2023. February 7. Table 32-10-0077-01 Farm product prices, crops and livestock. [Online] Available: <https://www150.statcan.gc.ca/t1/tbl1/en/tv.action?pid=3210007701&cubeTimeFrame.startMonth=07&cubeTimeFrame.startYear=2007&cubeTimeFrame.endMonth=11&cubeTimeFrame.endYear=2022&referencePeriods=20070701%2C20221101> [2023 Feb. 6].
- Steffen, W., Richardson, K., Rockström, J., Cornell, S.E., Fetzer, I., Bennett, E.M., Biggs, R., Carpenter, S.R., De Vries, W., De Wit, C.A., Folke, C., Gerten, D., Heinke, J., Mace, G.M., Persson, L.M., Ramanathan, V., Reyers, B., and Sörlin, S. 2015. Planetary boundaries: Guiding human development on a changing planet. *Science (1979)* **347**. American Association for the Advancement of Science. doi:10.1126/science.1259855.
- Stewart, W.M., Dibb, D.W., Johnston, A.E., and Smyth, T.J. 2005. The contribution of commercial fertilizer nutrients to food production. *Agron J* **97**: 1–6. American Society of Agronomy. doi:10.2134/agronj2005.0001.
- Thapa, R., Chatterjee, A., Awale, R., McGranahan, D.A., and Daigh, A. 2016. Effect of Enhanced Efficiency Fertilizers on Nitrous Oxide Emissions and Crop Yields: A Meta-analysis. *Soil Science Society of America Journal* **80**: 1121–1134. doi:10.2136/sssaj2016.06.0179.

- Thilakarathna, S.K., Hernandez-Ramirez, G., Puurveen, D., Kryzanowski, L., Lohstraeter, G., Powers, L.A., Quan, N., and Tenuta, M. 2020. Nitrous oxide emissions and nitrogen use efficiency in wheat: Nitrogen fertilization timing and formulation, soil nitrogen, and weather effects. *Soil Science Society of America Journal* **84**: 1910–1927. John Wiley and Sons Inc. doi:10.1002/saj2.20145.
- Ti, C., Xia, L., Chang, S.X., and Yan, X. 2019. Potential for mitigating global agricultural ammonia emission: A meta-analysis. *Environmental Pollution* **245**: 141–148. Elsevier Ltd. doi:10.1016/j.envpol.2018.10.124.
- Udvardi, M., Below, F.E., Castellano, M.J., Eagle, A.J., Giller, K.E., Ladha, J.K., Liu, X., Maaz, T.M.C., Nova-Franco, B., Raghuram, N., Robertson, G.P., Roy, S., Saha, M., Schmidt, S., Tegeder, M., York, L.M., and Peters, J.W. 2021. May 31. A Research Road Map for Responsible Use of Agricultural Nitrogen. *Frontiers Media S.A.* doi:10.3389/fsufs.2021.660155.
- United Nations Environment Programme 2014. *UNEP Year Book 2014 Emerging Issues in our Global Environment*. [Online] Available: <https://www.unep.org/resources/year-books> [2022 Jan. 9].
- Venterea, R.T., Halvorson, A.D., Kitchen, N., Liebig, M.A., Cavigelli, M.A., Grosso, S.J. Del, Motavalli, P.P., Nelson, K.A., Spokas, K.A., Singh, B.P., Stewart, C.E., Ranaivoson, A., Strock, J., and Collins, H. 2012. Challenges and opportunities for mitigating nitrous oxide emissions from fertilized cropping systems. *Front Ecol Environ* **10**: 562–570. doi:10.1890/120062.
- Venterea, R.T., Maharjan, B., and Dolan, M.S. 2011. Fertilizer Source and Tillage Effects on Yield-Scaled Nitrous Oxide Emissions in a Corn Cropping System. *J Environ Qual* **40**: 1521–1531. Wiley. doi:10.2134/jeq2011.0039.
- Wilson, M.L., Rosen, C.J., and Moncrief, J.F. 2010. Effects of Polymer-coated Urea on Nitrate Leaching and Nitrogen Uptake by Potato. *J Environ Qual* **39**: 492–499. doi:10.2134/jeq2009.0265.
- Yang, J.Y., Drury, C.F., Jiang, R., Yang, X.M., Worth, D.E., Bittman, S., Grant, B.B., Smith, W.N., and Reid, K. 2023. Simulating nitrogen balance in Canadian agricultural soils from 1981 to 2016. *J Environ Manage* **341**: 118015. doi:10.1016/j.jenvman.2023.118015.
- Yang, M., Zhu, X., Bai, Y., Sun, D., Zou, H., Fang, Y., and Zhang, Y. 2021. Coated controlled-release urea creates a win-win scenario for producing more staple grains and resolving N loss dilemma worldwide. *J Clean Prod* **288**. Elsevier Ltd. doi:10.1016/j.jclepro.2020.125660.
- Zebarth, B.J., Drury, C.F., Tremblay, N., and Cambouris, A.N. 2009. Opportunities for improved fertilizer nitrogen management in production of arable crops in eastern Canada: A review. *Can J Soil Sci* **89**: 113–132. doi:10.4141/CJSS07102.
- Zebarth, B.J., Rochette, P., and Burton, D.L. 2008. N₂O emissions from spring barley production as influenced by fertilizer nitrogen rate. *Can J Soil Sci* **88**: 197–205. doi:10.4141/CJSS06006.
- Zhang, W., Liang, Z., He, X., Wang, X., Shi, X., Zou, C., and Chen, X. 2019. The effects of controlled release urea on maize productivity and reactive nitrogen losses: A meta-analysis. *Environmental Pollution* **246**: 559–565. Elsevier Ltd. doi:10.1016/j.envpol.2018.12.059.