- **1** Spatially-distributed influence of agro-environmental factors
- 2 governing nitrate fate and transport in an irrigated stream-
- 3 aquifer system
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20 Abstract

Elevated levels of nitrate (NO₃) in groundwater systems pose a serious risk to human populations 21 and natural ecosystems. As part of an effort to remediate NO₃ contamination in irrigated stream-22 aquifer systems, this study elucidates agricultural and environmental parameters and processes 23 that govern NO₃ fate and transport at the regional (500 km²), local (50 km²), and field scales (< 1 24 km²). Specifically, the revised Morris sensitivity analysis method was applied to a finite-25 26 difference nitrogen cycling and reactive transport model of a regional-scale study site in the Lower Arkansas River Valley in southeastern Colorado. The method was used to rank the 27 28 influence of anthropogenic activities and natural chemical processes on NO₃ groundwater 29 concentration, NO₃ mass leaching, and NO₃ mass loading to the Arkansas River from the aquifer. Sensitivity indices were computed for the entire study area in aggregate as well as each 30 canal command area, crop type, and individual grid cells. Results suggest that fertilizer loading, 31 32 crop uptake, and heterotrophic denitrification govern NO₃ fate and transport for the majority of the study area, although their order of influence on NO₃ groundwater concentration and mass 33 leaching varies according to crop type and command area. Canal NO₃ concentration and rates of 34 autotrophic denitrification, nitrification, and humus decomposition also dominate or partially 35 dominate in other locations. Each factor, with the exception of O₂ reduction rate, is the 36 dominating influence on NO₃ groundwater concentration at one or more locations within the 37 study area. Results can be used to determine critical processes and key management actions for 38 future data collection and remediation strategies, with efforts able to be focused on localized 39 40 areas.

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42 **1 Introduction**

During recent decades, elevated concentration of nitrate (NO₃) C_{NO_3} in groundwater systems and at points of groundwater discharge to surface water bodies has become a serious environmental issue due to its adverse effects on human populations and natural ecosystems [Spalding and Exner, 1993]. Specific problems associated with high C_{NO_3} include methemoglobinemia for infants [Fan and Steinberg, 1996] and eutrophication in aquatic systems, which induces depletion

of dissolved oxygen (O₂) (hypoxia) due to increased biological activity. In addition, high C_{NO} can 48 lead to elevated concentrations of sulfate and selenium (Se) via oxidation of pyrite (FeS₂) and 49 seleno-pyrite (FeSe₂) from marine shale [Frind et al., 1990; Jørgensen et al., 2009; Bailey et al., 50 51 2012]. NO₃ also has been shown to mobilize uranium via oxidation [Wu et al., 2010]. Recent studies have revealed that certain rock formations can yield nitrogen (N) in response to a variety 52 53 of biogeochemical processes [Holloway and Dahlgren 2002, Montross et al 2013]. In most cases, 54 however, elevated concentrations result from excessive loadings of organic or inorganic N 55 fertilizer, inducing NO₃ leaching to the saturated zone of the aquifer [Korom, 1992; Spalding and Exner, 1993]. 56

57 To combat NO₃ contamination, numerous field and modeling studies have been performed to quantify NO₃ fate and transport processes in soil-groundwater systems, identify baseline 58 conditions of N sources and transport patterns, and investigate potential remediation strategies. 59 For the latter, simulation models typically are used to predict the effect of land use and best-60 61 managements practices (BMPs) such as reduction in fertilizer loading [Chaplot et al., 2004; Almasri and Kaluarachchi, 2007; Lee et al., 2010], reduction in applied irrigation water [Ma et 62 63 al., 1998; Rong and Xuefeng, 2011], and implementing or enhancing riparian buffer zones [Hefting and Klein, 1998; Spruill, 2000; Vaché et al., 2002; Sahu and Gu, 2009] on overall C_{NO_3} 64 and on NO₃ mass loading to and within streams. These studies have been conducted at various 65 scales [Ocampo et al., 2006], ranging from the soil profile and field scale [Johnsson et al., 1987; 66 Ma et al., 1998; Rong and Xuefeng, 2011], to the catchment scale [Birkinshaw and Ewen, 2000; 67 68 Conan et al., 2003; Wriedt and Rode, 2006; Lee et al., 2010], to the regional-scale watershed or 69 river basin scale [Chaplot et al., 2004; Almasri and Kaluarachchi, 2007; Bailey et al., 2015], and 70 include a variety of fate and transport processes such as soil N cycling, leaching, groundwater transport, and overland transport. 71

72 Besides assessing baseline conditions and predicting domain-scale effects on spatial

concentrations and loadings, numerical models also can be used in NO₃ remediation to determine

the system inputs, parameters, and processes (i.e., model factors) that govern these

- concentrations and loadings. In general, identifying the most influential processes on resulting
- 76 C_{NO_3} and mass loading can assist in establishing optimal remediation strategies. Additional

benefits of the analysis include guiding effective field sampling strategies by focusing on
influential system variables or inputs; facilitating model calibration and testing by focusing on
the identified key factors [Sincock et al., 2003; Almasri and Kaluarachchi, 2007]; identifying
factors that require additional research to improve model performance [Hall et al., 2009]; and
detecting non-influential parameters or processes that possibly could be eliminated to simplify
the model [Saltelli et al., 2008].

An appealing approach to determine the influence of model factors is sensitivity analysis (SA),
which relates changes in model output variables (e.g., concentration, mass loading) to prescribed

changes in model factor input values (e.g., initial conditions, system stresses, system
parameters). For studies assessing NO₃ fate and transport in groundwater systems using

87 physically-based spatially-distributed groundwater models, sensitivity analysis typically is

performed in a simple fashion due to model complexity and computational cost. For example,

Almasri and Kaluarachchi [2007] increased values of selected parameters (e.g., denitrification

90 rate, longitudinal dispersivity, initial concentration, soil mineralization rate, soil nitrification rate,

91 fertilizer loading) by 50% to determine their influence on simulated C_{NO_3} in a watershed in

92 Washington state, USA; Ehteshami et al. [2013], using the LEACHN model, investigated the

93 influence of low and high values of rainfall and initial C_{NO_3} for two soil types on soil C_{NO_3} . In a

field study using the RISK-N model, Oyarzun et al. [2007] modified values of soil initial N, $C_{NO_{1}}$

95 in irrigation water, fertilizer, N crop uptake, crop evapotranspiration (ET), and soil properties by

96 50%, 70%, 100%, 125%, and 150% to investigate their influence on NO₃ vadose zone mass flux

97 and C_{NO_3} in the groundwater. Also, Hartmann et al. [2013] used SA to estimate the influence of

98 model parameters on the time lag between spring discharge and NO₃ at several karst aquifer sites

across Europe. Whereas global effects of the model factor on system-response variables can be

assessed, local and interaction effects cannot be quantified.

101 A more rigorous SA method is global sensitivity analysis (GSA), which searches the entire

102 parameter space to identify the importance of model parameters and interactions thereof. Such

methods include the Elementary Effects (EE) method [Morris, 1991; Cacuci, 2003], a screening

104 method that identifies the most important model factors and is well-suited for large models

105 [Campolongo and Braddock, 1999], and variance-based methods that quantitatively decompose

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the variance of model output into fractions that are attributed to model factors [Saltelli et al.,

107 2008]. A number of hydrologic modeling studies have used GSA methods for assessing model

108 factor influence on overall watershed nutrient and sediment processes [White and Chaubey,

109 2005; Arabi et al., 2007; Sun et al., 2012, Ahmadi et al., 2014], flooding and hydraulic

110 characteristics [Hall et al., 2005; Hall et al., 2009], in-stream water quality [Cox and Whitehead,

111 2005; Deflandre et al., 2006; Liu and Zou, 2012; Bailey and Ahmadi, 2014], and in-stream solute

transport [Kelleher et al., 2013].

Sensitivity analysis is commonly used in hydrologic and water quality modeling to identify the 113 114 influence of model parameters on an aggregated measure of model responses such as average 115 annual stream discharge or contaminant loads. A few studies have assessed how the results of SA vary in time. For example Reusser et al. [2011] used hydrologic catchment models to investigate 116 the temporal-varying influence of model factors on a variety of watershed response variables for 117 118 catchments in Ecuador and Germany. However, the spatial variability of sensitivity indices has 119 been largely neglected. Specifically regarding this study, no studies have quantified the spatialvarying influence of factors on solute concentrations in large-scale groundwater systems. Such 120 information could be valuable in terms of implementing site-specific remediation strategies, 121 facilitating model calibration for specific model domain regions, and identifying system 122 variables that require additional field data collection, particularly for NO₃ due to its ubiquitous 123 presence in groundwater systems worldwide. 124

This study aims to identify the spatially-varying influence of system factors on NO₃ fate and transport in a regional-scale (506 km²) irrigated hydro-agricultural system. Specifically, the factors' influence on NO₃ groundwater concentrations, NO₃ leaching below root zone, and NO₃ groundwater mass loading to the stream network will be quantified for a variety of scales (cultivated field, canal command area, region). A calibrated and tested N fate and transport groundwater model is used for the assessment, with the modified Morris method used for the sensitivity analysis.

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134 2 Methods

135 A comprehensive SA method was applied to a regional-scale, intensively irrigated 506 km²

136 groundwater system in the Lower Arkansas River Valley (LARV) in southeastern Colorado to

identify the spatially-varying influence of system factors on NO₃ concentrations in groundwater,

138 NO₃ mass leaching in the shallow soil zone, and NO₃ mass loading to the Arkansas River. The

model used is UZF-RT3D [Bailey et al., 2013a, 2013b], a MODFLOW [Niswonger et al., 2011]

based, finite-difference model designed for N fate and transport at the regional scale and recently

calibrated and tested for the study area [Bailey et al., 2014]. The model accounts for major

agricultural inputs (fertilizer, canal seepage, irrigation water), processes (N cycling in the root

and soil zone, leaching, three-dimensional transport, heterotrophic and autotrophic

144 denitrification), and outputs (mass loading to the stream network).

As identifying the relative importance of parameters and processes in space is the objective of

this study, and since computational costs of UZF-RT3D are extremely high (run-time of

approximately 3.5 hours for a single simulation using an Intel® Core™ i7-3770 CPU @

148 3.40GHz desktop computer), the SA method used is an improved variant [Campolongo et al.,

149 2007] of the Morris method [Morris, 1991] rather than variance-based SA methods such as

Sobol' [Sobol', 1993] or FAST (Fourier Amplitude Sensitivity Test) [Cukier et al., 1973]. Nine

model factors are included in the assessment, with their overall influence on NO₃ fate and

transport evidenced in a previous study in the region [Bailey et al., 2014]. In conjunction with

the SA methodology, model results are processed to determine the dominant model factors

154 globally (i.e., averaged for the entire model domain), for each irrigation canal command area, for

each crop type (i.e., the set of model grid cells associated with each crop type), and for each grid

156 cell, thereby elucidating parameter influence at varying spatial scales. For the latter, spatial

157 contour maps depicting model sensitivity to individual model factors are shown. Due to the

dependence of N fate and transport on the presence of O_2 , the influence of the 9 model input

159 factors on C_{o_1} also is calculated and presented.

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162 2.1 Study Area

The semi-arid LARV in Colorado extends from the outlet of the Arkansas River from Pueblo 163 Reservoir eastward across southeastern Colorado to the border with Kansas (Figure 1), with the 164 Arkansas River fed primarily by snowmelt from the mountainous regions of the upper Arkansas 165 basin. In total, the valley supports approximately 109,000 irrigated ha (270,000 ac), and is one of 166 Colorado's most productive agricultural areas. Approximately 14,000 fields are cultivated, with 167 168 the majority using flood irrigation methods and a small minority using sprinklers or drip irrigation methods. Major crops include alfalfa, corn, grass hay, wheat, sorghum, dry beans, 169 170 cantaloupe, watermelon, melons, and onions.

The region of the LARV focused on in this study is shown in Figure 1. The boundary of the 171 study area is shown with a black line, and encompasses an area of 50,600 ha (125,000 ac), of 172 which 26,400 ha (65,300 ac) are irrigated. The fields receiving water from each of six main 173 174 irrigation canals (i.e. canal command areas) are shown in Figure 2a, with crop type cultivated in 2006 for each field shown in Figure 2b. Due to over-irrigation and poor subsurface drainage, 175 high water table elevations have been established in recent decades, with water table depth below 176 ground surface often between 1-3 m [Morway and Gates, 2012]. These high water tables have 177 178 resulted in salinization and waterlogging, in addition to substantial rates of groundwater return flows (i.e. discharge) to the Arkansas River and its tributaries [Morway et al., 2013]. The 179 180 thickness of the alluvial aquifer ranges from 4 to 34 m (Figure 4A), and is underlain by Cretaceous Shale [Scott, 1968; Sharps, 1976] in both solid and weathered form. 181

182 In addition to salinization and associated decrease in crop productivity [Morway and Gates,

183 2012], elevated groundwater C_{NO_3} has been observed, presumably due to over-fertilization on

184 cultivated fields. In a similar irrigated region of the LARV, located about 67 km upstream,

185 Zielinski et al. [1997] examined δ^{15} N isotopic signatures to conclude that NO₃ was derived

primarily from fertilizer and crop waste, not from proximate geologic sources. To assess the

- 187 C_{NO_2} in the study region, groundwater and surface water samples were collected (see locations in
- 188 Figure 2a) during 10 sampling events over the period 2006-2009 [Gates et al. 2009]. For
- groundwater, samples were taken routinely from 52 observation wells, with groundwater from 37

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190 additional observation wells sampled non-routinely (aperiodic). Surface water samples were taken from 10 locations along the Arkansas River and 5 locations in tributaries. Detailed results 191 192 of the monitoring scheme are shown in Supplementary Data. In summary, for groundwater the 85^{th} percentile values of $C_{_{NO_2-N}}$ were at or in excess of the 10 mg/L (85^{th} percentile) EPA 193 drinking water standard for the first three sample trips. The maximum measured value was 66 194 195 mg/L. The means for the samples gathered from the Arkansas River and its tributaries were 1.53 mg/L and 1.95 mg/L, respectively. The annual median values of the Arkansas River samples 196 197 were 0.95, 1.20, 1.10, and 2.20 mg/L for each of the successive years within the period 2006 -2009, compared to the Colorado interim standard of 2 mg/L [CDPHE, 2012] for total N 198 concentration ($C_{NO_2-N} + C_{NO_2-N} + C_{NH_4-N}$). The concentration of C_{NO_2-N} exceeded 2 mg/L in about 199 25% of the samples gathered in the river over this period and exceeded 2.5 mg/L in about 12% of 200 the samples, signifying the growing concern about N pollution in the river. Analysis of 22 river 201 samples and 15 tributary samples in 2013 revealed that C_{NO_3-N} made up greater than 80% of total 202 dissolved N in the river and about 76% of total dissolved N in the tributaries. 203

204 2.2 UZF-RT3D N Reaction Module and Baseline Application

UZF-RT3D simulates the reactive transport of multiple interacting chemical species in variably-205 saturated porous media using groundwater flow rates, water content, and a variety of 206 groundwater sources and sinks (e.g., applied irrigation water, pumping, canal seepage, 207 groundwater-surface water interactions) simulated by a MODFLOW-NWT model using the 208 209 UZF1 package. The N cycling and reaction module add-on package [Bailey et al., 2013b] was designed for model application in an irrigated agricultural groundwater system, and accounts for 210 the major hydrologic, chemical, and land management processes that govern N fate and transport 211 212 in an irrigated stream-aquifer system. Also, due to the dependence of N cycling and transport on the presence of O_2 , the fate and transport of O_2 is included. 213

A schematic of the fate and transport of N species and O₂ as simulated by the N reaction module of UZF-RT3D is depicted in Figure 3A. N mass (NO₃ or NH₄) enters the subsurface via fertilizer loading (single application or split application), canal seepage, infiltrating irrigation water (either from canal water or pumped groundwater), or seepage from the stream network (Arkansas River

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and its tributaries). N mass exits the subsurface via groundwater discharge to the stream network. 218 N cycling occurs in the root and soil zone, with organic N and carbon (C) added to soil organic 219 220 matter (manure M_N, fast-decomposing litter L_N, flow-decomposing humus H_N) via after-harvest plowing or decaying root mass and subsequently mineralized to NH₄, which can be volatilized, 221 nitrified to NO₃, or taken up with NO₃ into crop roots during the growing season. The timing of 222 land management actions, e.g. fertilizer loading (40%, 60% split application), irrigation events, 223 224 harvesting, and plowing, adopted in the module is shown in Figure 3B. NH₄ is sorbed readily to soil surface sites, whereas NO₃ is transported by one-dimensional transport in the unsaturated 225 zone and three-dimensional transport in the saturated zone, subject to heterotrophic 226 denitrification in near-surface areas and autotrophic denitrification in the presence of FeS₂-227 bearing marine shale (see Figure 1). O₂ also is subject to heterotrophic and autotrophic chemical 228

229 reduction.

UZF-RT3D solves a system of advection-dispersion-reaction (ADR) equations for interacting
dissolved-phase and solid-phase species using the finite-difference approach. Including ADR
processes and source/sink terms as depicted, the following mass conservation equations are
written for the dissolved-phase species (NO₃, NH₄, O₂) in the N reaction module:

$$\frac{\partial \left(C_{NH_{4}}\theta\right)}{\partial t}R_{NH_{4}} = -\frac{\partial}{\partial x_{i}}\left(\theta v_{i}C_{NH_{4}}\right) + \frac{\partial}{\partial x_{i}}\left(\theta D_{ij}\frac{\partial C_{NH_{4}}}{\partial x_{j}}\right) + q_{f}C_{f_{NH_{4}}} + F_{NH_{4}} - U_{NH_{4}} + \varepsilon\left(r_{s,N}^{min} - r_{s,N}^{imm}\right) + \theta\left(-r_{f}^{nit} - r_{f}^{vol}\right)$$

$$(1)$$

$$\frac{\partial \left(C_{NO_3}\theta\right)}{\partial t} = -\frac{\partial}{\partial x_i} \left(\theta v_i C_{NO_3}\right) + \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_{NO_3}}{\partial x_j}\right) + q_f C_{f_{NO_3}} + F_{NO_3} - U_{NO_3} + \theta \left(r_f^{nit} - r_{f,NO_3}^{het} - r_{f,NO_3}^{auto}\right)$$
(2)

$$\frac{\partial \left(C_{O_2}\theta\right)}{\partial t} = -\frac{\partial}{\partial x_i} \left(\theta v_i C_{O_2}\right) + \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_{O_2}}{\partial x_j}\right) + q_f C_{f_{O_2}} + \theta \left(-r_{f,O_2}^{het} - r_{f,O_2}^{auto}\right)$$
(3)

where C is solute concentration $[M_f L_f^{-3}]$, with f denoting fluid phase; v is the pore velocity $[L_b T^{-3}]$

¹], provided by MODFLOW-UZF1; θ is the volumetric water content $[L_f^3 L_b^{-3}]$, also provided by

MODFLOW-UZF1; D_{ij} is the hydrodynamic dispersion coefficient [L²T⁻¹]; q_f is the volumetric

flux of water representing sources and sinks $[L_f^3 T^{-1} L_b^{-3}]$ such as irrigation water, canal and river 237 seepage, groundwater discharge to the river, or pumped groundwater, with b denoting the bulk 238 phase; C_f is the concentration of the source or sink $[M_f L_f^{-3}]$; F is the inorganic fertilizer 239 application $[M_f L_b^{-3} T^1]$; U is the potential crop uptake rate $[M_f L_b^{-3} T^{-1}]$; ε is the volumetric solid 240 content $[L_s^3 L_b^{-3}]$ with s denoting the solid phase, and is equal to $1-\phi$, where ϕ is porosity $[L_f^3 L_b^{-3}]$ 241 ³]; r_f represents the rate of all reactions that occur in the dissolved-phase [M_fL_f⁻³T⁻¹]; *min, imm*, 242 nit, and vol signify mineralization, immobilization, nitrification, and volatilization of NH₄, 243 respectively; and *auto* and *het* represent autotrophic and heterotrophic chemical reduction, 244 respectively. ε is included for the min and imm reactions to denote a mass transfer between the 245 solid and dissolved phases. For NH₄, which is subject to sorption, R is the retardation factor and 246 is equal to $1 + (\rho_b K_{d, NH_a})/\theta$, where ρ_b is the bulk density of the porous media $[M_b L_b^{-3}]$ and 247 K_{d, NH_4} is the partitioning coefficient [L_f⁻³M_b]. The daily mass of potential N crop uptake during 248 the growing season is determined using a logistic equation [Johnsson et al., 1987] and is 249 distributed across the vertical column of grid cells encompassing the crop rooting depth 250 251 according to the mass density of the root system. Mass conservation equations (not shown) for solid-phase organic N (and C) species L_N, H_N, and M_N also are implemented. 252

The rate of chemical reactions r_f included in Equations (1-3) is governed by the dependence of the chemical reaction on soil temperature T, θ , and the presence of O₂ and C. These rates are simulated using first-order Monod kinetics. For example, the following rate law expression represents the process of heterotrophic denitrification, with others contained in Bailey et al. [2015]:

$$r_{f,NO_3}^{het} = \lambda_{NO_3}^{het} C_{NO_3} \left(\frac{C_{NO_3}}{K_{NO_3} + C_{NO_3}} \right) \left(\frac{CO_{2,prod}}{K_{CO_2} + CO_{2,prod}} \right) \left(\frac{I_{O_2}}{I_{O_2} + C_{O_2}} \right) E$$
(4)

where λ is the base rate constant for the reaction $[T^{-1}]$; K_j is the Monod half-saturation constant for species $j [M_f L_f^{-3}]$; I_{O_2} is the O₂ inhibition constant $[M_f L_f^{-3}]$ signifying the species concentration at which lower-redox species can undergo appreciable rates of reduction; $CO_{2,prod}$ is the total mass of CO₂ produced during organic matter decomposition and is used as an indicator of

available organic carbon (OC) for microbial consumption [Birkinshaw and Ewen, 2000]; and *E* [-] is an environmental reduction factor that accounts for θ and *T* and acts to temper microbial activity rates [Birkinshaw and Ewen, 2000; Bailey et al., 2013b]. Nitrification, mineralization, and denitrification each have uniquely specified relationships between θ and microbial activity.

The UZF-RT3D model used in this study is the same as that described in Bailey et al. [2014].

267 The model uses output from a calibrated and tested MODFLOW-NWT [Niswonger et al., 2011]

model of the study region [Morway et al., 2013], which uses the UZF1 unsaturated-zone flow

package [Niswonger et al., 2006]. The flow model uses weekly estimates of irrigation water,

270 precipitation, canal seepage, crop ET to estimate groundwater level and groundwater-surface

water interactions for the 1999-2009 time period. Figures 4b, 4c, and 4d show the finite-

difference grid, the simulated water content of the soil in June 2006, and the average simulated

water table elevation (m) during the 1999-2009 time period, respectively.

274 The UZF-RT3D model uses the same model domain and finite difference grid as the flow model (see Figure 4B). The model has 7 vertical layers, with Layers 1-2 (0.5 m each) corresponding to 275 the root zone, Laver 3 (1.0 m) corresponding to the leaching zone, Lavers 4-6 to the saturated 276 zone, and Layer 7 to the shale bedrock formation. Thickness of layers 4, 5, and 6 varies 277 278 according to saturated thickness, with layer thickness ranging from 2.8 m to 12.6 m. Each vertical column of cells in the 3D grid is assigned a set of crop parameter values according to the 279 portions of fields within the grid cell area. Crop parameters, with values shown in Table 1 for 280 each crop type in the study area, include: Planting Day; Harvest Day; Plowing Day; mass of 281 282 stover plowed into the soil P_{St} (kg/ha) after harvest; maximum rooting depth $d_{rt,max}$ (m), which controls N uptake; C-N ratio of root mass CN_{RT} ; fertilizer loading $F_{NH_{*}}$ (kg/ha), maximum 283 seasonal uptake values of N N_{up} (kg/ha), depth of plowing d_{pw} (m); mass of decaying roots P_{Rt} 284 (kg/ha); C-N ratio of stover mass CN_{ST}; and constants defining root growth and daily uptake rate 285 U. Chemical reaction parameter values are shown in Table 2, with an asterisk * indicating the 286 mean value of all the grid cells. C_{NO_3} and C_{O_2} of canal water and irrigation water were based on 287 observed data. The model was run for the 2006-2009 and tested against spatio-temporal averages 288 of groundwater C_{NO_3} and NO₃ mass loadings from the aquifer to the Arkansas River. 289

290 **2.3 Assessing Major Controls on NO₃ Fate and Transport**

291 2.3.1 Morris SA Methodology

292 The Morris screening method for global SA is based on an individually randomized one-at-a-

time (OAT) design that provides information regarding (i) the main effect of each input

294 parameter on model output responses and (ii) the overall effects including interactions between

parameters. For example, consider a model M with a vector of k parameters (ω_{i} i = 1,...,k) within

the feasible parameter space, Ω , that simulates *m* response vectors of the system (S_{i} , j = 1, ..., m):

$$\left[S_{1},\ldots,S_{m}\right] = M\left(\omega_{1},\ldots,\omega_{k}\right) \tag{5}$$

Similar to any standard SA practice, parameters are drawn from their predefined distributions, with each model input parameter ω_i varied across *p* discrete values [Saltelli et al., 2008]. After running model *M* for the given parameter sets, the local sensitivity measure (also referred to as the *elementary effect*, *EE*) is then computed for each parameter *i* for model response *j* as follows:

$$EE_{i,j}(\boldsymbol{\omega}) = \left(\frac{S_j(\omega_1, \dots, \omega_{i-1}, \omega_i + \Delta, \dots, \omega_k) - S_j(\boldsymbol{\omega})}{\Delta}\right)$$
(6)

where Δ is a value in the predefined increments (i.e. $\left[\frac{1}{(p-1),...,1-1}{(p-1)}\right]$) and $\boldsymbol{\omega} = \omega_1,...,\omega_k$ is a random sample in the parameter space so that the transformed point $(\omega_1,...,\omega_{i-1},\omega_i + \Delta,...\omega_k)$ is still within the parameter space $\boldsymbol{\Omega}$ [Saltelli et al., 2008]. The resulting distribution EE_i associated with each parameter ω_i is then analyzed to determine μ , the mean of the distribution which assesses the overall importance of the parameter on the model output; and σ , the standard deviation of the distribution, which indicates non-linear effects and/or interactions [Campolongo et al., 2007].

To determine sensitive and insensitive values, it is recommended to evaluate a graphical representation of σ vs. μ . However, for non-monotonic models, some *EE* values with opposite signs may cancel out when μ is calculated, and hence Campolongo and Saltelli [1997] proposed

the use of μ^* , the sample mean of the distribution of absolute values of *EE*. μ^* includes all types of effects that parameters can have on output responses and, therefore, is a global measure of output sensitivity to the parameters [Campolongo et al., 2007]. $\mu^*_{i,j}$ is defined as the mean of absolute values of the computed elementary effects *EE*_{*i,j*}. The total computational cost of the

Morris experiment is n = r(k+1) runs, where *r* is the selected size of each sample.

As noted above, an important objective of SA is to determine the most influential model input parameters. Hence, it is important to measure the level of agreement between results of SA experiments with an emphasis on the high-ranked parameters. Campolongo and Saltelli [1997] suggested the use of the Savage score to facilitate comparison of results from different SA experiments (see next section). The Savage score is defined as follows [Iman and Conover, 1987]:

$$SS_i = \sum_{h=i}^k \frac{1}{h} \tag{7}$$

where *i* is the rank assigned to the *i*th model parameter based on the Morris μ^* . For example, the highest ranked variable would have a score of $1/1 + \frac{1}{2} + \frac{1}{3} + ... + \frac{1}{k}$. The second ranked variable would have a score of $\frac{1}{2} + \frac{1}{3} + ... + \frac{1}{k}$, and so on. Savage scores typically are preferred because they place higher emphasis on the agreement of the key drivers (i.e. higher ranked parameters), rather than the overall agreement. The Savage score can be used in aggregating the results from different SA methods.

328 2.3.2 Model Input Factors Analyzed

In applying the SA method to the UZF-RT3D model of the study area, 9 model input factors were analyzed for impact on model results: F_{NH_4} , N_{up} , C_{NO_3} in canal water $Canal_{NO_3}$, rate of litter pool decomposition λ_L , rate of humus pool decomposition λ_H , rate of autotrophic reduction of O₂ in the presence of shale $\lambda_{O_2}^{auto}$, rate of autotrophic reduction of NO₃ in the presence of shale $\lambda_{NO_3}^{auto}$, rate of nitrification λ_{nit} , and rate of heterotrophic denitrification $\lambda_{NO_3}^{het}$. $Canal_{NO_3}$ conveys NO₃ mass into the subsurface system via applied irrigation water as well as seeped canal water. For each

simulation, separate values of F_{NH_a} and N_{up} were generated for each crop type, separate values of 335 $Canal_{NO_3}$ were generated for each of the six canal command areas, and separate values of $\lambda_{O_2}^{auto}$, 336 $\lambda_{NO_3}^{auto}$, and λ_{nit} were generated for each command area. The mean of each parameter value is 337 derived from the baseline simulation (see Tables 1 and 2), with the mean values of $\lambda_{O_2}^{auto}$, $\lambda_{NO_3}^{auto}$, 338 and λ_{nit} for each command area estimated during the calibration phase [Bailey et al., 2014]. 339 Setting the number of replications r and levels p of the Morris scheme to 20 and 10, respectively, 340 a total of 280 simulations were run. Parameter values were perturbed using a coefficient of 341 variation (CV) of 0.2 for all parameters except for $Canal_{NO_3}$, which was perturbed with a CV of 342 343 0.1 based on variance in observed canal water concentrations. Perturbation for the reaction rates $(\lambda_L, \lambda_H, \lambda_{O_2}^{auto}, \lambda_{NO_3}^{auto}, \lambda_{NO_3}^{het}, \lambda_{nit})$ was performed using log values since statistically these rates 344 typically conform to a lognormal distribution [Parkin and Robinson, 1989; McNab and Dooher, 345 1998]. CV values were selected by comparing the resulting spread of parameter values to values 346 found in the literature and from field data in the study area. The values of $F_{NH_{a}}$, $\lambda_{NO_{a}}^{auto}$, and 347 Canal_{NO2} for each of the 280 simulations are shown in Figure 5, with averages of 250 kg/ha, 348 $1.055 \times 10^{-4} \text{ day}^{-1}$, and 2.6 g m⁻³, respectively. The values shown in Figure 5A are for grid cells 349 that contain corn, and the values shown in Figures 5B and 5C are for the grid cells within the 350 351 Rocky Ford Highline canal command area (canal feeding the gray-shaded fields in Figure 2A). For each of the 280 simulations, the model was run for a 2-year spin-up period, followed by the 352 2006-2009 period. Model results were processed to determine the influence of the 9 targeted 353 model input factors on groundwater C_{NO_3} , NO₃ mass leached from the root zone, and total NO₃ 354 mass loading to the Arkansas River from the aquifer. Post-processing was implemented to 355 determine this influence (i) globally for the entire study area, i.e. averaging values from all grid 356 cells; (ii) for individual crop types, i.e. averaging values from all grid cells corresponding to a 357 given crop type; (iii) for individual canal command areas, i.e. averaging values from all grid cells 358 within a given command areas; and (iv) for individual grid cells. As total NO₃ mass loading to 359 360 the Arkansas River occurs along the entire reach of the river within the study area, parameter influence is assessed only for (i). Values of average concentration, average leaching, and total 361

mass loading were processed from the final year of the model simulation (i.e. 2009). For groundwater C_{NO_3} , concentration values were taken from Layer 4 of the model, which corresponds to the depth of observation well screens in the study area. For NO₃ leaching, values are taken from Layer 3 (i.e. the mass leached from Layer 3 to Layer 4). For parameter influence on C_{NO_3} for individual grid cells (item iv), the Savage score as calculated by Equation (7) will be used for presentation of results. Also for (iv), the parameter influence on C_{O_2} will be presented.

368

369 3 Results and Discussion

370 3.1 General Model Results

Model results from one of the 280 simulations is shown in Figure 6, with spatial distribution of 371 C_{O_2} and C_{NO_3} shown in Figures 6A and 6B, respectively for July 22, 2009, and the spatial 372 distribution of NO₃ mass loading shown for one week during the winter (December 2 2006, 373 Figure 6C) and one week during the summer (August 10 2008, Figure 6D). Mass loadings from 374 the aquifer to the stream network (discharge) are displayed in red, whereas loadings from the 375 stream network to the aquifer (seepage) are displayed in green. For concentrations in 376 groundwater, values of C_{O_2} range from 0.0 to 10.3 mg/L, with an average value of 2.7 g m⁻³ for 377 the 7,776 active grid cells. Values of C_{NO_2} range from 0.0 to 78.3 mg/L, with an average value of 378 1.84 mg/L. 379

Hotspots occur for both C_{O_2} and C_{NO_3} , with those of C_{NO_3} typically occurring in locations of corn cultivation due to the higher loading of F_{NH_4} as compared to other crop types. NO₃ mass loadings occur along the Arkansas River and the tributaries, with discharge and seepage both occurring along the length of the canals during the summer (Figure 6D). The spatio-temporal average value of C_{NO_3} in groundwater for each command area during the entire 2006-2009 time period is shown in Figure 7 for each of the 280 simulations. The average value for all grid cells in non-cultivated area also is shown. Average C_{NO_3} across all simulations for each command area are (average of

- observed field values are in parentheses) Highline 2.0 mg/L (3.1 mg/L); Catlin: 1.4 mg/L (6.1
- 388 mg/L); Rocky Ford: 1.5 mg/L (3.8 mg/L); Fort Lyon: 3.7 mg/L (1.6 mg/L); Holbrook: 1.9 mg/L
- 389 (3.5 mg/L); and non-cultivated areas: 3.5 mg/L (4.2 mg/L). Average values correspond closely to
- results from the tested baseline model [Bailey et al., 2014].

391 **3.2 Parameter influence on global concentration, leaching, and loading of NO₃**

The global influence of the 9 model input factors on NO₃ fate and transport in the study area is 392 shown in Figure 8. Global sensitivity plots are used, with non-linear effects and/or interactions σ 393 plotted against mean μ^* . The influence of the factors on C_{NO_2} in Layer 1 (top 0.5 m of the root 394 zone), C_{NO_3} in Layer 4 (shallow saturated zone), NO₃ leaching from Layers 3 to $4L_{NO_3Lay3\rightarrow 4}$ 395 (generally from the unsaturated zone to the saturated zone), and total NO₃ mass loading to the 396 Arkansas River Load_{NO3} are shown in Figures 8A, 8B, 8C, and 8D, respectively. As seen in 397 Figure 8A, C_{NO_3} in the root zone is governed principally by fertilizer loading (F_{NH_4}) and seasonal 398 NO₃ uptake by crops (N_{up}) and to a smaller degree by heterotrophic denitrification ($\lambda_{NO_3}^{het}$) and 399 400 nitrification (λ_{nit}). In the shallow saturated zone (Figure 8B), where NO₃ mass is received from the upper soil zone via leaching, F_{NH_4} and N_{up} still are dominant, but the concentration of NO₃ in 401 the canals ($Canal_{NO_3}$) has a stronger direct impact than $\lambda_{NO_3}^{het}$. The rate of humus decomposition (402 λ_H) and autotrophic denitrification ($\lambda_{NO_3}^{auto}$) also have a slight impact. NO₃ leaching also is 403 governed by F_{NH_4} , N_{up} , $\lambda_{NO_3}^{het}$, $Canal_{NO_3}$, and λ_H (Figure 8C), as higher F_{NH_4} , lower N_{up} , lower 404 $\lambda_{NO_3}^{het}$, and higher $Canal_{NO_3}$ increase the mass of NO₃ leached, and vice versa. $Load_{NO_3}$ is governed 405 by F_{NH_4} , N_{up} , and $\lambda_{NO_3}^{het}$ (Figure 8D), with $\lambda_{NO_3}^{het}$ influencing not only how much NO₃ is leached to 406 the water table and carried to the stream network via groundwater flow, but also how much NO₃ 407 undergoes denitrification in the riparian areas of the stream network. 408

409 The high σ values for N_{up} , F_{NH_4} , $\lambda_{NO_3}^{het}$ and $Canal_{NO_3}$ shown in Figure 8 signify the large spread in 410 *EE* values for these parameters, indicating that their influence on C_{NO_3} , NO₃ leaching, and NO₃ 411 mass loading is strongly dependent on the values of other parameters. For example, in reference

to C_{NO_3} in the shallow saturated zone (Figure 8B), the value of μ^* for N_{up} signifies the average 412 effect of N_{up} on C_{NQ} , but some values of *EE* for N_{up} are much smaller and larger than μ^* . 413 Smaller values of *EE* indicate that the combined influence of other parameter values produced a 414 small effect of crop uptake on C_{NO_3} , such as a lower N fertilizer loading and higher rates of 415 denitrification, whereas larger values indicate that other parameters produced a larger effect of 416 crop uptake on C_{NO_2} , such as a higher N fertilizer loading and lower rates of denitrification. Also, 417 higher values of $Canal_{NO_2}$ increase the influence of crop uptake on C_{NO_2} , as more NO₃ mass is 418 brought into the soil zone via canal seepage and infiltrating irrigation water. 419

420 **3.3 Parameter influence on** C_{NO_3} and leaching for each crop type

The influence of each of the 9 parameters on C_{NO_3} in the shallow groundwater zone and on NO₃ 421 leaching for each crop type in the study area is summarized in Tables 3 and 4, respectively using 422 values of μ^* . The μ^* values of the 3 most influential parameters for each crop type are bolded. 423 For the majority of crop types, C_{NO_3} in the shallow groundwater zone is governed by N fertilizer 424 loading (F_{NH_4}), seasonal crop N uptake (N_{up}), and heterotrophic denitrification $\lambda_{NO_3}^{het}$ (Table 3), 425 similar to the global analysis of C_{NO_3} in the shallow soil layers as presented in Section 3.2. For 426 example, μ^* for F_{NH_4} , N_{up} , and $\lambda_{NO_4}^{het}$ is 0.94, 0.72, and 0.30, respectively, for corn-cultivated 427 areas, and 0.84, 0.81, and 0.28 for sorghum-cultivated areas. The exception is areas that cultivate 428 onion, in which $Canal_{NO_2}$ ($\mu^*=0.45$) ranks in the top three behind F_{NH_4} (1.21) and N_{up} (0.99). For 429 many of the crops, λ_H and λ_{nit} have a small to moderate influence, whereas litter pool 430 decomposition rate (λ_L), autotrophic reduction of O₂ ($\lambda_{O_2}^{auto}$), and autotrophic denitrification (431 $\lambda_{NO_3}^{auto}$) have a negligible to small influence on C_{NO_3} . 432

The influence of the 9 parameters on NO₃ mass leaching to the shallow saturated zone (Table 4) follows the same pattern as for their influence on C_{NO_3} , with fertilizer N loading, uptake, and denitrification dictating the amount of NO₃ leached to the water table (values in boxes) and canal concentration, nitrification, and humus and litter pool decomposition having small to moderate 437 values of μ^* . For corn-cultivated areas, the average effect μ^* of F_{NH_a} , N_{up} , and $\lambda_{NO_a}^{het}$ is 486.3,

438 366.8, and 172.3, respectively, compared to 51.3 for λ_H , 41.3 for $Canal_{NO_3}$, and 26.4 for λ_L , with

439 15.2, 1.0, and 0.2 for λ_{nit} , $\lambda_{NO_3}^{auto}$, and $\lambda_{O_2}^{auto}$, respectively. Again, $Canal_{NO_3}$ is the third most

440 influential parameter for onion-cultivated areas, with $\mu^* = 1.6$, compared to 9.7 and 7.2 for F_{NH_4}

441 and N_{up} , respectively.

442 **3.4** Parameter influence on C_{NO_2} and leaching in individual canal command areas

Summaries of the influence of each of the 9 parameters on C_{NO_2} in the shallow groundwater zone 443 and on NO₃ leaching for each canal command area also are provided in Tables 3 and 4. The 444 results show importance differences between the command areas, with a mixture of F_{NH_a} , N_{up} , 445 λ_{nit} , $\lambda_{NO_3}^{het}$, $\lambda_{NO_3}^{auto}$, and $Canal_{NO_3}$ providing noteworthy impacts on C_{NO_3} and NO₃ mass leaching. For 446 influence on $C_{NQ_{1}}$ (Table 3), the top three influential parameters within the Catlin command area 447 are N_{up} ($\mu * = 0.26$), λ_{nit} (0.16), and F_{NH_4} (0.12), whereas the top three for the Rocky Ford 448 command area are Canal_{NO3} (0.51), λ_{NO3}^{auto} (0.20), and N_{up} (0.15), with the strong influence of λ_{NO3}^{auto} 449 due to the presence of outcropped shale in the command area and hence locations of autotrophic 450 denitrification. $\lambda_{NO_3}^{auto}$ also has a strong influence in the Holbrook command area, with the third 451 highest value of μ^* (0.11). Canal_{NO3} is ranked 3rd or higher in terms of μ^* in 3 of the 6 command 452 areas (Rocky Ford, Otero, Highline). F_{NH_4} , N_{up} , and $\lambda_{NO_3}^{het}$ govern NO₃ mass leaching for each of 453 the command areas (Table 4) except for the Catlin command area, in which λ_{nit} is ranked second 454 $(\mu^* = 38.0)$ and the Rocky Ford Ditch, in which $Canal_{NO_3}$ is ranked first $(\mu^* = 30.3)$. 455

456 **3.5 Spatial distribution of parameter influence on** C_{NO_3} and C_{O_2}

457 Cell-by-cell plots of Savage scores for the parameters according to their ranking in influencing 458 C_{NO_3} in shallow groundwater are shown in Figure 9. Plots are presented for each of the targeted 9 459 parameters except for $\lambda_{O_2}^{auto}$ due to the negligible influence of O₂ autotrophic reduction on C_{NO_3} .

460 The value for each cell represents the ranking (1-9) and associated Savage score for the given parameter. High ranking is displayed in maroon-red coloring, whereas low ranking is displayed 461 in blue. As seen in the plots, the ranking of each parameter in its influence on groundwater $C_{NQ_{h}}$ 462 is highly spatially-variable. For example, the locations where canal NO₃ concentration ($Canal_{NO_3}$) 463) has the strongest influence (maroon coloring) (Figure 9B) are scattered throughout the region, 464 with entire local areas (encompassed by circles in Figure 9B) governed by this parameter. For the 465 cultivated areas, the dominant intputs/processes are fertilizer loading (Figure 9A), crop N uptake 466 (Figure 9D), and heterotrophic denitrification ($\lambda_{NO_{*}}^{het}$) (Figure 9E), with humus decomposition 467 (Figure 9G) having a moderate influence and litter decomposition (Figure 9H) having a small 468 influence. Whereas fertilizer loading and N uptake have the most influence on C_{NO_1} in most of the 469 470 cultivated areas, some areas are governed principally by heterotrophic denitrification and humus decomposition (cells colored in maroon in Figures 9E and 9G). Denitrification is particularly 471 important in riparian areas along tributaries and the Arkansas River (Figure 9E), where dense 472 vegetation provides a natural filter of NO₃ before being loaded to surface water. Values of humus 473 474 decomposition (λ_H) and litter decomposition (λ_L) control the rate of organic C and organic N decomposition and hence the availability of C for heterotrophic denitrification to proceed. 475

No area has λ_L being the dominant influence on C_{NO_3} . Nitrification rate has a strong impact on 476 C_{NO_3} in the Holbrook command area (red-pink cell coloring in Figure 9C), with small impact 477 elsewhere in the study area. Autotrophic denitrification is the dominant parameter in areas along 478 the Arkansas River and several of the tributaries (Figure 9F) that are adjacent to shale formations 479 (see Figure 1). However, it is interesting to note that there are many locations in the study area 480 adjacent to outcropped shale in which $\lambda_{NQ_2}^{auto}$ is not the dominant parameter. These locations are 481 indicated by circles in Figure 9F. In these areas, other system inputs and processes such as $F_{NH_{*}}$, 482 N_{up} , $\lambda_{NO_3}^{het}$ and λ_H are the governing influences on C_{NO_3} , demonstrating that knowledge of shale 483 locations alone cannot be used to determine where C_{NO} will be affected the most by autotrophic 484 denitrification. 485

Similar cell-by-cell plots of parameter Savage scores are shown in Figure 10 for influence on 486 C_{O_2} in shallow groundwater. λ_H and λ_L govern C_{O_2} in the cultivated areas (Figures 10C,D), with 487 F_{NH_4} (Figure 10B), N_{up} (Figure 10E) and $Canal_{NO_2}$ (Figure 10A) exhibiting small to moderate 488 influence on $C_{O_{\lambda}}$ in the cultivated areas. The strong influence of λ_{H} and λ_{L} occurs due to their 489 control of the rate of organic C decomposition, and hence the availability of C for heterotrophic 490 reduction of O₂. The rate of autotrophic reduction of O₂ ($\lambda_{O_2}^{auto}$) is dominant in localized areas 491 492 where shale is present (see maroon-shaded cells in Figure 10F) with small influences in other 493 areas of the study region, mainly in areas down-gradient of the shale areas.

494

495 4 Discussion of Results

496 Results provide information regarding the system inputs and processes that control NO₃ fate and transport generally (across the entire study region), by crop type, by canal command area, and by 497 local regions. For the entire study region, detailed field sampling and observation of N fertilizer 498 loading, N crop uptake, heterotrophic denitrification in the shallow soil layers, and concentration 499 of NO₃ in canal water must be performed as often as possible to provide accurate model input 500 data. NO₃ in canal water not only seeps through the perimeter of the earthen irrigation canals into 501 the aquifer, but also is loaded to cultivated fields via applied irrigation water. In addition, results 502 indicate these inputs and processes must be controlled via implemented management practices if 503 NO₃ groundwater concentration, NO₃ leaching, and NO₃ mass loading to the river network are 504 expected to decline in future decades, whereas other processes (organic N decomposition, 505 506 nitrification of NH₄) are not critical target factors.

507 These results agree with other previous studies from regions worldwide, which indicated that key

controls on NO_3 fate and transport in groundwater and watershed systems, and hence targets for

509 management action, include N fertilizer application [Chaplot et al., 2004; Botter et al., 2006;

Almasri and Kaluarachchi, 2007; Arabi et al., 2007; Bailey et al., 2015] and rate of

denitrification [Wriedt and Rode, 2006; Almasri and Kaluarachchi, 2007; Schilling et al., 2007],

512 with the order of their influence varied depending on the study region. However, these studies

513 did not analyze the influence of NO₃ in canal irrigation water or the influence of crop N uptake.

514 Molénat and Gascuel-Odoux [2002] did demonstrate the strong influence of NO₃ leaching on in-

- 515 stream NO₃ concentration, similar to our assessment of N uptake and denitrification (which
- 516 influence NO3 leaching) on NO₃ loading from the aquifer to the stream network.

The same system parameters that govern NO₃ fate and transport at the regional scale also govern 517 NO₃ for each individual crop type. N fertilizer loading (less), N crop uptake (more), and 518 519 heterotrophic denitrification (more) typically must be controlled to decrease groundwater NO₃ concentration and NO₃ leaching, with NO₃ concentration in canal water controlled to lower these 520 521 values for onion-cultivated areas. For canal command areas, N fertilizer loading and N uptake 522 must be managed to decrease groundwater NO₃ concentration and NO₃ mass leaching in the majority of command areas. However, nitrification of NH₄ is an important control for the Catlin 523 command area, NO₃ concentration in canal water is important for the Highline, Otero, and Rocky 524 525 Ford command areas, heterotrophic denitrification is important for each command area except Catlin and Rocky Ford Ditch, and autotrophic denitrification is important for only the Holbrook 526 and Rocky Ford Ditch command areas. These reaction rate parameters must be focused on in 527 field data monitoring scheme and in model parameter estimation. Results demonstrate that 528 targeted inputs/outputs and processes vary depending on command area. 529

Similarly, different targets are required for controlling NO₃ fate and transport in localized areas 530 throughout the study region. In reference to Figure 9, each system parameter, with the exception 531 of litter pool decomposition, is the most influential in controlling NO₃ fate and transport in at 532 533 least several areas within the study region. N fertilizer loading is the dominant parameter in the majority of cultivated areas, although N uptake, heterotrophic denitrification, and NO₃ 534 concentration in canal water also are the most influential in much of the study area. The rate of 535 autotrophic denitrification ($\lambda_{NO_3}^{auto}$) is influential in many of the areas adjacent to outcropped 536 marine shale. However, it is interesting to note that there are many locations in the study area 537 adjacent to outcropped shale in which $\lambda_{NO_2}^{auto}$ is not the dominant parameter. These locations are 538 indicated by circles in Figure 9F. In these areas, other system inputs and processes are dominant, 539 540 demonstrating that knowledge of shale locations alone cannot be used to determine where groundwater NO₃ concentration will be affected the most by autotrophic denitrification. 541

542 Whereas other studies [Chaplot et al., 2004; Botter et al., 2006; Wriedt and Rode, 2006; Almasri

and Kaluarachchi, 2007; Arabi et al., 2007; Schilling et al., 2007; Bailey et al., 2015] have

focused on the response of the entire groundwater and/or watershed system, the novelty of this

study is the assessment of NO₃ transport control in localized areas within a region. Almasri and

546 Kaluarachchi [2007] stated that the importance of denitrification in controlling NO₃ in

547 groundwater may differ from location to location. In this study we quantify this difference

spatially for denitrification and for each of the other eight targeted parameters (see Figure 9).

549

550 5 Summary and Concluding Remarks

This study used a 506 km² regional-scale N fate and transport numerical model to examine the 551 552 influence of forcing terms (fertilizer loading, crop N uptake, N concentration of applied irrigation water and canal seepage Canal_{NO}) and chemical processes (litter and humus organic N 553 554 decomposition; nitrification of NH₄ to NO₃; heterotrophic and autotrophic reduction of NO₃, with the latter occurring in the presence of pyrite-bearing marine shale; and autotrophic 555 reduction of O₂, also occurring in the presence of shale) on NO₃ concentration in groundwater 556 C_{NO_3} , NO₃ leaching from the unsaturated zone to the saturated zone of the aquifer, and NO₃ mass 557 loading from the aquifer to the Arkansas River via groundwater discharge. The influence of each 558 559 of the 9 model factors was computed using the revised Morris method for sensitivity analysis, with results processed to determine parameter influence globally for the entire study region and 560 specific to crop type, canal command area (i.e. the group of fields receiving irrigation water from 561 a given canal), and individual grid cells. For the latter, spatial plots of sensitivity indices are 562 presented to display the spatial distribution of influence for each model factor. 563

Results indicate that, generally, fertilizer loading, crop N uptake, and heterotrophic

denitrification governed NO₃ mass transport, particularly in cultivated areas. However, their

order of influence on C_{NO_2} and NO₃ mass leaching varies according to crop type and command

- 567 area, and several command areas are influenced more, or at least to a significant degree, by
- nitrification, autotrophic denitrification, and *Canal_{NO₂}*. Spatial plots of cell-by-cell sensitivity

569 indices enhance further the understanding of localized model factor influence, with each factor except for rate of heterotrophic O_2 reduction having the dominant influence over C_{NO} at one or 570 more locations within the study area. Results also indicate that the concentration of O2 in 571 groundwater C_{O_2} is governed by rates of organic matter decomposition, which releases CO₂ and 572 hence enhances heterotrophic reduction of O₂. 573 In general, the procedure followed in this study provides key information regarding overall NO₃ 574 fate and transport in an agricultural groundwater system, guidance for future data collection and 575 monitoring programs, an indication of which parameters should be targeted during model 576 parameter estimation, and guidance for implementing best-management practices (BMPs) for 577 NO₃ remediation, i.e. decreasing groundwater concentrations and mass loading to the stream 578 network. For example, fertilizer loading, crop N uptake, and Canal_{NO3} should be targeted in field 579 data collection and observation, with Canal_{NO2} monitored for each irrigation canal as often as 580 possible, whereas first-order kinetic rate constants for nitrification, denitrification, and organic 581 matter decomposition should be targeted during parameter estimation efforts. Furthermore, the 582 procedure followed in this study also allows for data collection, management practice 583 implementation, and parameter estimation to be performed on location-specific basis. For 584 example, results suggest that a specific BMP (e.g., reduction in N fertilizer loading) may be 585 optimal for several of the command areas but not for others, or that decreasing Canal_{NO}, or the 586 amount of NO₃ denitrified in shale outcrop locations will help remediate NO₃ only in a few 587 specific locations within the study area. Also, data collecting points for specific model factors 588 can be restricted to sub-region areas, either to a given command area or, with the use of the 589 spatial plots of sensitivity indices, to even more localized sites. 590

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778 Table 1. Baseline agricultural management and crop parameter values for the model simulations.

Crop Type	Planting Day	Harvest Day	Plow Day	P_{St}	d _{rt,max}	CN_{RT}	$F_{_{N\!H_4}}$	N _{up}
Units	-	-	-	kg ha ⁻¹	m	-	kg ha ⁻¹	kg ha ⁻¹
Alfalfa	30-Apr	30-Sep	20-Oct	561.6	1.83	25	22.4	22.4
Bean	20-May	30-Sep	20-Oct	561.6	0.91	25	140	84.2
Corn	1-May	25-Oct	14-Nov	5616	1.22	70	252	224.6
Melon	15-May	10-Aug	30-Aug	561.6	1.22	25	112	112.3
Onion	20-Mar	15-Sep	5-Oct	561.6	0.46	25	140	78.6
Pasture	30-Aug	30-Sep	20-Oct	0	0.91	70	140	112.3
Pumpkin	1-Jun	30-Sep	20-Oct	561.6	0.91	25	140	84.2
Sorghum	20-May	15-Oct	4-Nov	1684.8	0.91	70	112	112.3
Spring Grain	1-Apr	15-Jul	4-Aug	1684.8	0.91	70	112	112.3
Squash	20-May	25-Jul	14-Aug	561.6	0.91	25	140	84.2
Sunflower	1-Jun	10-Oct	30-Oct	561.6	0.91	25	140	84.2
Vegetable	25-Apr	30-Aug	19-Sep	561.6	0.91	25	140	84.2
Winter Wheat	30-Sep	5-Jul	25-Jul	1684.8	0.91	70	112	112.3

 d_{pw} (depth of plowing) is 1.0 m for all crops except beans (0.8 m)

 P_{Rt} (seasonal mass of root mass) is 500 kg ha⁻¹ for all crop types

779 780 781 *CN_{st}* (carbon:nitrogen ratio in stover mass) is 50 for all crop types

783 Table 2. Parameters and values for chemical reactions involving organic matter decomposition, dissolved oxygen,

and nitrogen species for the baseline simulation model.

	Org. N	Matter Deco	omp.	Disso	olved Oxyge	en		Nitrogen			
	Param.	Value	Unit	Param.	Value	Unit	Param.	Value	Unit		
	λ_L	0.25	d ⁻¹	$\lambda_{O_2}^{het}$	2.0	d ⁻¹	$H_{C/N}$	12.0	-		
	λ_H	0.003	d^{-1}	$\lambda_{O_2}^{auto}$ *	0.58	d ⁻¹	$B_{C/N}$	8.0	-		
	f_e	0.5	-	K_{o_2}	1.0	$g m_{f}^{-3}$	I_{O_2}	1.0	$g m_f^{-3}$		
	f_h K	0.2	- a m ⁻³				λ_{nit}^*	0.98	d ⁻¹		
	IL CO2	0.75	g m _f				λ^{het}	0.1	u I-l		
							NO3 2 auto *	0.1	d-1		
							K	10.0	d-1		
							K	3.5	$g m_f^{-3}$		
785	* Indicates m	ean value,	with specifi	c values assign	ed to each o	command a	area according	to the value	s reported in	n Bailey et al.	(2014).
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- 803 Table 3. Sensitivity index (μ^*) for each of the model input factors investigated, indicating the degree of parameter
- 804 influence on C_{NO_3} in the shallow saturated zone of the aquifer (in layer 4 of the grid) for the grid cells associated with
- 805 each crop type and command area, with the values of the top three influential parameters for each crop type and
- command area bolded.

	N Fert.	N	Litter	Humus	O ₂	Nitrif.	Het.	Auto.	NO ₃ canal
	Loading	uptake	decomp.	decomp.	reduction		Denitrif.	Denitrif.	conc.
	$F_{_{N\!H_4}}$	N_{up}	λ_L	λ_H	$\lambda_{O_2}^{auto}$	λ_{nit}	$\lambda_{\scriptscriptstyle NO_3}^{\scriptscriptstyle het}$	$\lambda_{NO_3}^{auto}$	$Canal_{NO_3}$
Crop									
Alfalfa	0.46	0.56	0.03	0.09	0.00	0.06	0.23	0.04	0.11
Bean	0.70	0.43	0.04	0.09	0.00	0.03	0.34	0.00	0.06
Corn	0.94	0.72	0.04	0.10	0.00	0.03	0.30	0.03	0.09
Melon	5.46	3.02	0.10	0.15	0.00	0.23	0.92	0.00	0.47
Onion	1.21	0.99	0.02	0.14	0.00	0.03	0.19	0.01	0.45
Pasture	0.66	0.63	0.03	0.12	0.01	0.04	0.32	0.07	0.14
Sorghum	0.84	0.81	0.03	0.12	0.00	0.08	0.28	0.04	0.13
Spring Grain	0.79	0.70	0.04	0.13	0.00	0.02	0.32	0.02	0.06
Command Area									
Catlin	0.12	0.26	0.00	0.03	0.01	0.16	0.04	0.01	0.11
Fort Lyon	0.92	0.81	0.05	0.17	0.00	0.04	0.42	0.08	0.12
Highline	0.69	0.51	0.03	0.06	0.00	0.02	0.23	0.01	0.26
Holbrook	0.28	0.29	0.02	0.03	0.00	0.01	0.08	0.11	0.10
Otero	1.21	1.16	0.05	0.14	0.00	0.04	0.49	0.04	0.59
RF Ditch	0.14	0.15	0.01	0.03	0.02	0.01	0.14	0.20	0.51

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821 Table 4. Sensitivity index (μ^*) for each of the model input factors investigated, indicating the degree of parameter

822 influence on NO₃ mass leaching from the shallow soil zone for the grid cells associated with each crop type and

823 command area, , with the values of the top three influential parameters for each crop type and command area bolded.

	N Fert. Loading	N uptake	Litter decomp.	Humus decomp.	O ₂ reduction	Nitrif.	Het. Denitrif.	Auto. Denitrif.	NO ₃ canal conc.
	$F_{_{NH_4}}$	N _{up}	λ_L	λ_H	$\lambda^{auto}_{O_2}$	λ_{nit}	$\lambda_{NO_3}^{het}$	$\lambda^{auto}_{\scriptscriptstyle NO_3}$	$Canal_{NO_3}$
Crop Type									
Alfalfa	396	614	19	73	0.8	39	176	13	108
Bean	43	26	2.7	7.6	0.0	2.3	22	0.0	3.6
Corn	486	367	26	51	0.2	15	172	1.0	41
Melon	7.0	4.5	0.2	0.2	0.0	0.2	1.9	0.0	0.6
Onion	9.7	7.2	0.2	0.4	0.0	0.4	1.1	0.0	1.6
Pasture	431	382	16	76	0.4	9.0	162	12	49
Sorghum	271	221	11	29	0.1	11	94	2.1	26
Spring Grain	213	179	11	31	0.2	2.9	82	1.3	14
Command Area									
Catlin	35	63	0.9	5.3	0.1	38	7.5	0.3	9.2
Fort Lyon	852	777	35	140	1.0	33	335	13	70
Highline	125	103	4.2	12	0.0	2.7	41	0.1	37
Holbrook	70	71	3.6	5.7	0.1	2.6	21	3.6	10
Otero	196	176	8.4	21	0.0	4.7	85	2.0	62
RF Ditch	3.6	3.9	0.1	1.2	0.2	0.5	1.9	3.3	30



835 Figure 1. Location and hydrologic features of the study region in the Lower Arkansas River Valley in southeastern

Colorado, showing the Arkansas River and tributaries (red), cultivated fields (yellow), irrigation canals (light blue),

groundwater pumping wells (black dots), and the extent of near-surface shale (within 2 m of the ground surface)

- (green).



Figure 2. Features of the cultivation and data collection of the study region, including (a) canal command areas and

856 location of groundwater observation wells, with a command area defined as the collection of fields receiving

- 857 irrigation water from the same canal, and (b) the spatial distribution of crop cultivation during the 2006 growing
- season.



** Sources and Sinks of solutes during irrigation season include canal seepage, pumping, flows to and from rivers and tributaries, and crop uptake.

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Figure 3. Depiction of the main processes simulated by the N reaction module of the UZF-RT3D model, with (a)

872 conceptual model of the fate and transport of O_2 and N species in an irrigated soil-aquifer system wherein fertilizer,

873 irrigation, and canal seepage bring solute mass into the subsurface environment, and (b) the annual cultivation

schedule used in the N reaction module, including timing of planting, fertilizer loading, irrigation application,

harvest, and plowing. NH₄ fertilizer has a split loading, with 40% of the loading occurring 2 weeks before planting,

and the remainder applied 6 weeks after planting.



878 Figure 4. (a) The spatial distribution of aquifer thickness (m) of the alluvium in the study region, (b) the finite-

difference grid used in the calibrated and tested MODFLOW-UZF1 groundwater flow model, using 250 m by 250 m

grid cells, (c) spatial distribution of soil water content simulated by the MODFLOW-UZF1 model, for June 2006,

and (d) average-simulated water table elevation for the 1999-2009 time period.



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Figure 5. Values of (a) fertilizer loading F_{NH_4} (kg/ha) for corn, and (b) first-order rate constant of autotrophic

897 denitrification $\lambda_{NO_3}^{auto}$ (1/day) and (c) nitrate concentration of canal water $Canal_{NO_3}$ (mg/L) for the Rocky Ford Highline 898 canal command area, for each of the 280 simulations in the revised Morris SA scheme.

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903Figure 6. Summary of typical UZF-RT3D model results for the study region, showing spatial distribution of (a) C_{o_2} 904and (b) C_{NO_3} in shallow groundwater, and spatial distribution of mass loadings of nitrate to the Arkansas River905system (main stem and tributaries) for (c) December 2 2006, and (d) August 10 2008, showing the contrast between906the winter and summer seasons.



912 Figure 7. Spatio-temporal average value of C_{NO_3} in groundwater during the 2006-2009 simulation period for each

913 canal command area for each of the 280 UZF-RT3D model simulations. The spatio-temporal average for the non-

914 cultivated areas also is shown (small black crosses).



Figure 8. Global sensitivity plots (σ vs. μ^*) showing influence of the 9 targeted model input factors on (a) C_{NO_3} in Layer 1 of the model (top 0.5 m of the root zone), (b) C_{NO_3} in Layer 4 of the model (shallow saturated zone of the aquifer), (c) NO₃ mass leaching from Layer 3 to Layer 4 (unsaturated zone to saturated zone), and (d) total mass loading of NO₃ from the aquifer to the Arkansas River.

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Figure 9. Cell-by-cell (250 m by 250 m) plots of Savage scores for (a) F_{NH_4} , (b) $Canal_{NO_3}$, (c) λ_{nit} , (d) N_{up} , (e) $\lambda_{NO_3}^{het}$,

940 (f) $\lambda_{NO_3}^{auto}$, (g) λ_H , and (h) λ_L indicating the ranking of influence of that parameter on C_{NO_3} in groundwater for each of 941 the 7,776 cells in the study region.

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946 Figure 10. Cell-by-cell (250 m by 250 m) plots of Savage scores for (a) $Canal_{NO_3}$, (b) F_{NH_4} , (c) λ_H , (d) λ_L , (e) N_{up} , and

947 (f) $\lambda_{O_2}^{auto}$, indicating the ranking of influence of that parameter on C_{O_2} in groundwater for each of the 7,776 cells in 948 the study region.