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Early warning of global change effects on catchment nutrient exports

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Abstract

Global change scientists seek sentinels of change. On forested landscapes, first-order catchments serve as sentinels of global stressors and their effects on downstream surface waters. Here, I explored global stressors – including climate warming, hydrological intensification, and recovery from atmospheric acidic deposition – and their effects on nutrient exports in 22-year stream chemistry records from 41 forested first-order catchments in a network of North American long-term monitoring sites. First, I used multivariate autoregressive models to establish relationships between changes in global stressors and changes in catchment nutrient exports. Second, I analyzed the residuals of these relationships to determine if there was evidence of instability in the catchment nutrient exports. I found that changes in global stressors affected the nutrient exports of these catchments but that the global stressors having the largest impacts varied geographically, and that changes in these global stressors were leading to changes in the stability of these nutrient exports.

Keywords

Forest, climate warming, hydrological intensification, atmospheric acidic deposition, catchment, hydrology, biogeochemistry, first-order stream, stability, MARSS

Summary for Lay Audience

Global change scientists seek early warning systems to explore the effects of global atmospheric changes on ecosystems. First-order catchments with small, intermittent or ephemeral streams may be excellent early warning systems, as their signals are unencumbered by the confounding influences of the catchments into which they drain. However, their uniqueness in time and space create challenges in developing a predictive understanding of their responses to global changes.

I explored the effects of climate warming, hydrological intensification, and recovery from atmospheric acid deposition on first-order catchment nutrient exports in the temperate forest biome of North America. I asked two questions: Are global changes modifying catchment nutrient exports? and Are global changes leading to an increase in instability of catchment nutrient export magnitude and composition. To answer these questions, I mined 22-year records from a network of long-term monitoring sites where sulfur, nitrogen, and phosphorus exports were generally declining. I modeled the relationships between global changes and catchment nutrient exports, and then analyzed the residuals of these relationships for early warnings of changes in the stability of catchment nutrient exports. I found that global changes modify catchment nutrient exports, but that their effects were geographically dependent, with climate warming effects being greatest on northern sites, hydrological intensification effects being greatest on eastern sites and effects of recovery from acidic deposition being greatest near coastal sites, and with some sites responding to the interactive effects of climate change and the recovery from atmospheric acidic deposition. I also found that global changes were creating higher risks of changes in the magnitude and composition of catchment nutrient exports at all sites, particularly in nitrogen and phosphorus exports.

Development of a predictive understanding of global change effects on ecosystems is difficult to be generalized. Continued access to data from the network of long-term monitoring sites will be essential to reveal if the instabilities are indeed early warning of shifts to an alternative stable state in catchment nutrient exports that could have fundamental consequences on the productivity and diversity of downstream waters.

Co-Authorship Statement

This thesis will be reformatted for submission to an academic journal. Haibin (Rick) Dong will be the first author as he was responsible for writing the thesis and contributed to conceptualizing the analysis approach, improving the modeling structure, acquiring and assimilating data to parameterize the model, and operating the model for simulations. Irena F. Creed will be the second author as she was the primary editor of the thesis and contributed to conceptualizing the analysis approach, refining the model structure, and providing input at all stages of the project. Irena F. Creed also provided financial resources to support the research. Mark Scheuerell (NOAA) will be the third author as he contributed to developing and improving the model structure, and providing valuable feedback for the modeling results validations. Jim Hood (The Ohio State University), Tamara Harms (University of Alaska-Fairbanks), and all collaborators of the long-term ecological research sites will be co-authors as they provided feedback and contributed to the preparation of the manuscript.

Dedication

I dedicate this thesis to my high school teacher, Ling, who encouraged me to turn my life into a different direction with my own decision.

Thank my mother Hong, father Xiaoyong, and other family members for always supporting me to pursue my life decisions, loving me for the capricious I am, and pushing me to always stay independent.

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Finally, my spiritual model Master Yangming, a Chinese idealist Neo-Confucian philosopher, whose philosophy help me achieve the internal peace of my mind.

路漫漫其修远兮，

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--离骚

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Table of Contents

List of Tables

List of Figures

List of Abbreviations

General information

ACFs - Autocorrelation functions

AIC_c - Akaike's Information Criterion adjusted for small sample size

BMP - Best management practice

CI - Confidence interval

MARSS - Multivariate Auto-Regressive State Space

MNV – Multivariate normal distribution

Q-Q plot - quantile-quantile plot

RDA - redundancy analysis

LTER site

BBWM - Bear Brook Watershed in Maine

CWT - Coweeta Hydrologic Laboratory

DOR - Dorset Environmental Science Centre

ELA - Experimental Lakes Area

HBEF - Hubbard Brook Experimental Forest

HJA - H.J. Andrews Experimental Forest

LEF - Luquillo Experimental Forest

MEF - Marcell Experimental Forest

SEF - Santee Experimental Forest

TLW - Turkey Lakes Watershed

Biogeochemical response

Ca - Calcium

DIC - Dissolved inorganic carbon

DIN - Dissolved inorganic nitrogen

DOC - Dissolved organic carbon

NH_4-N – Ammonia-nitrogen

NO_3-N – Nitrate-nitrogen

PO_4-P – Phosphate-phosphorus

SO_4-S – Sulfate-sulfur

TDP - Total dissolved phosphorus

TP - Total phosphorus

Chapter 1

1 Introduction

1.1 Problem statement

Forest ecosystems perform important functions and provide important services such as the source areas of water upon which society depends (National Research Council, 2008; Smithwick, 2011; Hering et al., 2015). Damage to forest ecosystems places at risk these sources, with consequences that cascade downstream (Bishop et al., 2008; Xie et al., 2010; Pincebourde et al., 2012; Tamburello et al., 2013; Donohue et al., 2016; Creed et al., 2017). For example, forest hydrological and biogeochemical cycles are being pushed beyond thresholds that define “safe operating space” for humanity (Rockström, 2015; Steffen et al., 2015). Specifically, global atmospheric changes (e.g., climate warming, hydrological intensification, atmospheric pollution) together with local natural resource development activities (e.g., forest commercial harvesting, mining, recreational resort constructing) may lead to fundamental changes in forest condition (Wright, 1974; Smithwick, 2011; Ballantyne & Pickering, 2015; Biswas & Biswas, 2018). Changes in forest condition can be gleaned from the magnitude and composition of biogeochemical exports from source areas to surface waters (Woodward et al., 2012; Creed et al., 2017). Recent studies focused on exploring single relationships between the global stressors (i.e., climatic factors affected by global atmospheric changes) and stream biogeochemical export responses (Kerr et al., 2012) and do not consider multiple stressors and responses together to draw a larger picture of forested catchment health condition (Smithwick et al., 2011). This study attempts to remedy the lack of knowledge of the changes of the multiple global stressors and their impacts on the stream responses. This examination was done in the context of the presence or absence of forest management activities (named as local stressors) so that knowledge may be gained on the relative importance of global vs. local stressors on stream responses.

1.2 Scientific justification

1.2.1 Planetary boundary for biogeochemical cycles

Earth is a complex, self-regulating system with a certain capacity for resisting various external disturbances that alter the structure and dynamics of the earth systems (Rockström, 2015; Donohue et al., 2016). Biogeochemical cycles are the pathways through which chemicals flow in biotic (i.e., biosphere) and abiotic (i.e., atmosphere, hydrosphere and lithosphere) systems (Hedges, 1992). Planetary boundary analysis of the Earth system suggests that changes to biogeochemical cycles are exceeding "safe operating limits" for humanity due to global atmospheric changes and human intensification of land management activities (e.g., forestry, mining, recreations, etc.) (Smithwick et al., 2009; Smithwick, 2011; Rockström, 2015; Steffen et al., 2015; Bahn et al., 2015; Pickering, 2015; Schlesinger et al., 2016; Williamson et al., 2016; Ballantyne & Biswas, 2018). The effects of the global atmospheric changes (e.g., climate warming, hydrologic intensification, and atmospheric pollution), along with the effects of forest management activities are creating a source of substantial uncertainty and unpredictability in biogeochemical cycling of, and export from, forests. When biogeochemical cycles are altered, they may trigger consequences to the functioning of other ecosystems and the services they provide to humans.

1.2.2 First-order catchments as sentinels of change

Global change scientists seek sentinels to explore the effects of global stressor changes on forest ecosystems. Within forest ecosystems, first-order catchments that drain into small ephemeral, intermittent or permanent streams are particularly suitable to serve as sentinels of global stressors. First-order catchments are an important source of water (Bishop et al., 2008) that cascades down the river continuum, thus playing vital roles in downstream ecosystem functions and services. First-order catchments are sensitive to changes in hydrological (Strand et al., 2008) and biogeochemical (Alexander et al. 2007; Sleighter et al. 2014) cycling as their signals are unencumbered by the confounding influences of multiple, nested catchments draining into higher-order systems (Cirmo & Driscoll, 1996; Allan et al., 1997; Buttle et al., 2018). Furthermore, first-order catchments remain that are not disturbed by local stressors and therefore can be used as a reference in comparing the catchment response of natural to management catchments (Kreutzweiser et al., 2004; Creed & Beall, 2009; Buttle et al., 2018). However, the uniqueness of processes over time and across space creates challenges in development of a predictive understanding of these first-order catchments to global changes.

1.2.3 Detecting changes in biogeochemical trends

Global stressor changes are altering forest ecosystems (Gauthier et al., 2015; Trumbore et al., 2015). The frequency, magnitude, duration, and changing rate of these global stressor affects forest ecosystems at a variety of temporal and spatial scales (Pincebourde et al., 2012; Tamburello et al., 2013; Donohue et al., 2016). These global stressor changes are often reflected in hydrological flows that drain first-order catchments (Huntington, 2006; Déry et al., 2009; Wu et al., 2013; Creed et al., 2015) and in biogeochemical constituents carried in these flows (Prospero et al., 1996; Watmough et al., 2005; Mahowald et al., 2008; Creed et al., 2018). Alterations in hydrological and biochemical flows may reflect changes in terrestrial ecosystems (e.g., a degraded or regenerating forest) and may result in changes in aquatic ecosystems (e.g., downstream productivity, diversity and even toxicity) (Grimm et al., 2003; McClain et al., 2003; Guenet et al., 2010). Even though individual (or short-term) global stressors may have minimal effects on drainage waters, cumulative (or long-term) effects from a combination of global stressors have the potential to initiate a cascading sequence of difficult-to-reverse changes at regional, continental or even global scales (Kranabetter et al., 2016). Any of these changes may lead to instabilities that may drive a forest ecosystem from one stable state (with ecosystem functions and services that society has become dependent on) to another stable state (Groffman et al., 2006; Seidl et al., 2016).

A question that needs to be answered is, how to measure the effects of global changes in first-order catchments? There are many statistical techniques designed to develop models that are appropriate for testing “one-to-one”, “one-to-many” and “many-to-many” stressor-response relationships. However, the majority of these models are inappropriate for deciphering the complex stressor-responses relationships of ecosystems, because they were not designed to discriminate among multiple sources of response noise [i.e., both observation-based (human or measurement) noise and environmental and ecological variations (Schnute, 1994)]. Multivariate autoregressive state space (MARSS) models were specifically designed to model environmental and ecosystem changes taking into account both sources of noise and the fact that variances in these sources of noise in environmental processes are difficult to measure (Holmes, et al., 2014). MARSS models were originally developed in the fields of natural and environmental sciences (Holmes et al, 2014) for the purpose of studying ecosystem community stability and ecological interactions (Ives et al., 2003; Jorgensen et al., 2016), marine fish populations (Ohlberger et al., 2016; Zhu et al., 2017), and aquatic biogeochemistry (Smits et al., 2019). The state space means that the data collected from different locations (e.g., different catchments) can be modeled as one set of data (i.e., combining two or more catchments as one state space).

1.2.4 Detecting change in biogeochemical stability

Almost 50 years ago, Holling (1973: pp.17) defined ecological stability as "the ability of a system to return to an equilibrium state after a temporary disturbance. In this definition stability is the property of the system and the degree of fluctuation around specific states". Changes in ecological stability result from as the magnitude and composition shifts of energy and nutrient cycles in response to disturbances (Donohue et al., 2016). These system shifts can reduce ecosystem functions and services (e.g., water regulation, carbon sequestration, nutrient regulation, and biomass production) (Holling & Gunderson, 2002; Garmestani et al., 2009; Allen et al., 2010).

In this study, I defined biogeochemical stability as the ability of an ecosystem to maintain the size of biogeochemical pools and the rates of biogeochemical input and output processes in response to disturbances. The idea is that disturbances can modify biogeochemical dynamics within an ecosystem, leading to a potential shift to a new state in which the pathways of energy and nutrients and the influence of these pathways to the entire ecosystem are altered (Smithwick, 2011). Most troublingly, the biogeochemical pathways will not be easily restored to their original state once shifted.

In this thesis, I examined biogeochemical stability of first-order catchments and their drainage waters. I illustrate this using a simple univariate system (i.e., one stressor vs. one response) presented in **Figure 1.1**. An early warning signal of a regime shift (black point) occurs when there is a change in the response in the state of a stressor (i.e., from the dark gray point to the light gray point; **Figure 1.1.a**). The response residuals vary as the biogeochemical state changes (**Figure 1.1.b**). The residuals with a biogeochemical state closer to the threshold of the regime shift (the light gray point) will have a larger standard deviation than the residuals further from the threshold (the dark grey point). Early warning signals of a catchment becoming less stable are an increase in the standard deviation of residuals from the trend in biogeochemical flows in response to changes in global atmospheric stressors (**Figure 1.1.c**). In this study, I determined if there were trends in the standard deviations of residuals of stream responses within a moving window over time. Significant increasing trends indicate that a catchment is becoming less stable and may be more vulnerable to a regime shift in response to changes in global stressor changes (Wouters et al., 2015). Eventually, when the system state is pushed past tolerance thresholds (the black point), a regime shift (the dashed line) will occur.

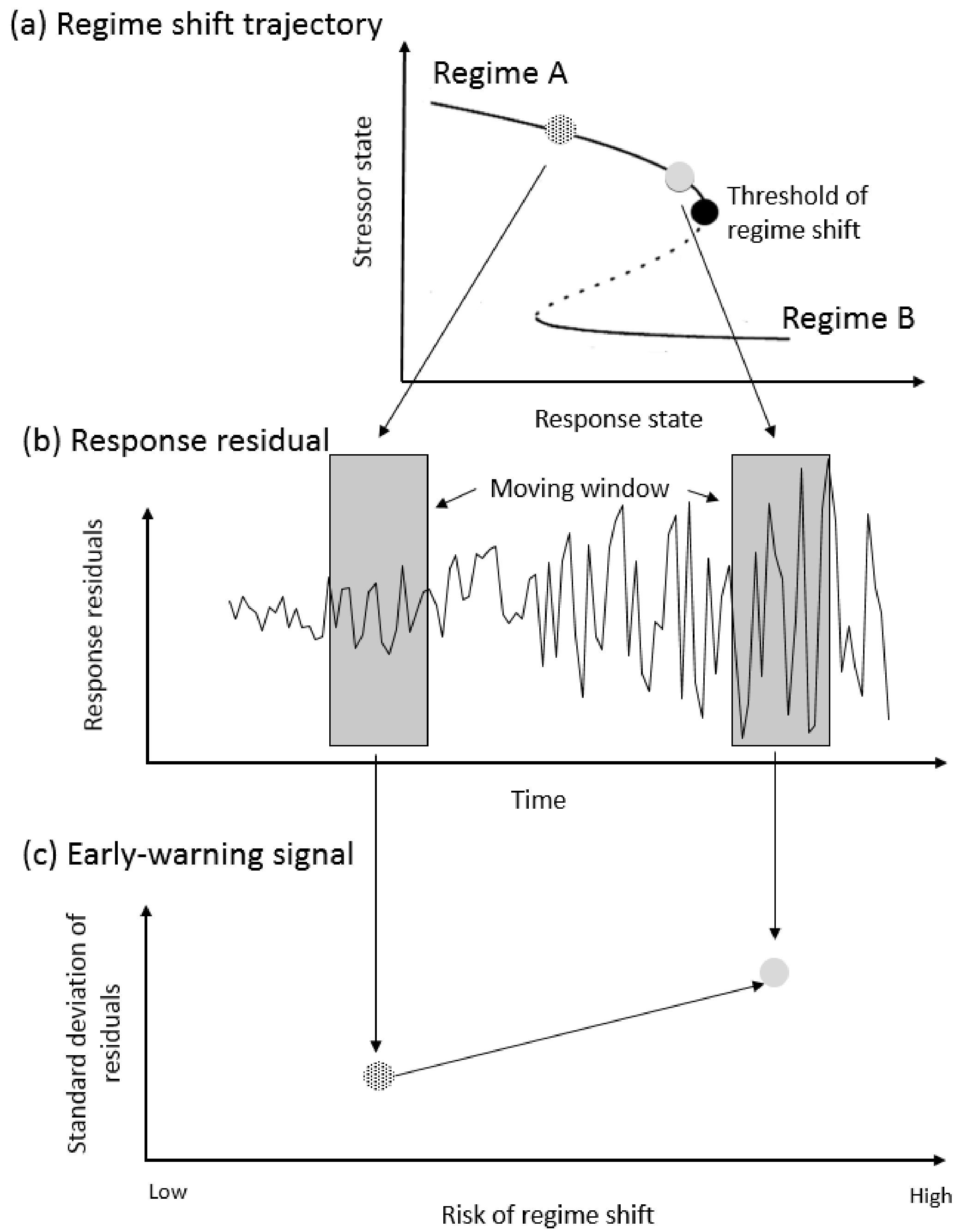

Figure 1.1 Conceptual model of early warning signal to detect decreased stability for this study: (a) system is approaching to the threshold of regime shift in regime A as stressor is changing; (b) response residuals become more fluctuated as approaching to the threshold of regime shift (from regime A to B) within same year range of moving window; (c) increased standard deviation of residuals can be considered as early warning signal of decreased stability (modified from Dakos et al., 2012 and Wouters et al., 2015)

1.3 Thesis goal, hypotheses, and predictions

The goal of this thesis was to explore if first-order catchments and their streams are effective early warning systems of the effects of global atmospheric changes on ecosystems. Early warning systems respond to changes in global and local stressors by altered biogeochemical flows in streams that can have consequences to downstream waters by altering ecosystem functions and associated services. Early warning systems can respond by changing the character of the stream response – either in terms of magnitude of a specific biogeochemical constituent (e.g., less SO_4-S deposition equals less SO_4-S export), or the stability of the stream response (e.g., a larger number and size of residuals from the modeled stressor-response relationship).

My guiding research question is, do global and local stressors have a ubiquitous effect on first-order catchment responses? My first hypothesis was that changes in global stressors are modifying the stream response from first-order catchments, and that the detection of these modifications is more problematic in managed forests given the diversity in the type, magnitude and extent of forest management activities. I tested this hypothesis using a series of statistical approaches, from simple ones with one stressor and one response, to more complex ones exploring the contributions of each stressor to multiple responses and their interactions. The use of increasingly complex models was in recognition of the need to determine the potential interactive effects within and between stressors and responses. I predicted that climate change is leading to warmer and wetter conditions that will lead to larger nutrient exports and that impact and recovery from atmospheric acidic deposition are leading to smaller nutrient exports, with the signals of atmospheric acidic deposition overriding those of climate changes because their rates of change are higher. I also predicted that signals in unmanaged catchments are more sensitive to global changes as there is no interference in the signal of the more subtle global effects by the less subtle local management effects.

My second hypothesis was that global changes are leading to decreases in stability (i.e., decreasing in stability) in catchment nutrient exports. I tested this hypothesis by examining the stream response residuals of the “best” statistical approaches from hypothesis 1 and looking for trends of increasing residual sizes – these would indicate decreasing stability in the global stressor-affected stream responses. I predicted that global change effects are increasing over time, creating greater instability (i.e., decreased stability) in stream responses.

These hypotheses were tested by data mining 22-year (16-year at one site) records of 41 first-order catchments from a network of ten long-term monitoring sites in North America forests. At each site, there were at least two first-order catchments and at least one unmanaged first-order catchment. The network of first-order streams was located in different forest types under different climate and atmospheric acidic deposition regimes across North America.

1.4 Thesis organization

This thesis is written as a monograph. Chapter 1 includes the problem statement of this study, the scientific justification for the problem statement, and the thesis objectives and hypotheses. Chapter 2 provides details of the study sites including descriptions of forestry experimental treatments at each site. Chapter 3 provides details of the methods, including the different statistical models developed in this study, used to identify trends and residuals in global stressor affected stream responses. Chapter 4 describes the results from the models. Chapter 5 discusses the modeling results and model limitations. Chapter 6 presents the scientific conclusions, management implications, and future research needs for this study.

Chapter 2

2 Study Area

2.1 Long-term monitoring sites

Biogeochemical data from 41 first-order forested catchment streams (25 unmanaged and 16 managed catchments) from ten long-term monitoring sites across North America (**Figure 2.1)** were selected in this study for the availability and accessibility of long-term (i.e., more than 16-year) daily or weekly stream discharge and biogeochemical export measurements. Unmanaged catchments are those that have been undisturbed by human activities; managed catchments are those that have experienced human modification (i.e., harvest or chemical treatments). Maps of ecological classifications (Commission for Environmental Cooperation, 2009; FAO, 2012) were used to describe the physical (i.e., soil and landform), climatic and ecological attributes of the long-term monitoring sites (**Table 2.1**). General information about the forests, climate, terrain and soil for the long-term monitoring sites is given in **Table 2.2**.

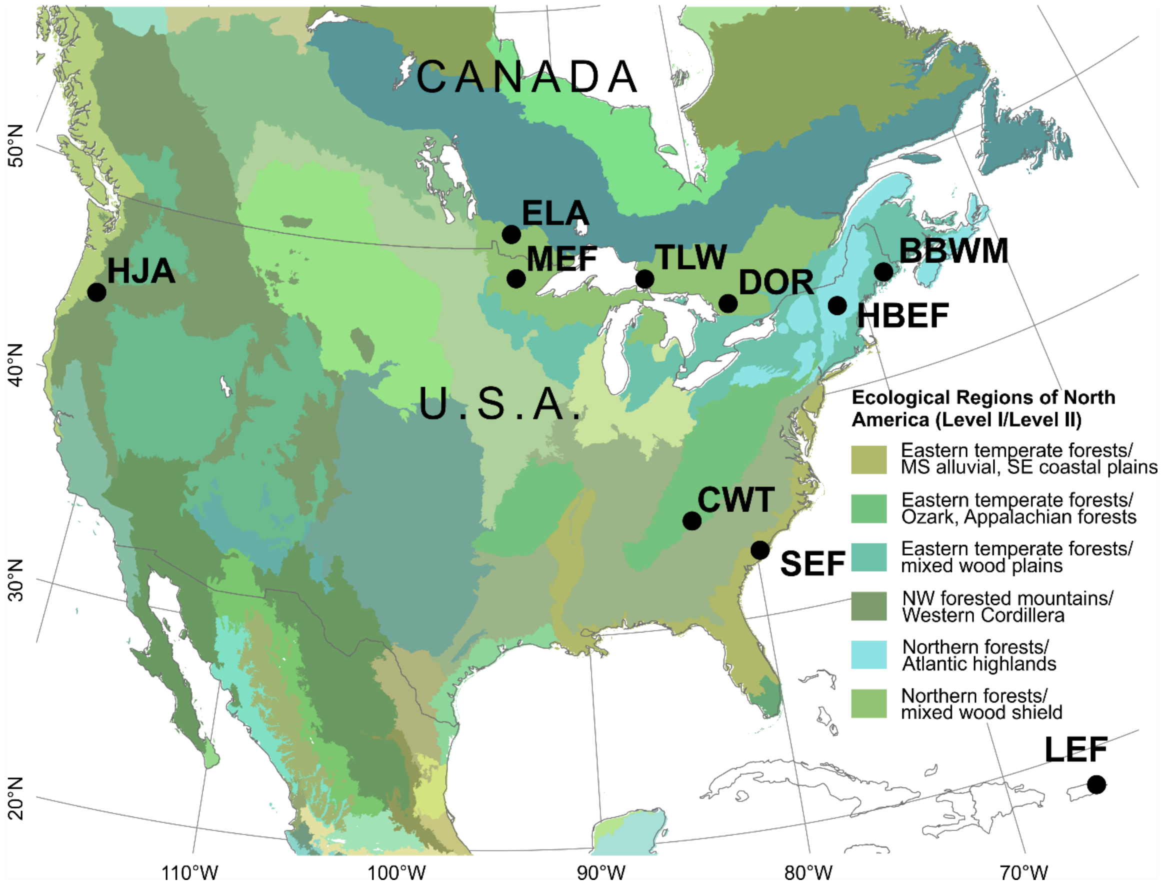

Figure 2.1 Location of study sites and Ecological Regions of North America (Commission for Environmental Cooperation, 2009). Site identifiers are: HJA – H.J. Andrews Experiment Forest; ELA – Experimental Lakes Area; MEF – Marcell Experiment Forest; TLW – Turkey Lakes Watershed; DOR – Dorset; BBWM – Bear Brook Watershed in Maine; HBEF – Hubbard Brook Experiment Forest; CWT – Coweeta Hydrologic Laboratory; SEF – Santee Experiment Forest; and LEF – Luquillo Experiment Forest.

Table 2.1 Ecological regions and descriptions of long-term monitoring sites in order of longitude (east to west) (Commission for Environmental Cooperation, 2009).

Site	Level I	Description	Level II	Description	Level III	Description
H.J. Andrews Experimental Forest (HJA), Oregon, USA	Northwestern Forested Mountains	Extends in western North America containing the highest mountains of the continent; Most diverse ecosystem types of North America; Most plains and valleys are covered by moraine and lacustrine deposits.	Western Cordillera	Extends from Alaska to southern border of Mexico; Most diverse ecosystem types of North America; Warm and dry summer, cold and snowy winter; Most plains and valleys are covered by moraine and lacustrine deposits.	Cascades	From west-central Washington State to the spine of Oregon and northern California; Warm and dry summers, mild to cool and wet winter; Mostly contains highly productive coniferous forest; Contains a dese drainage network with many alpine lakes and large reservoirs with high water quality.
Experimental Lakes Area (ELA), Ontario, Canada	Northern Forests	Extends from northern Saskatchewan east to Newfoundland and south to Pennsylvania; High percentage of boreal forests and high density of lakes on the Canadian Shield; Large area remains relatively undisturbed; Shallow to deep deposits of moraine on the top of Precambrian granitic bedrock; Cover soils are generally coarse-textured and nutrient-poor.	Mixed Wood Shield	Across the US-Canada border along Manitoba, Ontario, Minnesota, Wisconsin, and Michigan; Warm and humid summer, cold and snowy winter; Mostly contains coniferous and northern hardwood forests; Contains streams and wetlands.	Northern Lakes and Forests	Across the US-Canada border along Manitoba, Ontario, Minnesota, Wisconsin, and Michigan; Warm summer and sever winter with low humidity; Mostly contains coniferous and northern hardwood forests; Low gradient perennial streams and widespread wetlands.
Marcell Experimental Forest (MEF), Minnesota, USA						
Turkey Lakes Watershed (TLW), Ontario, Canada					Algonquin/Southern Laurentians	Extends from eastern shores of Lake Superior in Ontario to west Quebec; Warm summer, cold and snowy winter; Mixed wood frosts; Drainage network density varies from moderate to high with numerous lakes and ponds.
Dorset Environmental Science Center (DOR), Ontario, Canada						

Bear Brook Watershed in Maine (BBWM), Maine, USA	Eastern Temperate Forests	Extends from the Great Lakes in the north to the Gulf of Mexico in the south; Mildly humid climate; Consisting mostly of tall broadleaf, deciduous trees and needle-leaf conifers; Glacial lake deposits in the north; Cover soils vary from nutrient-poor to Ca rich.	Mixed Wood Plains	Extends from Ontario to Pennsylvania and New York; Warm summer and mild cold and snowy winter; Mixed wood frosts; Diverse hydrology.	Maine/New Brunswick Plains and Hills	Extends from Chaleur Bay in New Brunswick to Maine; Warm and moist summer, cold and snowy winter; Mixed wood forests; Contains low gradient drainage network with some large rivers.
Hubbard Brook Experimental Forest (HBEF), New Hampshire, USA	Northern Forests	Extends from northern Saskatchewan east to Newfoundland and south to Pennsylvania; High percentage of boreal forests and high density of lakes on the Canadian Shield; Large area remains relatively undisturbed; Shallow to deep deposits of moraine on the top of Precambrian granitic bedrock; Cover soils are generally coarse-textured and nutrient-poor.	Atlantic Highlands	Extends from northern New England to southern New York State; Warm and moist summer, cold and snowy winter; Contains mixed hardwood and spruce-fir forests; Contains perennial, high- to low-gradient streams with various sizes of lakes.	Northern Appalachian and Atlantic Maritime Highlands	Extends from northern New England to southern New York State; Warm and moist summer, cold and snowy winter; Contains mixed hardwood and spruce-fir forests; Contains perennial, high-gradient streams with various sizes of glacial lakes.
Coweeta Hydrologic Laboratory (CWT), North Carolina, USA	Eastern Temperate Forests	Extends from the Great Lakes in the north to the Gulf of Mexico in the south; Mildly humid climate; Consisting mostly of tall broadleaf, deciduous trees and needle-leaf conifers; Glacial lake deposits in the north; Cover soils vary from nutrient-poor to Ca rich.	Ozark, Ouachita-Appalachian Forests	Extends from New York to Alabama; Hot and humid summer, cold to mild winter; Mixed wood forests; Various density of perennial streams.	Blue Ridge	Extends from southern Pennsylvania to northern Georgia; Hot summer, cold to mild winter; Contains rich temperate broadleaf forests; High density of perennial, high gradient, cool, clear streams.
Santee Experimental Forest (SEF),			Mississippi Alluvial and Southeast	Extends from southern New Jersey to Massachusetts;	Middle Atlantic Coastal Plain	Extends from southern New Jersey to the South Carolina/Georgia border;

South Carolina, USA			USA Coastal Plains	Hot summer, cold to warm winter; Mixed wood forests; Various density of perennial streams and lakes		Hot and humid summer, mild winter; Dominated by longleaf pine, with more oak-hickory-pine to the north; Contains low gradient streams and rivers with swamps, marshes, and estuaries.
Luquillo Experimental Forest (LEF), Puerto Rico	Tropical mountain forest[1]	Mostly widespread in South America and in (semi-)humid mountain areas; High biodiversity at different scales; Landscape varies with elevations; Forests are seasonal disturbed by climate. (Richter, 2008)	N/A		N/A	

[1]Global Ecological Zones (FAO, 2012).

Table 2.2 General information (number of catchments, forest, climate, terrain and soil) about long-term monitoring sites in order of longitude and latitude.

Site	# Unmanaged catchments	# Managed catchments	Forest type	Forest age (yrs)	Dominant forest species	Mean annual temperature 1989-2010 (°C)	Mean annual precipitation 1989-2010 (mm)	Mean elevation (m.a.s.l.)	Relief (m)	Soil type
HJA	2	3	Coniferous	>100	Douglas-fir *(Pseudotsuga menziesli)*, western hemlock *(Tsuga heterophylla)*	7.81	2302.13	899	705	Holocene
ELA	3	0	Deciduous	>100	Jack pine *(Pinus banksiana)*, black spruce *(Picea mariana)*	3.05	414.56	392	61	Till veneer
MEF	2	2	Mixed	>80	Aspen *(Populus)*, birch, black spruce *(Picea mariana)*	3.88	624.02	444	37	Glacial till
TLW	3	3	Deciduous	>140	Sugar maple (*Acer saccharum)*	4.86	1198.56	373	300	Till veneer
DOR	4	0	Deciduous	>100	Sugar maple (*Acer saccharum*), red maple (*Acer rubrum)*	5.02	886.08	316	95	Till veneer (thin & discontinuous)
BBWM	1	1	Deciduous	>100	Northern hardwoods[1] and red spruce *(Picea rubens)*	7.38	802.56	370	210	Haplorthods in stony lodgement till
HBEF	4	1	Deciduous	>100	Sugar maple (*Acer saccharum*), North American beech *(Fagus)*, yellow birch *(Betula alleghaniensis)*	6.16	1155.13	500	260	Haplorthods and Fragiorthods
CWT	2	2	Deciduous	>60	Oak *(Quercus)*, hickory *(Carya)*, cove hardwoods[2]	15.24[4]	1264.37[4]	687	728	Holocene to Tertiary
SEF	1	1	Coniferous	>60	Loblolly pine *(Pinus taeda)*, longleaf pine *(Pinus palustris)*, and bottomland hardwoods[3]	18.49	925.48	5	12	Aquic alfisols & ultisols
LEF	3	3	Deciduous	100	Candlewood (*Pterocelastrus tricuspidatus*), swamp cyrilla (*Cyrilla racemiflora*), Sierran palm (*Prestoea acuminate*)	25.45	1998.94	400	400	Volcanoclastic

[1]*North American beech (*Fagus*), red maple* (Acer rubrum), *sugar maple* (Acer saccharum), *yellow birch* (Betula alleghaniensis), *paper birch (Betula papyrifera),* and *striped maple (Acer pensylvanicum)*.
[2]Sugar *maple* (Acer saccharum), yellow buckeye (Aesculus flava), white ash (Fraxinus americana), silverbell (Halesia), and basswood (Tilia Americana).
[3]Gum (Eucalyptus), oak (Quercus), and bald cypress (Taxodium distichum).
[4]2002-2017.

2.2 Experimental treatments

At sites with both unmanaged and managed catchments, unmanaged catchments were selected based on (1) proximity to and similarity of forest species, relief and soil type with managed catchments, and (2) an absence of recorded experimental treatments or disturbances (i.e., harvesting or chemical treatments). Unmanaged disturbances occurred at two sites as a result of Hurricane Hugo in 1989 – at LEF, 7% damage in unmanaged catchments and 50% damage in managed catchments were reported by Walker (1991), and at SEF, 80% damage in both unmanaged and managed catchments were reported by Hook et al. (1991).

Managed catchments included various physical treatments (e.g., clear cut, shelterwood cut, selection cut, thinning treatment, overstory cut, salvage cut) and chemical treatments (e.g., acid and base treatments, and fertilization). Salvage cut is applied after severe damage of the forest; for example, a salvage cut was used to remove the damaged trees in the managed catchment at SEF after Hurricane Hugo in 1989. Managed catchments typically received one type of management activity, but exceptions were recorded at HJA06 where a 9% operational road was built in addition to the 100% clear cut, and at MEF where a clear cut was followed by fertilization. The management activities at many sites (CWT, HJA, LEF, and MEF) were applied before the modeling period (1989-2010); LEF was unmanaged for 100-years, and the other sites were unmanaged for at least 10-years. Full details of management activities in the catchments are presented in **Table 2.3**.

Table 2.3 Treatment and disturbance information for catchments at long-term monitoring sites.

Unmanaged catchment	Area (ha)	Managed catchment	Area (ha)	Experimental treatment
HJA08	21	**HJA06**	13	Clear cut (100%) in 1974; operational road (9%)
		HJA07	15	Overstory cut (60%) in 1974; remaining canopy cut (40%) in 1984; non-commercial thin treatment (12%) in 2001
HJA09	9	**HJA10**	10	Clear cut (100%) in 1975
ELA01	157			
ELA02	16			
ELA03	60			
MEF05	53	**MEF04**	34	Clear cut (34%) in 1971; clear cut (71%) in 1972; NH_4NO_3 addition (340 kg ha^{-1} yr^{-1}) in 1978 (Sebestyen et al., 2011)
MEF02	10	**MEF06**	9	Clear cut (78%) in 1981; Na_2SO_4 addition (11% basal area) from 2001 to 2009 (Sebestyen et al., 2011)
TLW32	8	**TLW31**	5	Clear cut (89%) in the late summer and fall of 1997
TLW35	4	**TLW33**	24	Selection cut (29%) in the late summer and fall of 1997; operational road (< 1%)
TLW38	6	**TLW34**	68	Shelterwood cut (42%) in the late summer and fall of 1997
DOR00	542			
DOR03	46			
DOR05	190			
DOR06	100			
BBWM01	10	**BBWM02**	11	HNO_3 (126~262 kg ha^{-1} yr^{-1}) and H_2SO_4 (196~39 2kg ha^{-1} yr^{-1}) additions from 1987 to 1993; $(NH_4)_2SO_4$ (264 kg ha^{-1} yr^{-1}) addition from 1989 to 2010
HBEF06	13	**HBEF01**	12	$CaSiO_3$ addition (3800 kg ha^{-1} yr^{-1}) to increase the soil base saturation (10% to 19%) in 1999
HBEF07	77			
HBEF08	59			
HBEF09	68			
CWT02	12	**CWT07**	60	Clear cut (100%) in 1977 with no BMP[1] and buffer zones along the stream channels (Ford et al., 2011)
CWT18	12	**CWT17**	13	Clear cut (100%) between 1941 and 1955; white pine replanted at a 2 × 2 m spacing in 1956 and protected from hardwood competition by cutting and chemicals to present (Ford et al., 2011)
SEF80	206	**SEF77**	155	Various silvicultural management treatments from 1960 to 1980 (Richter et al., 1982); salvage cut (80%) after Hurricane Hugo in 1989
LEF01	6	**LEF04**	273	100-year harvest legacy; Hurricane Hugo damaged (50%) in 1989 (Walker, 1991)
LEF02	6	**LEF05**	8780	100-year harvest legacy; Hurricane Hugo damaged (50%) in 1989 (Walker, 1991)
LEF03	33	**LEF06**	1771	100-year harvest legacy; Hurricane Hugo damaged (50%) in 1989 (Walker, 1991)

[1]Best management practices in forestry (Ice et al., 2010).

Chapter 3

3 Methods

3.1 Data collection and processing

Data were provided by the managers of the long-term monitoring sites (**Appendix A**). Global stressor data were obtained at daily or weekly intervals from 1989-2010 (and for 2002-2017 at CWT where earlier measurements were not available) at each site, including air temperature, effective precipitation (runoff), and atmospheric acidic deposition (sulfate-sulfur (SO_4-S), nitrate-nitrogen (NO_3-N), and ammonium-nitrogen (NH_4-N). There were exceptions to the source of global stressor data: where site-measured air temperature (ELA, BBWM, HBEF, CWT, and LEF) or atmospheric acidic deposition data (all sites except HJA and TLW) were not available, air temperature data were acquired from nearby National Oceanic and Atmospheric Administration climate monitoring stations, and atmospheric acidic deposition data were extracted from the National Atmospheric Deposition Program (2018). Local response data were also obtained at daily or weekly intervals from 1989-2010 (and for 2002-2017 at CWT where earlier measurements were not made) at each site, including stream solute concentration of SO_4-S, NO_3-N, NH_4-N, total dissolved phosphorus (TDP), dissolved organic carbon (DOC) and calcium (Ca). There were variations to the definitions of stream exports at some sites. At MEF, total organic carbon and total phosphorus (TP) concentrations were considered as equivalent to DOC and TDP concentrations because the particulates of carbon and phosphorus in water samples were not detectable. At LEF and HBEF, the dissolved organic phosphorus fraction in water samples was negligible; therefore, observations of phosphate-phosphorus (PO_4-P) concentrations were used as TDP concentrations.

3.2 Data preparation

3.2.1 Global stressor and local response data

Global stressor and local response data needed to be compiled and converted to meet the requirement of the different analysis in this study. The daily or bi-weekly data were aggregated to water year data, and statistical analyses were performed on these water year data.

Water years were used to align the seasonal cycles of data across sites. Water years were defined based on consultations with collaborators; they were October to September for BBWM, ELA, HJA, and SEF; May to April for CWT; June to May for DOR, HBEF and TLW; and November to October for MEF. Precipitation is distributed equally through the year at LEF, and therefore the calendar year was used at this site for data aggregation.

For global stressors, air temperature at each site (or catchment where available) was provided as daily means (°C) and averaged to create water year mean daily temperatures. Stream discharge at each catchment was provided as mean rates (L s^{-1}, ft^3 s^{-1}, or m^3 s^{-1}) at daily (late spring, summer, and early fall) or bi-weekly intervals, with missing daily discharge values estimated using simple linear interpolations, and then daily discharge values converted to daily runoff (mm day^{-1}) as ratios of flow (mm^3) to catchment area (mm^2) and finally summed to create water year accumulated daily runoff. Wet atmospheric acidic depositions of SO_4-S, NO_3-N, and NH_4-N were provided as daily totals (kg ha^{-1} day^{-1}) and were summed to create water year mean daily totals. Dissolved inorganic nitrogen (DIN) deposition was included to explore the impacts of total inorganic N deposition on the stream responses, where DIN deposition was calculated as the sum of NO_3-N and NH_4-N depositions (kg ha^{-1} day^{-1}).

For local responses, six stream solutes (i.e., SO_4-S, NO_3-N, NH_4-N, TDP, DOC and Ca annual concentrations) were selected. Stream nutrients were provided as mean solute concentrations (mg L^{-1}) at daily (late spring, summer, and early fall) or bi-weekly intervals.

Mann-Kendall tests were applied to determine if there were any significant trends in time series of global stressors (i.e., temperature, runoff, SO_4-S deposition, NO_3-N deposition, NH_4-N deposition, and DIN deposition) and stream responses (i.e., SO_4-S, NO_3-N, NH_4-N, TDP, DOC, Ca) over the measuring periods. The magnitudes of the trends were measured as the significant

($p < 0.1$) Theil-Sen slope of the linear regressions of stressors or stream responses vs. water year. A significance level of $p<0.1$ was applied thoroughly out all regression analysis in this study because it is commonly used and recommended in various research fields (e.g., Lancaster, 1961; Rhoads & Morse, 1971; Wahlby et al., 2001).

3.2.2 Correlation analysis

Correlations among global stressors and between global stressors and stream responses were tested using non-parametric Spearman rank-order correlation analysis, with significant correlations identified as those with $\rho > \rho$-crit at $\alpha = 0.1$.

3.2.3 Multivariate analysis

Redundancy analysis (RDA) was performed using global stressors as explanatory variables for stream responses in each catchment using the vegan package (Oksanen et al., 2007) in R. RDA is an extension from principal component analysis that is used to analyze the correlations between the global stressors and stream responses in a multi-variate log-linear environment (i.e., including multiple global stressors and stream responses in one analysis process) (Zuur et al., 2007). Stream response data were natural log-transformed. Both untransformed global stressor data and transformed stream response data were then scaled to adjust the data to a mean of zero and variance of one following **Equation 3.1**, where x is the measurement and n is the data size.

$$\text{scaled value} = \sqrt{\frac{\sum x^2}{n-1}} \qquad \text{(Equation 3.1)}$$

For each catchment, scaled values of the six global stressors (i.e., temperature, runoff, SO_4-S deposition, NO_3-N deposition, NH_4-N deposition, and water year) were fitted into RDA models as explanatory variables for the transformed and scaled values of the six stream responses (i.e., SO_4-S, NO_3-N, NH_4-N, TDP, DOC, Ca). P-values from RDA analysis were used to evaluate the significance (< 0.1) of the RDA models as well as of each of the explanatory variables in the RDA models.

3.3 MARSS models

Multivariate autoregressive state space (MARSS) models were developed and converted as an R package based on the algorithm of the maximum likelihood framework (i.e., Expectation-Maximization algorithm) with Gaussian errors (Harvey, 1990; Durbin & Koopman, 2001; Holmes et al., 2014).

3.3.1 MARSS general equations

MARSS models are based on two linear models: an observation model (**Equation 3.2**) and a process model (**Equation 3.3**) (Durbin & Koopman, 2001; Homes et al., 2014). The observation model uses measured stream responses to produce modeled stream responses (i.e., processed estimations) with the observation errors (i.e., human-, equipment- or technique-based errors) that can be input to the process model.

$$\mathrm{y_t} = \mathrm{Zx_t} + \mathrm{v_t};\ v_t \sim MVN(0, R) \qquad \text{(Equation 3.2)}$$

In the observation model, *y* is an *i* × *j* spatial temporal matrix contains datasets of the six stream responses; *x* is a *k* × *j* matrix of the processed estimations based on values of *y*; *v* is an *i* × *j* matrix of the observation errors (residuals) of *y* based on the multivariate normal distribution (MVN) of an *i* × *i* covariance matrix *R*; *t* presents the specific time based on *y* (i.e., the water year from 1989 to 2010 for all catchments except for CWT where it was from 2002 to 2017); *Z* is an *i* × *i* state space matrix which defines the spatial scale of the processed estimations *x* (i.e., how many *x* need to be estimated); *i* is equal to the number of catchments × the number of stream responses; *j* is the measuring period of the responses (i.e., 22 years in this study or 16 years for CWT); and *k* is equal to the number of state spaces × the number of stream responses (the number of state spaces depends on the size of the *x* matrix) (Ives et al., 2003; Hampton et al., 2013; Holmes et al., 2014; Smits et al., 2019).

$$\mathrm{x_t} = \mathrm{Bx_{t-1}} + \mathrm{Cc_t} + \mathrm{w_t};\ w_t \sim MVN(0, Q) \qquad \text{(Equation 3.3)}$$

In the process model, *c* is a *k* × *j* matrix temporal-spatial matrix containing datasets of the seven global stressors; *w* is a *k* × *j* matrix of the process errors (residuals) of *x* based on the MVN of *k* × *k* covariance matrix *Q*; *B* is a *k* × *k* response interaction matrix which presents the strength of chemical interactions within the response pool; C is a $k \times l$ stressor-response interaction matrix which presents the relationship between the stressor and responses; and l is equal to the number of state spaces (Ives et al., 2003; Hampton et al., 2013; Holmes et al., 2014; Smits et al., 2019).

3.3.2 MARSS matrix structures

MARSS models require two types of input: fixed inputs and unfixed inputs. Fixed inputs are the spatial-temporal data (i.e., the global stressors and stream responses); unfixed inputs are changeable coefficient matrices (i.e., *B*, *C*, *Z*, *R*, and *Q* matrices). The different structures of changeable coefficient matrices will affect the modeling outputs; therefore, choosing the appropriate structure of the matrices with consideration for biogeochemical meaning is important.

Many types of matrix structures can be applied in the equations; the following are some of the most commonly used in studying ecological stability (**Figure 3.1**).

Zero

$$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Identity

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Unconstrained

$$\begin{bmatrix} \sigma_1^2 & \sigma_{1,2} & \sigma_{1,3} \\ \sigma_{2,1} & \sigma_2^2 & \sigma_{2,3} \\ \sigma_{3,1} & \sigma_{3,2} & \sigma_3^2 \end{bmatrix}$$

Diagonal and equal

$$\begin{bmatrix} \sigma^2 & 0 & 0 \\ 0 & \sigma^2 & 0 \\ 0 & 0 & \sigma^2 \end{bmatrix}$$

Diagonal and unequal

$$\begin{bmatrix} \sigma_1^2 & 0 & 0 \\ 0 & \sigma_2^2 & 0 \\ 0 & 0 & \sigma_3^2 \end{bmatrix}$$

Equal variate covariate

$$\begin{bmatrix} \sigma^2 & \beta & \beta \\ \beta & \sigma^2 & \beta \\ \beta & \beta & \sigma^2 \end{bmatrix}$$

Figure 3.1 Examples of coefficient matrix structures, where σ and β are estimations from MARSS modeling process, $\sigma_{1,2}$ indicates the matrix parameter in column 1 and row 2 (modified from Holmes et al., 2014).

Zero and *Identity* matrices have fixed values. When the *zero* matrix is applied, the related matrix is ignored during the modeling process (e.g., if the *C* matrix is set to "*zero*", the global stressor will be ignored and the model considered as a “no-stressor” model). When the *Identity* matrix is applied, a constrained matrix fixes interaction along the diagonal of the matrix (e.g., response vs. response or stressor vs. response). For example, a *3 × 3 Identity B* matrix (**Table 3.1**) means that the three parameters interact with themselves only at different time steps (e.g., x_1 at time *t-1* only interacts with x_1 at time *t*). In contrast, an unconstrained matrix (not commonly used) provides the option for the MARSS modeling process to estimate all interactions in the matrix.

Table 3.1 Example of *B* matrix structure.

	$x_{1,t-1}$	$x_{2,t-1}$	$x_{3,t-1}$
$x_{1,t}$	1	0	0
$x_{2,t}$	0	1	0
$x_{3,t}$	0	0	1

Diagonal and Equal, *Diagonal and Unequal*, and *Equal Variate Covariate* matrices are used for the *Q* and *R* matrices and influence the variance and covariance of the process and observation error matrices. The *Diagonal and Equal* matrix indicates observation or process errors for all catchments in a model share the same variance with no covariance. The *Diagonal and Unequal* matrix indicates that observation or process errors for all catchments in a model have different variance with no covariance). The *Equal Variate Covariate* matrix indicates that observation or process errors for all catchments in a model share the same variance and covariance) (Smits et al., 2019).

3.3.3 MARSS model development assumptions

Several assumptions were used in the development of the MARSS models as applied in this study. *First*, MARSS models treat interactions between global stressors and stream responses as linear. However, contemporary climate change studies often suggest a non-linear relationship between stressors and responses (Tayleur et al., 2016). To account for this, many studies have applied log-linear models to study climate change impacts and consequences (Kroiss & HilleRisLambers, 2015; Arbuthnott et al., 2016; Tayleur et al., 2016). In this study, stream response input data were therefore natural log-transformed (both global stressor and transformed stream response data were scaled using **Equation 3.1**). *Second*, chemical interactions between different stream responses in the same catchment are assumed to be negligible due to the short retention time for internal cycling in streams (Ives et al., 1999; Chapin et al., 2011). In this study, the *B* matrix was therefore defined as an *Identity* matrix so that a response *x* at time *t* is only dependent on the same response at time *t-1* (i.e., the interaction coefficients of the same response at a different time are equal to 1). Additionally, there is no dependence of a response *x* at *t* to any different responses at *t-1* (i.e., the interaction coefficients of a response to other responses are equal to 0). *Third*, observation errors in stream responses between sites are not correlated to each other because measurements were taken by different people using different equipment and/or procedures at each site. In this study, MARSS models were therefore developed separately for each site.

Assumptions of observation and process errors are incorporated in the structure of *Q* and *R* matrices as explained in **Chapter 3.3.4**. Other studies have tested different structures of these matrices that assume different variance of observation and process errors (e.g., Jorgensen et al., 2016; Ohlberger et al., 2016; Zhu et al., 2017; Smits et al., 2019) because these errors can vary randomly between different study areas. In this study, I assume that there is no covariance between observation errors or process errors in different stream responses; therefore, the *Equal Variate Covariate Q* and *R* matrices are not tested. Similarly, I assume that observation errors and process errors could share the same variance (because they may have been measured by the same person, equipment, and procedure) or have different variance within the same stream response. In this study, both *Diagonal and Equal*, *Diagonal and Unequal Q* and *R* matrices are tested at each site. The variance of observation errors or process errors may be different at each site.

3.3.4 MARSS model development

MARSS models were developed for each site using the configurations shown in the flow chart presented in **Figure 3.2**. At each site, six stream responses and six global stressors were selected as the fixed inputs for the modeling process. Ives et al. (2003) indicate that correlated global stressors should not be input into the same model; therefore, at sites where two or more global stressors were found to be correlated, the stressors were fitted into separate models. A no-stressor and a water year stressor model were also applied at each site. No-stressor models are commonly used in MARSS modeling studies as a validation to test the significance of the applied global stressors (i.e., if the influence of global stressors on MARSS model estimations is random) (Ives et al., 1999; Smits et al., 2019). The water year stressor model fitted year (e.g., a year from 1989 to 2010) as an alternative "stressor" to capture the evidence of a systematic trend in the modeling process (i.e., to test if there were other influences to the stream response changes other than the applied global stressors).

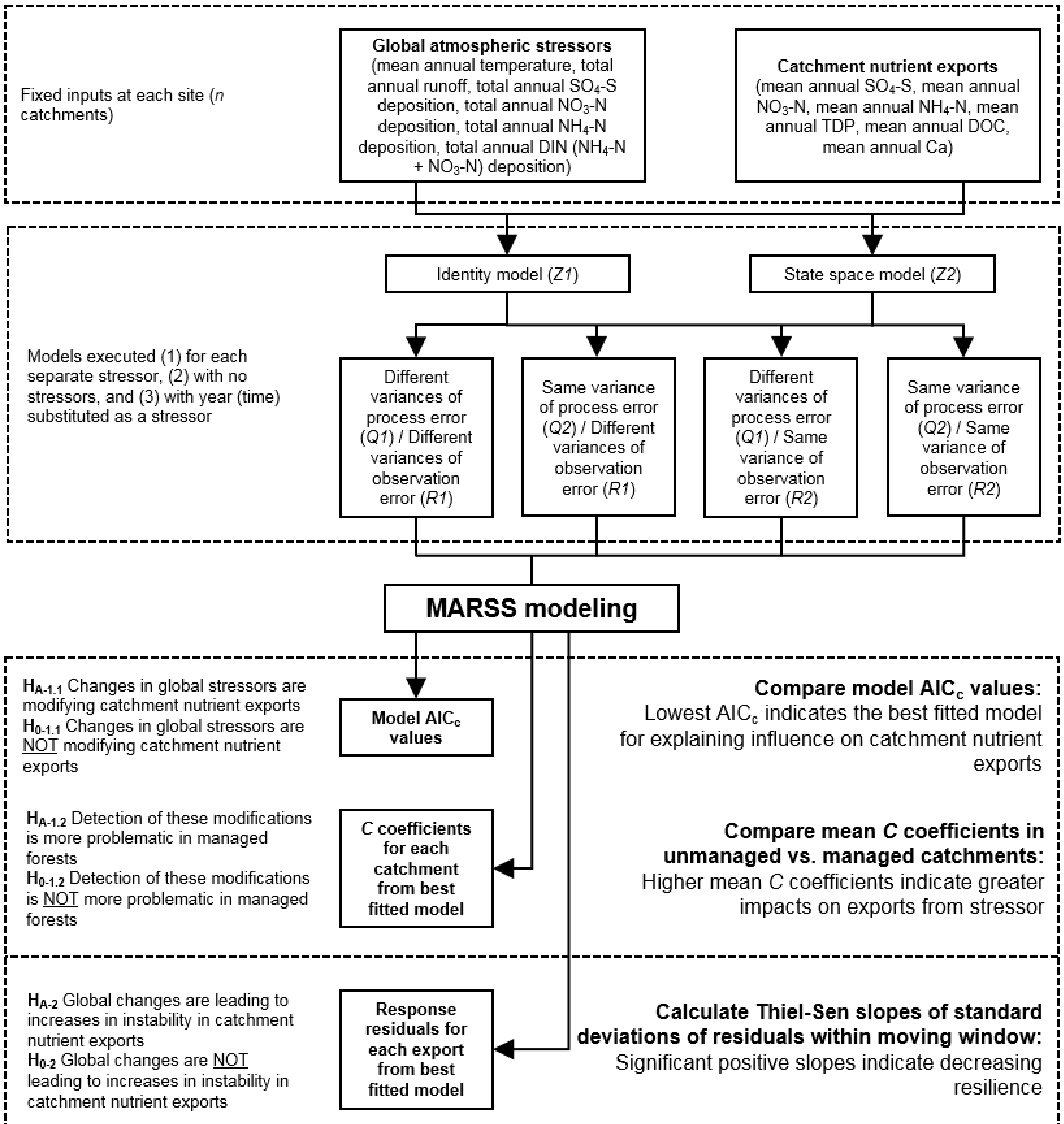

Figure 3.2 MARSS modeling flow chart for this study.

For the unfixed inputs, one type of *B* and *C* matrices and two types each of *Z*, *Q* and *R* matrices were applied (**Table 3.1**). For the *Z* matrix, an *Identity* structure means that number of catchments is equal to number of state spaces. In contrast, the state space structure of the *Z* matrix treated all unmanaged catchments at the same site as a single state space in which these unmanaged catchments shared same global stressors, observation, and process errors. Unmanaged catchments across different long-term monitoring sites were not combined into state spaces because: (1) The purpose of this study does not include exploring if there are regional differences in catchment biogeochemical stability; (2) There is no universal template for defining regions (i.e., using climate zones or forest eco-regions results at all sites except three being part of the same region or state space); and (3) The long-term monitoring sites vary along with a number of independent gradients or categories (including but not necessarily limited to latitude, longitude, elevation, relief, aspect, soils, geology, species, etc.) that make the definition of a template arbitrary. This study also did not consider managed catchments either within or across different sites to be single state spaces because the management treatments in the managed catchments were different between sites and even between catchments at the same site. Therefore, assumptions about the *R* matrix cannot be made for this study. Example of MARSS codes can be found in **Appendix B**.

Table 3.2 MARSS matrix structures used in this study.

Matrix	Description	Structure	Purpose
B	Interactions between response at the time of *t-1* and time of *t* (response impact)	*Identity*: Each response has fixed interaction only with itself	To assume no interactions between different responses, and interactions of the same response are fixed.
C	Stressor-responses interactions at the time of t (stressor impact)	Each catchment has a different stressor	To follow the data measurement method (i.e., stressor data were measured in each catchment)
Z	State space matrix to group catchments	*Identity*: Each catchment is its own space	To test the difference between the two types of *Z* matrix structure (identity model vs. state space model)
		State space: Unmanaged catchment at same sites as one space	
Q	Estimations of process error (white noise for process equation)	*Q1*: Different variance of process errors in each catchment	To simulate the process errors of the response: *Q1* each catchment had different process errors; *Q2* the response across different catchments shared same process errors
		Q2: Same variance of same process errors in each catchment	
R	Estimations of observation error (white noise for observation equation)	*R1*: Different variance of observation errors in each catchment	To simulate the observation errors of the response: *R1* each catchment had different observation errors; *R2*

	R2: Same variance of same observation errors in each catchment	response across different catchments shared same observation errors

3.3.5 MARSS model performance

Models developed in this study were examined using the diagnostics method suggested in Ives et al. (2003). The three diagnostics that were used included: (1) Bootstrapping for all no-stressor models and best fitted models to estimate the validation and accuracy of the models (Kosmidis, 2018); a Hessian function was used to bootstrap the confidence interval of each model, with large confidence interval values indicating that the models might not be accurate enough to explain changes in stream responses. (2) Autocorrelation functions (ACFs) for the residuals of the natural log-transformed responses (i.e., if the response residuals were correlated to each other); ACFs values beyond the 95% confidence intervals indicate that the model is not adequate to detect all the systematic changes in the related response distributions (Holmes et al., 2014). And (3) Quantile-Quantile (Q-Q) plots for the standardized residuals (**Appendix C**) of the responses were used to test the normality of the response residuals; if the residuals sit approximately on the line of y = x, it can be concluded that the residuals are normally distributed (Gibbons & Chakraborti, 2011). A normal distribution of the standardized residuals indicates that the models are adequate; in contrast, non-normal distribution of the standardized residuals might indicate that the models are inadequate.

3.4 MARSS model applications

MARSS outputs including Akaike's Information Criterion adjusted for small sample size (AIC_c), *C* matrix coefficients, and process errors from the process models were used to test the hypotheses posed in this thesis (**Figure 3.2**).

3.4.1 Hypothesis 1 – Global stressors are driving trends in stream responses

Hypothesis 1 was that global stressors are driving trends in stream responses. To test this hypothesis, 304 models were examined (i.e., 32 or 64 models at each site), including all possible combinations of (1) eight stressor types (no-stressor, water year, and six global stressors), (2) two types of *Z* matrix structures (state space vs. identity matrix structures) at sites where there was more than one unmanaged catchment, (3) two types of *Q* matrix structures (different variances vs same variance of process errors), and (4) two types of *R* matrix structures (different variances vs same variance of observation errors). The model with the lowest AIC_c at each site was selected as the best-fitted model for that site for explaining changes in stream responses (Anderson & Burnham, 2002; Ohlberger et al., 2016; Smits et al., 2019). AIC_c weights were used to estimate the likelihood that the selected model was the most likely model among the evaluated models. AIC_c weight is an estimation of the likelihood that the targeted model is the best-fitted model and is calculated as the ratio of the targeted AIC_c and the sum of AIC_c values (**Equation 3.4**).

$$\mathrm{AIC_c\ weight} = \frac{\exp\left\{-\frac{1}{2}\Delta \mathrm{AIC_C}\right\}}{\sum \exp\left\{-\frac{1}{2}\Delta \mathrm{AIC_C}\right\}} \qquad \text{(Equation 3.4)}$$

where ΔAIC_c is the difference between the AIC_c of the targeted model and the lowest AICc. AIC_c weight has a value range from zero to one. A higher AIC_c weight indicates that the model is more likely to be the best-fitted model (Anderson & Burnham, 2002).

At each site, the most likely identity model for all combinations of *Q* and *R* matrices for each stressor type (no-stressor, water year, and six global stressors) was identified as the model with the lowest AIC_c. At sites where a stressor model was found to produce a better-fitted model than no-stressor or water year models, changes in that stressor were assumed to have produced modifications in stream responses. If a stressor model (i.e., neither the no-stressor model nor the water year model) was found to be the best-fitted model at a site, it indicated that the global stressor changes were highly correlated to the changes of the stream responses at that site; i.e., that the global stressor had a larger impact on stream responses at that site than random influences, other global stressors or unknown stressors. If a no-stressor model was found to be the best-fitted model at a site, it was assumed that the effects of the applied global stressor changes on the stream response changes were random at that site (i.e., none of the global stressor changes had strong correlations to the stream responses changes). If a water year model found to be as the best-fitted model at a site, it was assumed that there were untested influences (either unidentified global stressors or by the interacting effects of an unidentified combination of the applied global stressors) on the stream response changes. Because the accuracy of MARSS models will be reduced with multiple correlated stressors, multivariate linear regressions were used to test correlations between years and all possible combinations of the global stressors (excluding DIN which is itself a combination of NO_3-N and NH_4-N) at sites where a water year model was found to be the best-fitted model. AIC_c weights of the coefficients of determination (r^2) values from the top five best fitted linear models were calculated to explore the unknown influences.

At sites where a global stressor provided the best-fitted model, the model's *C* matrix coefficients were used to determine the effects of the global stressors on the individual stream responses in each catchment. The *C* matrix coefficients have a range from positive to negative infinity. A higher absolute value of the *C* matrix coefficient indicates a higher direct impact level from the global stressor to the individual stream response. Mean *C* matrix coefficients in the same types of catchments (i.e.., unmanaged catchment or managed catchment) at each site were used to compare the impact differences between the global and local stressors (i.e., the impact of the global stressor between unmanaged and managed catchments). If unmanaged catchments in a site had a higher absolute mean *C* matrix coefficient than managed catchments, then it can be concluded that unmanaged catchments are more sensitive to the impacts of the global stressor than the managed catchments.

3.4.2 Hypothesis 2 – Global stressors are driving instabilities in stream responses

Hypothesis 2 was that global stressors are creating instabilities in stream responses. To test this hypothesis, process errors from the process models were used to detect signals of decreased biogeochemical stability using a method modified from Wouter et al. (2015). Process errors were considered as the residuals from trends in stream responses that reflect the internal changes of the catchment biogeochemical flows or the external changes of global stressors. Observation errors from the observation equations were not examined. These types of errors only occurred over the water sampling process and did not influence the estimations of *B* and *C* matrix; therefore the process errors should be considered as part of the catchment biogeochemical cycling process. The models produced process errors for each stream response in each catchment at each site.

The standard deviations of process errors of each response in each catchment were calculated within various lengths of moving windows (i.e., 3-year, 4-year, 5-year, and 7-year). Trends in the standard deviations of the process errors were tested using Mann-Kendall analysis, and the direction and magnitude of the change were tested evaluated using Theil-Sen slope analysis. The tau values from the Mann-Kendall analysis were used to select the length of the moving window; the largest number of significant ($p < 0.1$) trends in different moving window lengths indicated the appropriate length. An increasing significant trend (i.e., positive Theil-Sen slope) in standard deviations of process errors indicates that the stream response in that catchment is destabilizing, representing higher risk of regime shift of that stream response (i.e., the biogeochemical stability of the stream response decreased) (Wouters et al., 2015). Further, if there were multiple increasing significant trends at a site, it might indicate that the biogeochemical structure and function of that site had higher potential risks of regime shifts.

Chapter 4

4 Results

4.1 Trends in global stressors and stream responses

Summaries of the presence of trends for each global stressor and stream response are provided in **Tables 4.1** and **Table 4.2**, with more details on the statistical tests presented in **Appendix D**.

Trends varied among global stressors, both within and among long-term monitoring sites (**Table 4.1**). However, fewer than half (41.7%) of all global stressor trends for all sites were significant at $p < 0.1$ over the span of the study period (1989-2010, except 2002-2017 at CWT). Four sites showed significant climate changes [i.e., increasing temperature (LEF) or increasing (HBEF) or decreasing (TWL and BBWM) runoff], and seven sites (i.e., MEF, TLW, DOR, BBWM, HBEF, CWT, and SEF) showed significant declines in two or more atmospheric acidic depositions. Some sites had multidirectional changes in stressors (i.e., temperature increased or runoff increased or decreased while atmospheric acidic depositions declined). Further details are presented in **Table D.1** of **Appendix D**.

Table 4.1 Summary of presence of significant trends in global stressors at long-term monitoring sites ($p < 0.1$).

Sites (n = 10)	Mean annual temperature (°C yr^{-1})	Total annual runoff (mm yr^{-1})	Total annual SO_4-S deposition (kg ha^{-1} yr^{-1})	Total annual NO_3-N deposition (kg ha^{-1} yr^{-1})	Total annual NH_4-N deposition (kg ha^{-1} yr^{-1})	Total annual DIN deposition (kg ha^{-1} yr^{-1})
# significant trends	1	3	7	6	3	5
% significant trends	10	30	70	60	30	50
# significant increasing trends	1	1	0	0	0	0
% significant increasing trends	10	10	0	0	0	0
# significant decreasing trends	0	2	7	6	3	5
% significant decreasing trends	0	20	70	60	30	50

Over the same time period, more significant trends (50.0% for all catchments at $p < 0.1$) were found in stream responses than in global stressors (18.3% increasing and 31.7% decreasing) (**Table 4.2**). SO_4-S exports most frequently had significant trends; 28 catchments (68.3%) had significant trends, with 9 (22.0%) increasing and 19 (46.3%) decreasing. DOC exports had the smallest number of significant trends; 11 catchments (26.8%) had significant trends, with 5

(12.2%) increasing and 6 (14.6%) decreasing. Nineteen catchments (46.3%) had significant trends in NO_3-N exports, with 3 (7.3%) increasing and 16 (39.0%) decreasing. Twenty-six catchments (63.4%) had significant trends in NH_4-N exports, with 12 (29.3%) increasing and 14 (34.1%) decreasing. Twenty-two catchments (53.7%) had significant trends in TDP exports, with 8 (19.5%) increasing and 14 (34.1%) decreasing. Seventeen catchments (41.5%) had significant trends in Ca exports, with 8 (19.5%) increasing and 9 (22.0%) decreasing. Further details are presented in **Table D.2** of **Appendix D**.

There were no major differences in significant trends between unmanaged and managed catchments (**Table 4.2**); unmanaged catchments had only slightly fewer significant trends (47.3%) than managed catchments (54.2%). The largest number of significant trends in both unmanaged and managed catchments were for SO_4-S and NH_4-N exports, followed by TDP (48.0% of unmanaged vs. 62.5% of managed catchments), NO_3-N (40.0% of unmanaged vs. 56.3% of managed catchments), Ca (44.0% of unmanaged vs. 37.5% of managed catchments) and finally DOC exports (24.0% of unmanaged vs. 31.3% of managed catchments). In unmanaged catchments, the majority of trends were decreasing (except for DOC where there was no difference between increasing and decreased trends). In management catchments, the majority of trends were also decreasing, except for NH_4-N and Ca. There were no major differences in the likelihood of increasing significant trends in TDP and DOC exports between unmanaged catchments (20.0% and 12.0% respectively) and managed catchments (18.8% and 12.5% respectively). SO_4-S and NO_3-N had more varied trends (82.4% and 70.6% of catchments) than other stream response in northern forests (i.e., ELA, MEF, TLW, and DOR).

Table 4.2 Summary of significant trends in mean daily concentration (mg L^{-1} yr^{-1}) of stream responses in unmanaged and managed catchments at long-term monitoring sites ($p < 0.1$). Northern forests are ELA, MEF, TLW, DOR.

	Mean daily SO_4-S	Mean daily NO_3-N	Mean daily NH_4-N	Mean daily TDP	Mean daily DOC	Mean daily Ca
Unmanaged catchments (n = 25)						
# significant trends	17	10	15	12	6	11
% significant trends	68.0	40.0	60.0	48.0	24.0	44.0
# significant increasing trends	5	1	6	5	3	3
% significant increasing trends	20.0	4.0	24.0	20.0	12.0	12.0
# significant decreasing trends	12	9	9	7	3	8
% significant decreasing trends	48.0	36.0	36.0	28.0	12.0	32.0
Managed catchments (n = 16)						
# significant trends	11	9	11	10	5	6
% significant trends	68.8	56.3	68.8	62.5	31.3	37.5
# significant increasing trends	4	2	6	3	2	5
% significant increasing trends	25.0	12.5	37.5	18.8	12.5	31.3
# significant decreasing trends	7	7	5	7	3	1
% significant decreasing trends	43.8	43.8	31.3	43.8	18.8	6.3
Northern forest catchments (n=17)						
# significant trends	14	7	12	4	6	4
% significant trends	82.4	41.2	70.6	23.5	35.3	23.5
# significant increasing trends	5	2	5	4	5	1
% significant increasing trends	29.4	11.8	29.4	23.5	29.4	5.9
# significant decreasing trends	9	5	7	0	1	3
% significant decreasing trends	52.9	29.4	41.2	0.0	5.9	17.6

4.2 Relationships between global stressors and stream responses

4.2.1 Univariate regression tests

Spearman correlation analysis between single global stressors and single stream responses revealed that no stream response was correlated to any global stressor in the majority of catchments (**Table 4.3**). Stream responses were most often correlated with water year (i.e., trends in responses were detected but they were generally not correlated to the selected stressors). Stream SO_4-S was the most frequently correlated to global stressors; however, stream SO_4-S was correlated to SO_4-S deposition in only 37% of catchments, while stream NO_3-N concentration was similarly correlated to NO_3-N deposition in only 20% of catchments and stream NH_4-N concentration was correlated to NH_4-N deposition in only 32% of catchments.

Table 4.3 Spearman correlation matrices of global stressors and mean daily concentration (mg L^{-1} yr^{-1}) of stream responses. Each value indicates the percentage of catchments for which a pair of stressors and responses were significantly correlated (ρ > ρ-crit, 2-tailed test, α = 0.1)

	Rank mean daily SO_4-S	Rank mean daily NO_3-N	Rank mean daily NH_4-N	Rank mean daily TDP	Rank mean daily DOC	Rank mean daily Ca
Rank water year	66	49	56	56	29	44
Rank mean annual temperature (°C)	24	5	17	10	12	22
Rank total annual runoff (mm)	39	17	15	27	7	39
Rank total annual SO_4-S deposition (kg ha^{-1})	37	32	44	17	15	27
Rank total annual NO_3-N deposition (kg ha^{-1})	37	20	37	22	12	12
Rank total annual NH_4-N deposition (kg ha^{-1})	24	22	32	10	10	7

4.2.2 Multivariate regression models

Multivariate RDA models were significant ($p < 0.1$) in 80.0% of the catchments (**Table 4.4**). NH_4-N deposition was a significant component in 82.9% of catchment RDA models, a much larger percentage than the next largest percentage (51.4% for NO_3-N deposition). Runoff and water year were significant in the smallest percentage of catchment RDA models (25.7% and 20.0% respectively). Details of RDA results can be found in **Table E.1** in **Appendix E**.

Table 4.4 Percentage of catchments with significant RDA models of global stressors as explanatory variables for stream responses, and percentage of catchments for which individual global stressors were significant parts of the RDA models ($p < 0.1$).

	Percentage
RDA model	80.0
Water year	20.0
Mean annual temperature (°C)	42.9
Total annual runoff (mm)	25.7
Total annual SO_4-S deposition (kg ha^{-1})	37.1
Total annual NO_3-N deposition (kg ha^{-1})	51.4
Total annual NH_4-N deposition (kg ha^{-1})	82.9

4.2.3 Multivariate autoregressive models

Prior to MARSS analysis, correlations between water year and stressors and among global stressors were examined. There were a large number of significant correlations between year and global stressors, and among the global stressors (especially among atmospheric acidic depositions which were correlated to another deposition in a minimum of 88% of sites) (**Table 4.5**). Therefore, global stressors were fitted into separate models at each site (see **Chapter 3.3.4**).

Table 4.5 Spearman correlation matrices of global stressors; each value indicates the percentage of sites for which a pair of stressors were significantly correlated (ρ > ρ-crit, 2-tailed test, α = 0.1).

	Rank water year	**Rank mean annual temperature (°C)**	**Rank total annual catchment runoff (mm)**	**Rank total annual SO_4-S deposition (kg ha^{-1})**	**Rank total annual NO_3-N deposition (kg ha^{-1})**	**Rank total annual NH_4-N deposition (kg ha^{-1})**
Rank water year	--					
Rank mean annual temperature (°C)	22	--				
Rank total annual catchment runoff (mm)	22	5	--			
Rank total annual SO_4-S deposition (kg ha^{-1})	66	24	34	--		
Rank total annual NO_3-N deposition (kg ha^{-1})	63	27	29	90	--	
Rank total annual NH_4-N deposition (kg ha^{-1})	27	2	12	88	95	--

MARSS modeling diagnostics, including bootstrapping, ACFs and Q-Q plots, indicated that the models developed for this study were reasonable and can be accepted as valid results. Specifically, bootstrapping results (**Appendix F**) showed no errors and the confidence interval (CI) values indicating low deviation from the mean of the modeling results confirming the goodness of fit of MARSS models; ACF results were all below the 95% confidence intervals indicating that the models were well fitted; and Q-Q plots showed all response residuals were normally distributed.

Hypothesis 1 was that global changes are modifying stream responses at long-term monitoring sites. To test this hypothesis, stressor models were compared with no-stressor and water year models for each site. State space models in which all unmanaged catchments at a single site were treated as a single state space had stronger statistical explanations for stream responses at each site (i.e., lower AIC_c; **Appendix G)** than *Identity* models. However, the state space models assume that process errors are the same for all catchments sharing a state space and therefore do not yield residuals for individual catchments. In addition, modeling results in each unmanaged catchments at the same site were different, which indicated that correlations between global stressors and stream response were different in unmanaged catchments. Because I wanted to examine the differences in response residuals for all unmanaged catchments, the results of the *Identity* models are given in this chapter.

For the *Identity* models, a *Q* matrix structure forcing the same variance of process errors in all catchments produced the best-fitted model in eight sites (excluding HBEF and SEF), and a *R* matrix structure forcing different variances of observation errors in all catchments produced the best-fitted model at eight sites (excluding MEF and SEF). A combination of these *Q* and *R* matrix structures produced the best-fitted model at seven sites (excluding MEF, HBEF, and SEF).

Among *Identity* models, global stressors had the largest impacts on stream responses at six sites, although there was no clear pattern of which global stressor was having these impacts. Climate change stressors had the largest impact on stream responses at sites located at the interior of the continent, whereas atmospheric acidic pollution stressors had the largest impact on stream responses at sites located closer to the coastal areas of the continent (**Figure 4.1**). The best fitted stressor models at most sites had AIC_c weights greater than 95% except at LEF where the best-fitted stressor model was a DIN deposition model that had an AIC_c weight of 60% (but the second best-fitted model at LEF with an AIC_c weight of 15% was a NO_3-N deposition model (a component of DIN) (**Table 4.6**). Stream responses in coastal long-term monitoring sites (HJA, BBWM, SEF, and LEF) were impacted by atmospheric acidic deposition stressors, with HJA, BBWN and SEF driven by atmospheric acidic deposition decreases and LEF affected by atmospheric acidic deposition increases (NO_3-N, NH_4-N and DIN deposition respectively) (**Figure 4.1**; **Table 4.6**).

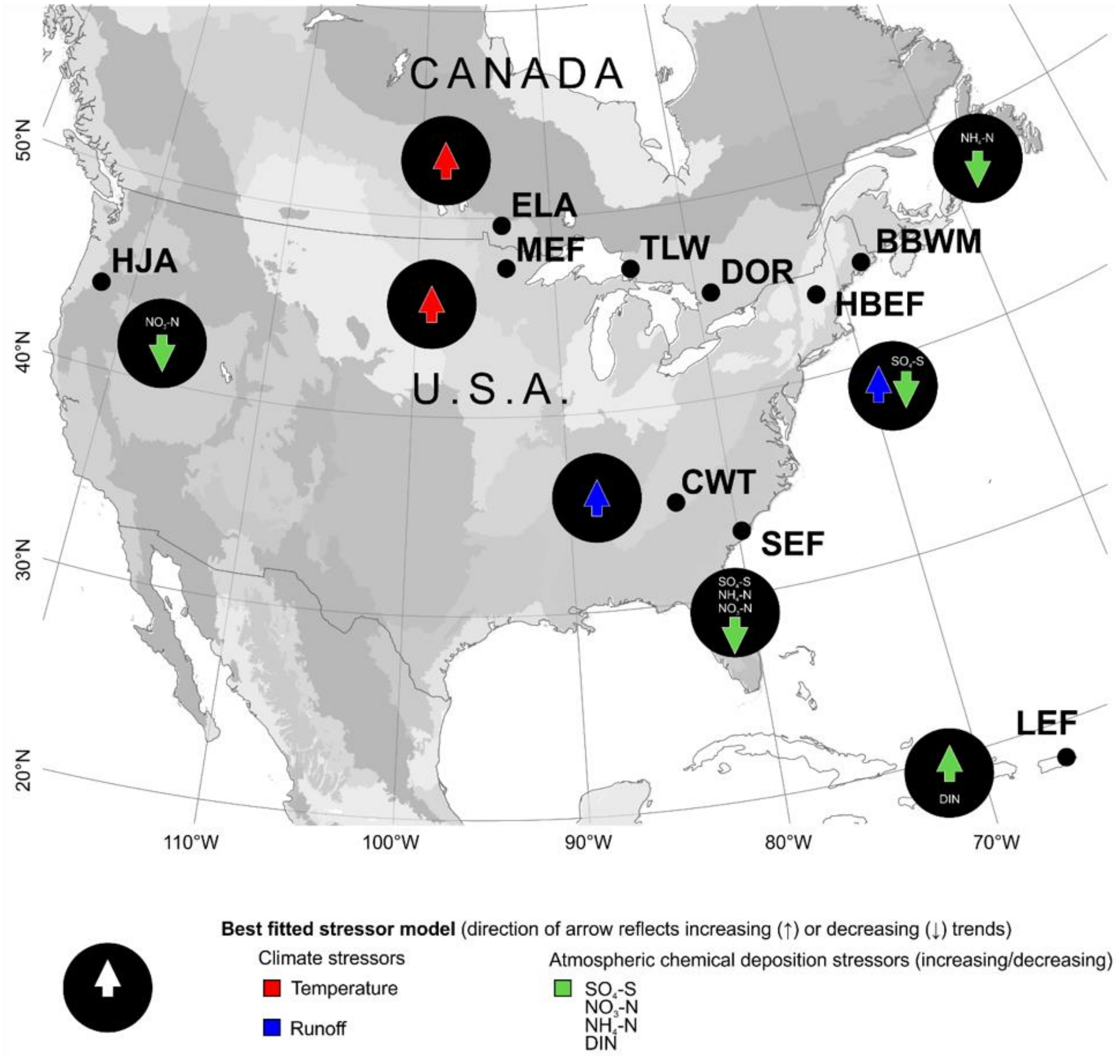

Figure 4.1 The global stressors with largest contribution to the stream response changes across ten long-term monitoring sites. The direction of the arrow indicates the trends of global stressor changes.

Table 4.6 Best fitted and second best-fitted stressor models and AIC_c weights at each site. Model ranks were based on AIC_c values of all models for each site, from lowest to highest.

		Best fitted model		2^{nd} best-fitted model	
		Stressor	**AIC_c weight**	**Stressor**	**AIC_c weight**
Impacted by climate stressors	**ELA**	Temperature	1.00	none	0.00
	MEF	Temperature	1.00	DIN deposition	0.00
	CWT	Runoff	0.97	none	0.03
Impacted by acidic deposition stressors	**HJA**	NO_3-N deposition	1.00	SO_4-S deposition	0.00
	BBWM	NH_4-N deposition	1.00	DIN deposition	0.00
	LEF	DIN deposition	0.60	NO_3-N deposition	0.15
Impacted by no stressor (i.e., random)	**TLW**	none	1.00	Temperature	0.00
	DOR	none	1.00	SO_4-S deposition	0.00
Impacted by unknown stressor (i.e., water year)	**HBEF**	Water year	1.00	none	0.00
	SEF	Water year	0.97	NO_3-N deposition	0.02

Water year models produced the best fit at HBEF and SEF, indicating that stream responses at these sites may be impacted either by unidentified stressors or by the interacting effects of a combination of two or more global stressors that led to synergistic or antagonistic responses that could not be captured by an individual stressor. At HBEF, a multivariate linear regression of runoff and SO_4-S deposition as a function of water year had the highest AIC_c weight with an $r^2 = 0.82$ (**Table 4.7**). At SEF, a multivariate linear regression of all three atmospheric acidic pollutants (i.e., SO_4-S, NO_3-N, NH_4-N deposition) as a function of water year had the highest AIC_c weight with an $r^2 = 0.76$ (**Table 4.7**). Combinations of climate change and atmospheric acidic deposition declines appeared more frequently as independent variables among the top performing multivariate linear regressions as a function of water year at HBEF than at SEF.

Table 4.7 Performance of top five stressor combinations in multivariate linear regressions vs. water year at HBEF and SEF, ranked by AIC_c weight.

Site	Stressor combination	AIC_c weight	r^2
HBEF	Runoff + SO_4-S deposition	0.41	0.82
	Temperature + Runoff + SO_4-S deposition	0.17	0.83
	Runoff + SO_4-S deposition + NH_4-N deposition	0.11	0.83
	Runoff + SO_4-S deposition + NH_4-N deposition	0.08	0.83
	Runoff + NO_3-N deposition + NH_4-N deposition	0.05	0.82
SEF	SO_4-S deposition + NO_3-N deposition + NH_4-N deposition	0.29	0.76
	NO_3-N deposition + NH_4-N deposition	0.22	0.72
	SO_4-S deposition + NO_3-N deposition	0.16	0.71
	Temperature + SO_4-S deposition + NO_3-N deposition	0.06	0.73
	Runoff + SO_4-S deposition + NO_3-N deposition	0.06	0.73

At sites where a global stressor was found to have influenced stream responses, *C* matrix coefficients from the largest impact stressor model were used to identify which stream responses were most impacted and to determine if unmanaged catchments were more sensitive to the impacts from that stressor than managed catchments.

Stream NO_3-N, NH_4-N and Ca were more likely to be impacted by global stressors in unmanaged catchments than in managed catchments, while stream SO_4-S, TDP, and DOC were more likely to be impacted in managed catchments than in unmanaged catchments (**Figure 4.2**). At sites affected by declines in atmospheric acidic depositions (HJA, BBWM, and LEF) stream NO_3-N and NH_4-N were more impacted in unmanaged catchments while stream DOC was more impacted in managed catchments. At sites affected by climate change – increasing temperatures or changing runoff – there were no differences in the impacts to stream NO_3-N, NH_4-N or DOC between unmanaged or managed catchments, but stream Ca was more impacted in unmanaged catchments and stream SO_4-S and TDP were more impacted in managed catchments.

The specific impacts on stream responses varied among sites (**Figure 4.2**). Stream DOC and Ca had the highest levels of impact from NO_3-N deposition declines at HJA. Stream SO_4-S had the highest levels of impact from temperature increases at ELA and MEF, but impacts on other responses were different. Stream TDP had the highest levels of impact from NH_4-N deposition change at BBWM. Stream TDP and DOC had the highest levels of impact from runoff changes at CWT, stream DOC had the highest levels of impact from DIN deposition change at LEF.

Both unmanaged and managed catchments were impacted by global stressors, but there was no recognizable pattern of relative sensitivity of unmanaged catchments vs. managed catchments to global stressors within or across sites or stream responses (**Table 4.8**). At HJA and MEF, managed catchments were generally more impacted by global stressors. In contrast, at BBWM and CWT, unmanaged catchments were generally more impacted by global stressors. All responses were more impacted in unmanaged catchments at LEF where 7.0% of the forest cover was damaged by Hurricane Hugo in 1989 vs. 40.0% damage of the forest cover in managed catchments.

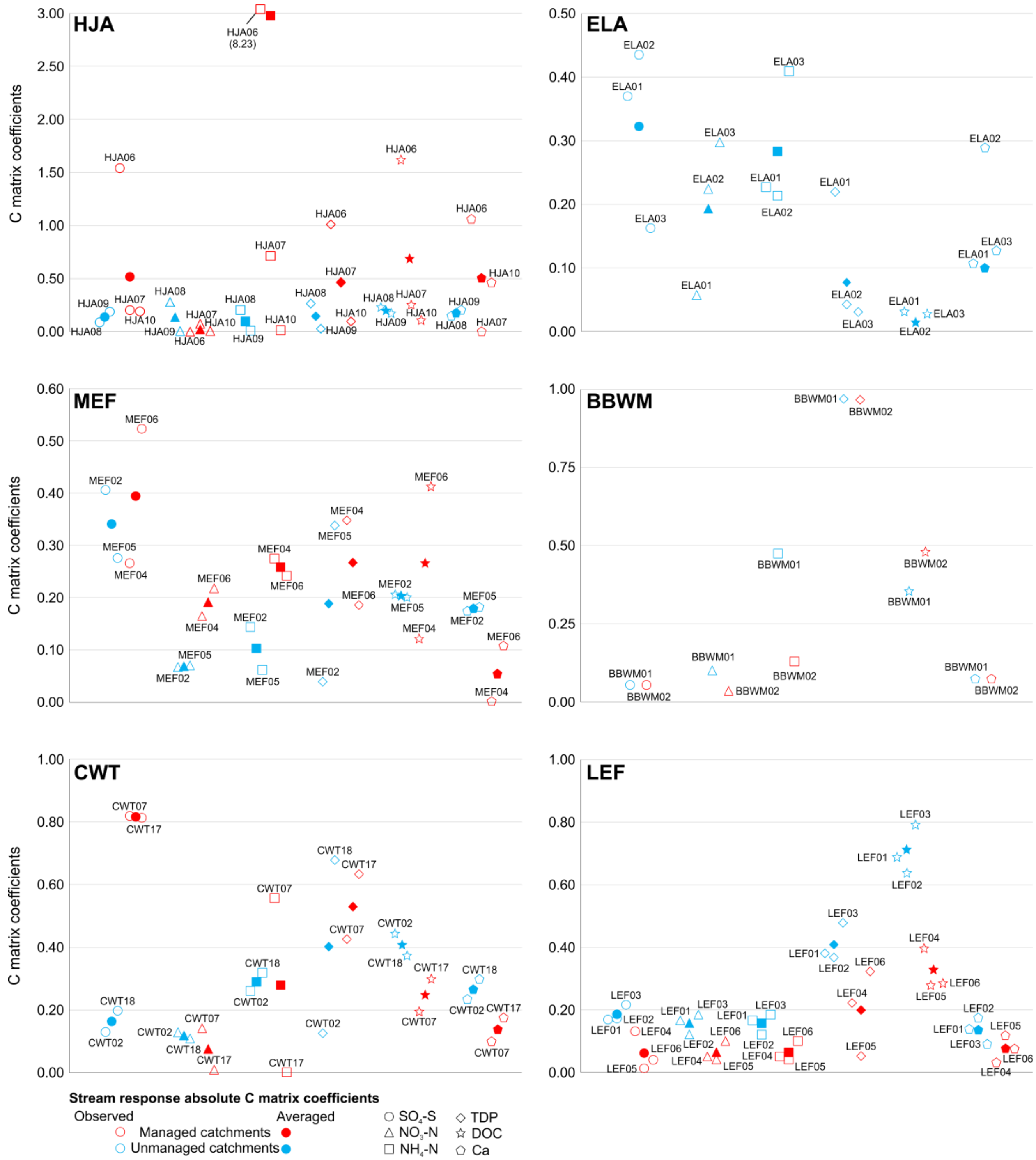

Figure 4.2 *C* matrix coefficients from best fitted global stressor models in all unmanaged and managed catchments at each site (note: axis scales are not standardized across all sites because the coefficient values are from different models). Larger *C* matrix coefficients indicate larger effects from the best fitted global stressor models. HJA was impacted by NO_3-N deposition changes; ELA and MEF were impacted by air temperature changes. BBWM was impacted by NH_4-N deposition changes; CWT was impacted by runoff changes; LEF was impacted by DIN deposition changes.

Table 4.8 Absolute mean *C* matrix coefficients from best fitted global stressor models in unmanaged and managed catchments; **bolded** coefficient indicates a higher value. There were no managed catchments at ELA with which to make a comparison.

Site	Stressor	Response	Unmanaged catchments	Managed catchments
HJA	**NO_3-N deposition**	SO_4-S	0.14	**0.52**
		NO_3-N	**0.14**	0.02
		NH_4-N	0.10	**2.98**
		TDP	0.15	**0.46**
		DOC	0.20	**0.66**
		Ca	0.18	**0.51**
ELA	**Temperature**	SO_4-S	0.32	N/A
		NO_3-N	0.19	N/A
		NH_4-N	0.28	N/A
		TDP	0.08	N/A
		DOC	0.01	N/A
		Ca	0.10	N/A
MEF	**Temperature**	SO_4-S	0.34	**0.40**
		NO_3-N	0.07	**0.19**
		NH_4-N	0.10	**0.26**
		TDP	0.19	**0.27**
		DOC	0.20	**0.27**
		Ca	**0.18**	0.05
BBWM	**NH_4-N deposition**	SO_4-S	0.05	0.05
		NO_3-N	**0.10**	0.04
		NH_4-N	**0.48**	0.13
		TDP	0.05	0.05
		DOC	0.35	**0.47**
		Ca	0.07	0.07
CWT	**Runoff**	SO_4-S	0.16	**0.82**
		NO_3-N	**0.12**	0.00
		NH_4-N	**0.29**	0.28
		TDP	0.40	**0.53**
		DOC	**0.41**	0.25
		Ca	**0.27**	0.04
LEF	**DIN deposition**	SO_4-S	**0.19**	0.06
		NO_3-N	**0.16**	0.04
		NH_4-N	**0.16**	0.04
		TDP	**0.41**	0.20
		DOC	**0.71**	0.32
		Ca	**0.13**	0.01

Hypothesis 2 was that global changes are creating instabilities in stream responses at the long-term monitoring sites. To test this hypothesis, trends in the standard deviations of process errors (**Appendix H**) of stream response in moving windows were used to detect signals of changes in biogeochemical stability. The largest number of significant trends in the standard deviations of process errors of stream responses in all catchments was observed in 7-year moving windows (67% of response trends vs. 20% in 5-year, 9% in 4-year, and 4% in 3-year moving windows). Therefore, 7-year moving windows were used to calculate the standard deviations of process errors of stream responses for all catchments.

Decreased stability was observed in one or more stream responses in one or more catchments at all sites, and in 35 (85.4%) of all catchments, in 21 (84.0%) of unmanaged catchments, and in 12 (87.5%) of managed catchments. However, more stream responses showed signals of decreased stability in unmanaged catchments (average 2.04 stream responses per unmanaged catchment) than in managed catchments (average 1.81 stream responses per managed catchment).

While signals of decreased stability in at least two stream responses were observed in 29 (53.7%) of all catchments, only one stream response in four catchments at MEF showed a signal of decreased stability (NH_4-N), and ten (83.3%) responses in the two catchments at BBWM showed signals of decreased stability (**Table 4.9**). Signals of decreased stability were detected in all stream responses, most frequently in stream TDP (43.9%) and least frequently in stream DOC (22.0%) (**Table 4.9**). However, signals of decreased stream TDP stability were not found in unmanaged or managed catchments at three sites (i.e., MEF, DOR, and SEF) or in unmanaged catchments at BBWM and LEF. Further, signals of decreased stream NO_3-N and NH_4-N stability were more frequently detected (41.2% and 35.3% respectively) in northern forests (i.e., ELA, MEF, TLW, and DOR) than for stream TDP (29.4%) (**Table 4.9**).

Unmanaged catchments showed a larger number and percent of occurrences of decreased stability compared to the managed catchments (**Figure 4.3**). In the unmanaged catchments, signals of decreased stability were more frequently detected in stream NO_3-N, NH_4-N and TDP (i.e., 40% of the catchments; **Table 4.9**).

Relatively strong signals of decreased stability in unmanaged catchments were observed at HJA, ELA, TLW, CWT, HBEF, and BBWM, and relatively weak signals of decreased stability in unmanaged catchments were observed at MEF and SEF (**see Table I.1 in Appendix I**). Stream NO_3-N, NH_4-N, and TDP showed relatively more signals of decreased stability, and stream SO_4-S, DOC and Ca showed relatively fewer signals of decreased stability in unmanaged than in managed catchments (**Table 4.9**).

Table 4.9 Summary of the number and percent of significant trends ($p < 0.1$) in standard deviations within 7-year moving windows (1989-2010) of process errors in mean annual concentrations (mg L^{-1}) of stream responses in the catchments.

	Mean daily SO_4-S	Mean daily NO_3-N	Mean daily NH_4-N	Mean daily TDP	Mean daily DOC	Mean daily Ca
All catchments (n = 41)						
# significant increasing trends	12	15	12	18	9	14
% significant increasing trends	29.3	36.6	29.3	43.9	22.0	34.2
Unmanaged catchments (n = 25)						
# significant increasing trends	8	10	10	10	5	8
% significant increasing trends	32.0	40.0	40.0	40.0	20.0	32.0
Managed catchments (n = 16)						
# significant increasing trends	4	5	2	8	4	6
% significant increasing trends	25.0	31.3	12.5	50.0	25.0	37.5
Northern forest catchments (n = 17)						
# significant increasing trends	1	7	6	5	2	3
% significant increasing trends	2.4	17.1	14.6	12.2	4.9	7.3

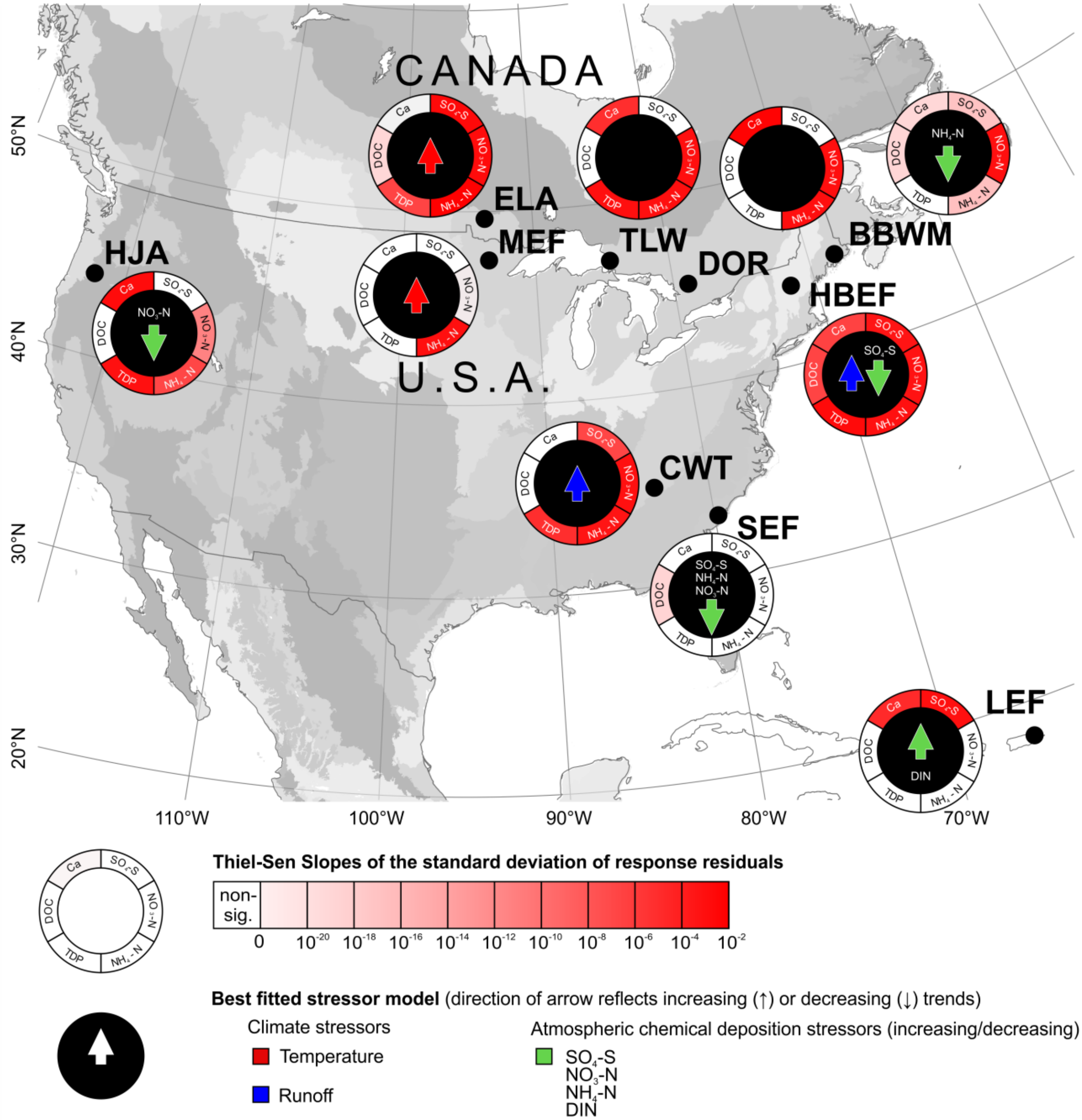

Figure 4.3 Signals of decreased stream biogeochemical stability; Color of out-ring represents the Thiel-Sen slope of the standard deviations of the stream response residuals with 7-year moving windows. No-sig. means no significant Thiel-Sen slope ($p \geq 0.1$).

Chapter 5

5 Discussion

There are many studies exploring the relationships between global changes and local hydrological or nutrient cycles at the long-term monitoring sites (e.g., Knoepp et al., 2008; Sebestyen et al., 2011; Creed et al., 2014); however, only Creed et al. (2014) discussed the ideas of catchment hydrological stability in response to changes in global stressors. The overall signals of the effects of global stressors on catchment biogeochemical cycles (i.e., the correlations between the global stressors and stream responses) remain unclear. The purpose of this study was to explore the effects of global stressors (i.e., changes in air temperature, hydrological cycles, and atmospheric pollution) and local forestry management activities (i.e., physical and chemical treatments) on stream biogeochemical changes in various types of forests.

5.1 Univariate vs. multivariate modeling environments

Univariate linear trend analyses indicated that there were no clear links between changes in a specific global stressor and its effect on a stream response. A global stressor did not show any significant trend, but a related stream response at many sites did. For example, stream SO_4-S concentration decreased significantly at ELA but atmospheric SO_4-S deposition at this site did not change significantly. In contrast, a managed catchment at MEF (MEF04) received treatment in the form of additions of NH_4-N and NO_3-N during the study period but there was no increasing trend in either nutrient in streams. Stream responses depend on local site conditions and management activities (Sebestyen et al., 2011) in addition to changes in global stressors, amplifying or dampening these responses. Therefore, it is difficult to qualify or quantify correlations between changes in global stressors and stream responses through comparison of simple linear trends, especially given the relatively short time series in which significant trends are difficult to discover.

Multivariate linear models had greater explanatory power for the stream responses than univariate linear trend analyses, suggesting that there are “new stories” (i.e., more correlations) to be found in the relationships between global stressors and stream response. However, although RDA results indicated which stressors are significant components in the models, the analysis did not indicate which and how the stressors affect responses (i.e., what is in the black box of the stream responses?). Despite the lack of insights that RDA makes between stressors and responses – especially between corresponding stressors and responses such as stream SO_4-S, NO_3-N, and NH_4-N – the significance of these models indicated that there may be interacting effects between both stressors and responses which may be predicted in a multivariate modeling environment. MARSS models were used to explore what is in the black box of the stream responses.

MARSS models are unique among multivariate model methods in that they analyze and estimate for the specific contributions of environmental processes and observation errors to the measurements of environmental variables (Holmes et al., 2014). The unmanaged variability of environmental processes (referred to in MARSS as process errors) and observation errors together represent the differences between modeled and observed responses (i.e., MARSS modeling residuals); process errors are those portions of the residuals that can be attributed to environmental processes and observation errors are those portions of the residuals that can be attributed to human or technical errors. By estimating process and observation errors separately, MARSS models are able to take into account that there may be similarities or differences in the variances of either or both of these errors in any given ecosystem or between ecosystems, allowing for finer parameterization of equations and more robust models relating stressors to responses. Furthermore, the separation of process errors from overall residuals allows for evaluation of changes in trends of ecological process residuals independent of any change in observation errors; in this study, process errors were used to evaluate stream stability.

Although MARSS modeling is a powerful tool for predicting the relationships between global stressors and stream responses, the modeling results depend on the number and type of stressors that are input into the models. In this study, other atmospheric depositions that may affect catchment biogeochemistry such as atmospheric phosphorus deposition were not available for input. Similarly, MARSS cannot discriminate between the effects of different but correlated stressors, even if two or more stressors may combine to impact stream responses. In this study, the large number of correlations between stressors dictated that separate models were developed for single stressors. I compensated for this by including time (water year) as a stressor and interpreted its impact to indicate the impacts of multiple stressors that may be correlated with time. MARSS results are also highly dependent on the structures of equation matrices (i.e., *B, Z,* *Q*, *R* matrices). In environmental sciences, the interactions and variances between populations (*B*), geographic areas or scales (*Z*), and observation or process errors (*Q* and *R*) are frequently poorly understood (especially the interactions between constituents in streams with different but usually short retention times). I made assumptions in structuring these matrices based on expert opinion, but it cannot be said that the structures were comprehensive in representing the relationships between observation errors and between process errors at any or all sites. Nonetheless, while the *Q* and *R* matrix structures of the best fitting models varied between sites, one combination of same variance in *Q* matrix and different variances in *R* matrix (**Appendix G**) was found to have provided the best fits at seven of the ten sites, and these results are similar to those found in Ohlberger et al. (2016) and Zhu et al. (2017).

5.2 Hypothesis 1: Global change effects on stream responses

5.2.1 Geographic dependency of global stressor-stream response relationships

Global change effects were geographically dependent – with climate warming effects greatest on northern sites, runoff change effects greatest on eastern sites, and recovery from atmospheric acidic deposition greatest near coastal sites, and with some sites responding to the interactive effects of climate change and the recovery from atmospheric acidic deposition. Global stressors had effects on stream responses at eight sites. Atmospheric acidic deposition changes were found to be stronger predictors of stream response changes at four sites, whereas climate changes were found to be stronger predictors at three sites, and only one site was affected by both atmospheric acidic deposition and climate changes. The hypothesis that global stressors were driving changes in trends in stream responses was supported by the findings in this study, but the prediction that the effects of the rapid reduction in at least some of the atmospheric acidic pollutants were stronger than the effects of less rapid changes in climate was more difficult to assess.

The rise in atmospheric acidic deposition prior to the 1970s and the subsequent reduction (Shannon, 1999; Stoddard et al., 1999; Watmough et al., 2005) may lead to shifts in biogeochemical interactions in soils that could then affect stream exports (Schulze, 1989; Lawrence et al., 2015). Declines in atmospheric acidic deposition are due to the effectiveness of the air pollution policies (e.g., Clean Air Act in U.S. and Eastern Canada Acid Rain Program in Canada) initialed during the 1970s in North America (Shannon, 1999). These policies and programs regulated industrial and municipal air pollutions (especially SO_2 and NO_x emissions) to the atmosphere (Stoddard et al., 1999). SO_4-S depositions reduced substantially; e.g., Lawrence et al. (2015) found that atmospheric SO_4-S depositions declined between 5.7% and 70% in eastern Canada and northeastern U.S. between 1985 and 2010, with the largest decreases in northern Ontario. In this study, seven sites had significant declines in SO_4-S depositions between 1989 and 2010 (between 2002 and 2017 at CWT). N depositions were not well recorded as part of the air pollution control programs (Stoddard et al., 1999). In this study, six sites had significant declines in NO_3-N depositions and three sites had significant declines in NH_4-N depositions during the study period. However, there was no correspondence between atmospheric acidic deposition rates and their effects on stream responses. For example, TLW and DOR experienced significant atmospheric acidic deposition declines, but stream responses were not affected by atmospheric acidic deposition or any other global stressors at these sites. Therefore, rapid declines in atmospheric acidic deposition did not significantly affect all long-term monitoring sites.

The rise in temperatures and changes in runoff affected the two northern long-term monitoring sites (ELA and MEF). The rates of climate warming, which are among the highest at the northern latitudes that were part of this study (Smith et al., 2015), may also lead to shifts in biogeochemical interactions in soils that could then affect stream exports (Smithwick et al., 2009). For example, increased temperatures can increase the primary productivity of forests that leads to the retention of major nutrients (Boisvenue et al., 2006). Changes in runoff affect nutrient concentrations in streams, either by concentrating or diluting the nutrients (Wu et al., 2013; Creed et al., 2015, 2018). In catchments with large topographic relief, precipitation is more quickly converted to runoff with shorter retention times in soils (Mengistu et al., 2013). These catchments will frequently also have thinner soil layers, further reducing the opportunities to mitigate the deposited acidic pollutants as they flow through the catchment to the stream. In catchments with small topographic relief, precipitation is more likely to be retained in deeper soils, including wetlands that act to store runoff (Devito et al., 1999; Creed et al., 2003) and transform nutrients from particulate to dissolved, or from dissolved to gaseous forms (Creed et al., 2003; Eimers et al., 2004). In this study, there were significant runoff changes at TLW, BBWM, and HBEF – among these sites, stream responses were affected only at the site with the largest terrain relief (HBEF). However, it must be noted that the effects of increased or decreased runoff on stream nutrient concentrations vary more within years (as a result of short-term drought or extreme precipitation events or contrasts between wet and dry seasons) than between years. For example, despite the absence of a significant trend in runoff during the study period, seasonal changes in runoff are considered to have influenced the stream response at CWT which had the second largest terrain relief of the study sites.

5.2.2 Management activities modify global stressor-stream response relationships

There was no evident pattern in the relative sensitivity of the catchments to global stressors vs. local stressors. *C* matrix coefficients were used to compare the effects of global stressors in unmanaged catchments within local stressors to managed catchments where local stressors were applied. Among the sites, LEF, was the only site in which the average impacts (*C* matrix coefficients) for all stream responses were larger in unmanaged catchments than for managed catchments. This difference in impacts between unmanaged and managed catchments is likely due to the difference in the proportion of damaged forest between unmanaged and managed catchments from Hurricane Hugo in 1989, especially as the potential legacy effects of harvests that occurred over 100 years ago were likely small.

There was some evidence of a pattern in the relative sensitivity of the catchments to the intensity of local stressors. For example, at MEF, the average impacts on stream responses for SO_4-S, TDP, DOC, and Ca were smaller in MEF04 than in MEF06. MEF06 had a larger percentage of clear cut and, following the clear cut, had Na_2SO_4 applied in solution to 11% of the catchment area to augment the atmospheric SO_4-S deposition by a factor of four for study purposes (Sebestyen et al., 2011); together, these may have induced higher impacts on stream responses. Furthermore, at CWT, the average impacts on stream responses for NH_4-N and TDP were smaller in CWT07 than in CWT17. Both CWT07 and CWT17 were clear cut at the same time and to the same extent but harvesting was done in CWT07 with best management practices to protect riparian zones that can help mitigate changes in runoff (Frelich et al. 2018). Finally, at HJA, among the three managed catchments (HJA06, HJA07, and HJA10), the average impacts on stream responses were largest for HJA06, where in addition to clear-cutting an operational road covering 9% of the catchment area was built. Operational roads frequently connect upstream drainage areas to streams and enhance rapid runoff (Wemple et al., 1996; Tague & Band, 2001). The higher the intensity of management activities within the catchment, the higher the magnitude of effect of the global stressor on the stream response.

5.3 Hypothesis 2: Global change effects on stream stability

5.3.1 Stream response stability

Signals of decreased stability were found in one or more stream responses in catchments at all sites, including those in which stream responses were impacted by changes in global stressors as well as those in which stream responses were not impacted by changes in global stressors (DOR and TLW). At a significance level (p) of 0.1, these signals were found in exactly half of all stream responses from all catchments, meaning that on average half of the stream responses in any given catchment at any of these sites is showing signs of decreased stability. The hypothesis that global stressors are leading to decreased stability in stream responses is supported by the findings of this study.

Signals of decreased stream response stability were only slightly more likely to be found in unmanaged catchments than in managed catchments. This suggests that management activities may interfere with the effects of global stressor changes on stream stability – in some cases increasing and in other cases decreasing stability. For example, at MEF and TLW, signals of decreased stability in stream responses were less likely to be found in unmanaged catchments (average 1.0 stream responses per unmanaged catchment) than in managed catchments (average 1.6 stream responses per managed catchment). However, there was substantial heterogeneity in stream responses among managed catchments; e.g., MEF04 (clear cut in 1971) and MEF06 (clear cut in 1981) showed no signals of decreased stability, and TLW31 (clear cut in 1997), showed signals of decreased stability.

The ubiquity of decreased stability signals in unmanaged catchments at all long-term monitoring sites, even at sites that have not been shown to have been impacted by global stressors, suggests that something may be amplifying or diminishing the effects of global stressors on stability. This suggestion is reinforced by the fact that the difference in the average number of stream responses in which signals of decreased stability were observed varied regionally. The sites are located in different ecoregions in which different soil and vegetation characteristics may play a part in modifying changes in biogeochemical cycling in response to subtler atmospheric changes.

Signals of decreased biogeochemical stability were detected in each of the stream responses, but the distribution of responses in which these signals were found varied spatially. Stream NO_3-N, NH_4-N, and TDP had more significant trends ($p < 0.1$) than other stream responses and were more likely to have shown signals of decreased stability than other responses, suggesting that they are more susceptible to change than other stream responses. Among all catchments, stream TDP had most significant trends (53.7% catchments) and had the most frequently detected signals of decreased stream stability (43.9% of catchments). However, the dominant signal had regional differences. Particularly vulnerable were northern sites (ELA, MEF, TLW, DOR), where stream NO_3-N and NH_4-N trends were more frequently varied (41.2% for NO_3-N and 70.6% for NH_4-N), but signals of decreased stream stability were larger (41.2% of northern catchments for NO_3-N, and 35.3% of northern catchments for NH_4-N) compared to stream TDP (29.4% of northern catchments) suggesting early warnings of a shift to higher nitrogen in streams. In contrast, stream SO_4-S trends were decreasing (47.1% catchments), but signals of decreased stream stability were detected in only one (5.9%) of the northern catchments. Stream Ca trends were increasing (reflecting recovery from atmospheric acidic deposition, as increasing soil pH raises soil Ca content (Watmough et al., 2005) which is then mobilized to streams), but signals of decreases stream stability which would be indicative of a shift to a state of higher Ca, were detected in only 17.6% of northern catchments. The decreases stream stability in Ca reflect a potential for even higher Ca concentrations in streams that are not realized due potentially to delays in recovery from acidification, perhaps due to the interactive effects of climate changes. If decreases in stability herald regime shifts, these signals in first-order catchments may portend negative consequences for downstream ecosystems and their functions and services.

Chapter 6

6 Conclusion

Forests are important source areas of water for society. Global atmospheric changes are leading to alterations in biogeochemical loads and decreases in biogeochemical stability in first-order catchment drainage waters on forested landscapes. Global atmospheric changes are not in lockstep with biogeochemical responses, but there early warnings that ecosystems are being pushed past tolerance thresholds towards a regime shift. Such a regime shift would create a "new reality" for first-order catchments, and fundamental changes with cascading consequences in the freshwater ecosystem functions and associated services upon which society depends.

6.1 Scientific findings

New concepts in fields studying systems with great complexity and large uncertainties (e.g., biogeochemical cycles in forest ecosystems) can help guide researchers in the selection of data and analysis tools. In this study, the concepts of multivariate auto-regression and biogeochemical stability were applied using various types of analysis tool to explore the relationship between the changes of the global stressors and stream responses in different types of forest streams across North American with different experimental treatments. The major findings of this study were:

- Finding 1: The effects of global changes on stream response variations were geographically dependent. Climate warming (i.e., temperature raising) effects were greatest in northern sites, runoff changes effects greatest in eastern sites, and recovery from acidic deposition greatest in coastal sites with higher elevations. Impacts of global stressor to stream responses in managed catchments varied geographically [i.e., the same forestry treatments (e.g., clear cut) can induce different changes in stream responses and biogeochemical stability at different sites]. There was no recognizable pattern in the relative sensitivity of unmanaged and managed catchments to global changes within or across sites.
- Finding 2: The effects of global changes were creating instability in the magnitude and composition of stream nutrient exports at all sites, particularly for N and P exports.

Signals of instability in stream SO_4-S can still be detected at many eastern sites after the large declines in atmospheric acidic depositions from 1970s to 1990s.

Development of a predictive understanding of these global change effects is not a generalizable process. Global changes are driving changes and creating instabilities that vary as a function of the uniqueness of the catchment in time and space. Continued access to data from the network of long-term monitoring sites will be essential to revealing if the instabilities are indeed early warning of shifts to an alternative stable state in catchment nutrient exports, which will have fundamental consequences on the productivity and diversity of downstream ecosystem.

6.2 Management implications

The study of forest streams is important to environmental management, especially in forestry. Forest streams are significant sources of freshwater supplies for human consumption (Brown et al., 2008). Traditional forest management focuses on maintaining ecosystem sustainability based on the range of historical ecosystem conditions, but global atmospheric changes have pushed global and regional climates beyond the boundaries of the old conditions (Intergovernmental Panel on Climate Change, 2007). In addition to the effects of global atmospheric changes, local forestry management also plays a vital role in biogeochemical cycles. Many nutrients (e.g., N and P) strongly disturbed by global changes have the potential to cause hazardous algal blooms in large water bodies (Burford, 2005; Chapin et al., 2010; Razon, 2014; Creed et al., 2018).

Concepts of ecosystem stability are also important to environmental management and have been promoted by researchers in ecological and biogeochemical fields as the most popular recommendations in the context of global environmental changes (Dale et al., 2001; Price & Neville, 2003; Spittlehouse & Stewart, 2003). These concepts have been introduced in sustainable forest management developments (Price & Neville, 2003; Spittlehouse & Stewart, 2003). The idea is that stable forests will adapt to gradual environmental shifts and will be resistant to rapid disturbances (Millar et al., 2007).

At local management scales, large amounts of energy and resources are needed to maintain or restore forest ecosystems back to optimum conditions but with a high level of uncertainty in the results. A set of short- and long-term strategies enhancing ecosystem stability needs to be developed in response to the inevitable ecosystem changes that occur with global and local disturbances (Millar et al., 2007). For example, drainage systems should be developed for operational roads to contain or reduce rapid nutrient fluxes to streams. More wetlands should be created as barriers between terrestrial to aquatic systems. More dry-tolerant tree species should be introduced to regions that experience more frequent drought events.

At regional scales, the findings of nutrient export differences in streams among the various forestry treatments can be used as a supportive reference for future best management practice policy and regulation development in forestry. For example, many catchments under clear cut treatment (e.g., MEF04 and MEF06) showed no signals of decreasing biogeochemical stability while others (e.g., HJA06 and TLW31) did show these signals. Further research is needed to test if young forests are more stable to the global changes and if this can be generalized to other forest types or regions, and to determine whether this analysis method is applicable to other catchments with different land-use properties.

The approaches used in this study can contribute to environmental management at global scales as well. At global scales, this study provided an alternative view to conventional studies by examining the relationships between multiple global stressors and forest and stream ecosystems, and exploring the impacts of global changes to biogeochemical stability. A large proportion of nutrients in streams come directly from long-range transport of air pollutants produced from human activities such as industry and agriculture (Lovett & Kinsman, 1990; Camarero et al., 2017); more comprehensive and sophisticated air pollution prevention and energy conservation policies should be written or enhanced to avoid injecting large quantities of N and P into the atmosphere from industry and agricultural practices.

The network of international long-term monitoring sites that provides data to support these kinds of studies should be promoted to increase monitoring and share resources, as well as to inspire more research interests in environmental protection. Many long-term monitoring sites are facing problems of decommissioning or funding shortages. This study shows the importance of keeping these sites.

6.3 Future research

More long-term monitoring sites could be included as an international network for future study of the approaches used in this study. This study used biogeochemical observations and other types of data (i.e., ecological regions, forest type, and forestry treatment information, etc.) from ten long-term monitoring sites in North America. Data from numerous long-term monitoring sites around the world (Kim, 2006; Porter, 2010) with similar and different climatic, geological, biological and vegetation characteristics and different types of global and local disturbances (e.g., hurricanes, wildfires, and mining, etc.) could be used to enrich the database in this study for an expanded study. Further, the feasibility and reliability of MARSS models could also be tested with more modeling samples at other long-term monitoring sites.

It may be anticipated that the same global stressors applied in this study also play vital roles in changing stream biogeochemical concentration and stability globally, especially in the northern regions (i.e., temperate climate with snow and fully humid warm summer) where there are more rapid acidic deposition declines (Pardo et al., 2011; Lawrence et al., 2015; Richon et al., 2018). It may also be expected that future studies would provide similar empirical supports for the idea that forest stream ecosystems are showing signs of shifting towards a “new normal” which can be exacerbated by local management activities.

The concepts of biogeochemical stability have evolved to include cross-scale analysis with a greater appreciation of how spatial interactions govern landscape stability (Smithwick, 2011). Methods similar to those used in this study can be used in the exploration of downstream cascading effects using nutrient export from up-streams as stressors. Biogeochemical observations from higher-order streams or downstream rivers/lakes could be used to as responses to test the correlations between biogeochemical correlations and stability up- and down-stream. It may be anticipated that biogeochemical cycle changes in first-order catchments would affect the biogeochemical stability downstream. However, nutrient interactions in lake systems are more complex than in first-order streams, thus more sophisticated MARSS models should be developed for these types of studies.

Future studies can also be expanded by increasing the number of stream responses that are input and modeled to explore more deeply the correlations between global stressors and stream responses. For example, traditional studies are often focused on the dynamics of inorganic N (Dittman et al., 2007), and this study also only used inorganic forms of N as responses. However, many studies also suggest studying DON (Neff et al., 2003). DON analysis at TLW showed that DON exports can also be affected by runoff changes (Creed & Band, 1998) or increases in temperature (Boisvenue et al., 2006). Therefore, adding DON to a stream response pool may produce different modeling results and different conclusions about stream response stability.

Finally, MARSS modeling could be applied to the study of the biogeochemical correlations and stability in different ecosystems. This approach could be utilized in various contexts such as agricultural fields [e.g., in Maumee River (Ohio) where there are increasing occurrences of algal blooms (Bridgeman et al., 2012; Michalak et al., 2013; Stow et al., 2015)], or in fish farming waterbodies [e.g., in the eastern coasts of Canada where large amounts of nutrients have been dumped in the ocean (Brager et al., 2015; Lalonde et al., 2015)].

To summarize, similar approaches in the study of correlations between global atmospheric changes and biogeochemical changes could be applied in more forest ecosystems globally with more types of observations (i.e., more stream nutrient exports) or in other types of ecosystems such as downstream lake and coastal systems. The scientific findings could inform more comprehensive environmental policies and management strategies to ensure protection or conservation of biogeochemical stability in surface waters.

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Appendices

Appendix A Collaborators' information of the study sites

This section contains the title and contact information of the collaborators at ten LTER sites. Their roles for this study are data provider and consultant of many detailed site information such as water year period and forestry treatment details.

- HJA – Sherri Johnson (Research Ecologist of H.J. Andrews Experimental Forest)
- ELA – Scott Higgins (Research Scientist of IISD Experimental Lakes Area)
- MEF – Stephen Sebestyen (Research Hydrologist of Northern Forest Science and Application)
- TLW – Kara Webster (Forest Soil Ecologist for Natural Resources Canada) and Dean Jeffries (Research Scientist of Environment and Climate Change Canada)
- DOR – Huaxia Yao (Hydrology and Meteorology Research Scientist of Dorest Environmental Science Centre) and James Rusak (Scientist & Group Leader of Dorset Environmental Science Centre)
- BBWM – Sarah Nelson (Associate research professor in Watershed Biogeochemistry)
- HBEF – John Campbell (Research Ecologist of Northern Forest Science and Applications)
- CWT – Chelcy Miniat (Project leader of Coweeta Hydrological Laboratory)
- SEF – Carl Trettin (Project leader and Research Soil Scientist of Center for Forested Wetlands Research)
- LEF – Bill McDowell (Lead investigator of NH Water Research Center)

Appendix B MARSS scripts for this study

The MARSS scripts for the ten LTER sites were similar. The core scripts include data scaling, unfixed matrix structure set up, MARSS modelling (no stressor model, stressor models, and water year model), model selection, residual generation, and model diagnostics. A sample MARSS scripts for TLW was illustrated to show the details of R codes.

The section below showed the codes of scaling the stream response. Each catchment at TLW must be scaled individually to demean the natural logged data in an appropriate way. The data in each catchment are in a series as TLW32, TLW35, TLW38, TLW31, TLW33, TLW34.

````
#### Read stream response
```{r}
# Natural log of the responses
vars <- scale(log(vars))
# subtract the mean for each catchment separately
TLW32 <- scale(vars[1:n_yrs,], center = TRUE, scale = FALSE)
...
TLW34 <- scale(vars[1:n_yrs+n_yrs+n_yrs+n_yrs+n_yrs+n_yrs,], center = TRUE, scale = FALSE)
# combine the response
vars <- rbind(TLW32,...,TLW34)
```
````

This section showed the structure for B and C matrix. B is a 36×36 matrix with “identity” structure. C is a 36×6 matrix, where each row indicates the steam responses in each catchment and the columns indicate the six catchments. C matrix coefficients in TLW32 should only be estimated from row one to six in column one.

````
#### B & C matrix structure
```{r}
## B matrix structure (independent and identically distributed)
BB <- "identity"

## The stressor has impact only in its own catchment
CC <- matrix(list(0),n_vars*n_sites,n_sites) # n_vars*n_sites = number of y
CC[1,1] <- "TLW32_NO3"
CC[2,1] <- "TLW32_NH4"
CC[3,1] <- "TLW32_Ca"
CC[4,1] <- "TLW32_SO4"
CC[5,1] <- "TLW32_DOC"
CC[6,1] <- "TLW32_TDP"
...
CC[31,6] <- "TLW34_NO3"
CC[32,6] <- "TLW34_NH4"
CC[33,6] <- "TLW34_Ca"
CC[34,6] <- "TLW34_SO4"
CC[35,6] <- "TLW34_DOC"
CC[36,6] <- "TLW34_TDP"
```
````

Two types of *Z* matrix structure were applied in this study. The first model is the identity model and the second model is the state space. *Z* in the identity model can be simply coded as "*ZZ* <– "identity"", but the outputs of MARSS will not show the catchment and response for the specific estimations. Therefore, it is recommended to set up the identity *Z* matrix as below.

```
#### Z matrix structure
```{r}
# each catchment is its own space
ZZ <- factor(c("TLW32_NO3","TLW32_NH4","TLW32_Ca","TLW32_SO4","TLW32_DOC","TLW32_TDP",
               "TLW35_NO3","TLW35_NH4","TLW35_Ca","TLW35_SO4","TLW35_DOC","TLW35_TDP",
               "TLW38_NO3","TLW38_NH4","TLW38_Ca","TLW38_SO4","TLW38_DOC","TLW38_TDP",
               "TLW31_NO3","TLW31_NH4","TLW31_Ca","TLW31_SO4","TLW31_DOC","TLW31_TDP",
               "TLW33_NO3","TLW33_NH4","TLW33_Ca","TLW33_SO4","TLW33_DOC","TLW33_TDP",
               "TLW34_NO3","TLW34_NH4","TLW34_Ca","TLW34_SO4","TLW34_DOC","TLW34_TDP"))

## Reference catchments as one space
ZZ <- factor(c("TLW_NO3","TLW_NH4","TLW_Ca","TLW_SO4","TLW_DOC","TLW_TDP",
               "TLW_NO3","TLW_NH4","TLW_Ca","TLW_SO4","TLW_DOC","TLW_TDP",
               "TLW_NO3","TLW_NH4","TLW_Ca","TLW_SO4","TLW_DOC","TLW_TDP",
               "TLW31_NO3","TLW31_NH4","TLW31_Ca","TLW31_SO4","TLW31_DOC","TLW31_TDP",
               "TLW33_NO3","TLW33_NH4","TLW33_Ca","TLW33_SO4","TLW33_DOC","TLW33_TDP",
               "TLW34_NO3","TLW34_NH4","TLW34_Ca","TLW34_SO4","TLW34_DOC","TLW34_TDP"))
```
```

The structure set up of *Q* and *R* matrix were same. The two types of *Q* and *R* were put in a combination for the different type of model (e.g., the combination of *Q* structure 1 and *R* structure 2). Matrix *U*, *A*, *D*, and *d* were not used in this study thus were set up as "zero".

```
#### Q matrix structure
```{r}

## Different variance of white noise in each catchment
QQ <- "diagonal and unequal"

## Same variance of same response noise in each catchment
QQ <- matrix(list(0),n_vars*n_sites,n_vars*n_sites) # n_cat is number of y
diag(QQ) <- list("q_TLW_NO3","q_TLW_NH4","q_TLW_Ca","q_TLW_SO4","q_TLW_DOC","q_TLW_TDP",
                 "q_TLW_NO3","q_TLW_NH4","q_TLW_Ca","q_TLW_SO4","q_TLW_DOC","q_TLW_TDP",
                 "q_TLW_NO3","q_TLW_NH4","q_TLW_Ca","q_TLW_SO4","q_TLW_DOC","q_TLW_TDP",
                 "q_TLW_NO3","q_TLW_NH4","q_TLW_Ca","q_TLW_SO4","q_TLW_DOC","q_TLW_TDP",
                 "q_TLW_NO3","q_TLW_NH4","q_TLW_Ca","q_TLW_SO4","q_TLW_DOC","q_TLW_TDP",
                 "q_TLW_NO3","q_TLW_NH4","q_TLW_Ca","q_TLW_SO4","q_TLW_DOC","q_TLW_TDP")
```
```

```
#### R matrix structure
```{r}
## Different variance of white noise in each catchment
RR <- "diagonal and unequal"

## Same variance of same response noise in each catchment
RR <- matrix(list(0),n_vars*n_cat,n_vars*n_cat) # n_cat is number of y
diag(RR) <- list("r_TLW_NO3","r_TLW_NH4","r_TLW_Ca","r_TLW_SO4","r_TLW_DOC","r_TLW_TDP",
                 "r_TLW_NO3","r_TLW_NH4","r_TLW_Ca","r_TLW_SO4","r_TLW_DOC","r_TLW_TDP",
                 "r_TLW_NO3","r_TLW_NH4","r_TLW_Ca","r_TLW_SO4","r_TLW_DOC","r_TLW_TDP",
                 "r_TLW_NO3","r_TLW_NH4","r_TLW_Ca","r_TLW_SO4","r_TLW_DOC","r_TLW_TDP",
                 "r_TLW_NO3","r_TLW_NH4","r_TLW_Ca","r_TLW_SO4","r_TLW_DOC","r_TLW_TDP",
                 "r_TLW_NO3","r_TLW_NH4","r_TLW_Ca","r_TLW_SO4","r_TLW_DOC","r_TLW_TDP")
```
```

```
#### Other not used matrix
```{r}
UU <- "zero"
AA <- "zero"
DD <- "zero"
dd <- "zero"
```
```

The core scripts of MARSS models are listed in the following two sections. *y* is the stream response, and *cc* is the global stressor. *i* indicates the type of global stressor (e.g., $i = 1$ indicates the temperature in this study). *maxit* indicates the maximum iterations for process modelling. The inputs for *allow.degen*, safe, and trace were set up this way to increase the accuracy of the models in this study, but the set up does not default for all study. The details of the three inputs can be found in Holmes et al. (2014). Method of bootstrapping was set up as "*hessian*" with 1000 iterations. For larger models (e.g., combining all LTER sites together), a method of "*parametric*" is recommended. The differences between no stressor model and stressor model are that the *C* and *c* matrix were set up as "*zero*" in no stressor model. Each *i* indicates an individual model. For TLW, there were 8 models (1 no stressor + 7 stressor models) for this study.

```
#### No stressor model and Bootstrapping
```{r}
mod_LTER <- MARSS(y=LTER,
                  model=list(B=BB, U=UU, Q=QQ, c="zero", C="zero",
                             Z=ZZ, A=AA, R=RR, D=DD, d=dd),
                  control=list(maxit=5000, allow.degen=TRUE, safe=TRUE, trace=-1))

## Bootstrapping for Confidence Interval
CIs = MARSSparamCIs(mod_LTER, method="hessian", nboot=1000)
print(CIs)
```
```

```
#### Model with other stressors
```{r}
for(i in 1:n_covs) {
  cc <- t(matrix(covs[,i],nrow=n_yrs,ncol=n_sites)) # n_vars*n_sites is the number of x
  mod_res_LTER[[i]] <- MARSS(y=LTER,
                        model=list(B=BB, U=UU, Q=QQ, c=cc, C=CC,
                                   Z=ZZ, A=AA, R=RR, D=DD, d=dd),
                        control=list(maxit=5000, allow.degen=TRUE, safe=TRUE, trace=-1))
  mod_res_LTER[[i]]$cov <- colnames(covs)[i]
}
```
```

Model selection was based on AIC_c. The best fitted model was selected based on ΔAIC_c which is equal to the difference between AIC_c of the model and the lowest AIC_c among all models. The best fitted model was the one with a ΔAIC_c value of zero.

```
#### Model selection
```{r}
## AICc for each model
tbl_mod_sel_LTER <- data.frame(Model=sapply(mod_res_LTER,function(x) x[["cov"]]),
                        AICc=round(sapply(mod_res_LTER,function(x) x[["AICc"]]),3))
tbl_mod_sel_LTER$delta_AICc <- tbl_mod_sel_LTER$AICc - min(tbl_mod_sel_LTER$AICc)
tbl_mod_sel_LTER

##Best fitted model
mod_top_LTER <- mod_res_LTER[[which(tbl_mod_sel_LTER$delta_AICc==0)]]
```
```

There are many types of model residuals for MARSS. Two were used for this study which is the standardized residuals (*std.residuals*) and process residuals (*state.residuals*). Observation models produce observation residuals whereas process models produce process residuals. The overall residuals of MARSS models (i.e., observation residuals + process residuals) is named as the conditional residuals. The standardized residuals are equal to the ratio of the conditional residuals and the sum of standard deviations of the conditional residuals. The standardized residuals were used for modelling diagnostics. The process residuals were used to detect the early warning signals of decreased biogeochemical stability.

```
#### Modeling residuals
```{r}
## Standardized residuals for TLW31
resids_top_LTER <- residuals(mod_LTER)$std.residuals[1:n_vars,]
t(resids_top_LTER)

## Process residuals for TLW31
resids_top_LTER <- residuals(mod_top_LTER)$state.residuals[1:n_vars+n_vars,]
t(resids_top_LTER)
```
```

Two modelling diagnostics method illustrated as below. Both of them used the standardized residuals.

```
#### Model diagnostics
```{r}
## ACF estimations
par(mfrow=c(n_vars,2),mai=c(0.1,0.4,0.2,0.2),omi=c(0.5,0,0.2,0))
for(i in 1:n_vars) {
  plot.ts(resids_top_LTER[i,], xaxt="n", xlab="", main=colnames(vars)[i])
  if(i==n_vars) {
    axis(1)
    mtext(side=1,"Time", line=2.5)
    }
acf(resids_top_LTER[i,], lag.max=10, xaxt="n", xlab="")
if(i==n_vars) {
  axis(1)
  mtext(side=1,"Time", line=2.5)
  }
}

## QQplot
par(mfrow=c(n_vars,1), mai=c(0.1,0.4,0.2,0.2), omi=c(0.5,0,0.2,0))
for(i in 1:n_vars) {
  ## Q-Q plot of innovations
  qqnorm(t(resids_top_LTER), main=colnames(vars)[i], pch=16, col="blue", xaxt="n", xlab="")
  ## add y=x line for easier interpretation
  qqline(t(resids_top_LTER))
  if(i==n_vars) {
    axis(1)
    }
}
par(mfrow=c(1,1))
```
```

Appendix C Standardized residuals

Standardized residual is a measure of the strength of the difference between observed and expected values (Holmes, 2014). It is used to help detect outliers, whereas raw residuals might not be acceptable identifiers of outliers due to the non-constant variance. Standardized residual greater than 2 and less than -2 are usually considered large. A +/-3 residual means that something extremely unusual is happening.

Standardized residual can be calculated as in **Equation C.1**:

$$\text{Standardized residual} = \frac{\varepsilon_t^*}{\sqrt{\Sigma_t^*}} \qquad \text{Equation C.1}$$

where ε_t^* is the conditional residual from the models which is the combination of the observation and process errors from MARSS models; Σ_t^* is the variance of conditional residual; * means that missing values are considered as part of the modeling process.

References cited

Holmes, E. E. (2014). Computation of Standardized Residuals for MARSS Models. arXiv preprint arXiv:1411.0045.

Appendix D Tend analysis results of the global stressors and stream responses

Many sites had multidirectional changes in stressors (i.e., temperature increased while atmospheric acidic depositions and/or runoff decreased; **Table D.1**). Unidirectional (decreasing) changes in all stressors occurred only at SEF; however, only the atmospheric chemical deposition trends at this site were significant.

Mean annual temperature increased significantly only at LEF. The direction of trends in mean annual "effective precipitation," measured as runoff, varied among sites between increases and decreases, but most of these trends were also not significant within the time (significant increase at HBEF, and significant decreases at BBWM and TLW). Many more atmospheric deposition trends were significant at $p < 0.1$ (52.2%); atmospheric acidic depositions generally decreased, especially at the eastern LTER sites, and all significant trends were decreasing.

Table D.1 Trends in global stressors (1989-2010). Negative values indicate decreasing trends; positive values indicate increasing trends; * indicates $p < 0.1$, ** indicates $p < 0.05$.

Site	Mean annual temperature (°C yr^{-1})	Total annual runoff (mm yr^{-1})	Total annual SO_4-S deposition (kg ha^{-1} yr^{-1})	Total annual NO_3-N deposition (kg ha^{-1} yr^{-1})	Total annual NH_4-N deposition (kg ha^{-1} yr^{-1})	Total annual DIN deposition (kg ha^{-1} yr^{-1})
HJA	-0.02	-9.13	$+4\times10^{-2}$	-2×10^{-2}	$+1\times10^{-2}$	-1×10^{-2}
ELA	+0.06	+57.26	-0.01	-3×10^{-2}	$+4\times10^{-2}$	$+1\times10^{-2}$
MEF	+0.04	-10.84	-0.02**	-0.01**	+0.01	-0.01
TLW	+0.05	-39.13*	-0.25**	-0.10**	-0.06**	-0.16**
DOR	+0.05	+3.14	-0.06**	-0.03**	-0.01	-0.04**
BBWM	+0.01	-147.85**	-0.05**	-0.02**	-2×10^{-2}	-0.03**
HBEF	+0.02	+204.83**	-1.01**	-0.06	-1.94**	-2.00
CWT[1]	+0.14	+1.20	-0.17**	-0.05**	-0.01	-0.06*
SEF	-0.03	-10.78	-0.07**	-0.03**	-3×10^{-2}*	-0.03*
LEF	+0.07*	-66.37	+0.04	+0.01	$+3\times10^{-2}$	+0.01

[1]2002 to 2017 at CWT

Over the same time period, more significant trends (50.0% for all catchments at $p < 0.1$) were found in stream responses than in global stressors (18.3% increasing and 31.7% decreasing) (**Table D.2**). SO_4-S exports most frequently had significant ($p < 0.1$) trends; 28 catchments (68.3%) had significant trends, with 9 (22.0%) increasing and 19 (46.3%) decreasing. Twenty-six catchments (63.4%) had significant ($p < 0.1$) trends in NH_4-N exports, with 12 (29.3%) increasing and 14 (34.1%) decreasing. Nineteen catchments (46.3%) had significant ($p < 0.1$) trends in NO_3-N exports, with 3 (7.3%) increasing and 16 (39.0%) decreasing. Twenty-two catchments (53.7%) had significant ($p < 0.1$) trends in TDP exports, with 8 (19.5%) increasing and 14 (34.1%) decreasing. Seventeen catchments (41.5%) had significant ($p < 0.1$) trends in Ca exports, with 8 (19.5%) increasing and 9 (22.0%) decreasing. DOC exports had the smallest number of significant ($p < 0.1$) trends; 11 catchments (26.8%) had significant trends, with 5 (12.2%) increasing and 6 (14.6%) decreasing.

Table D.2 Trends in stream responses (1989-2010); * indicates p value < 0.1, ** indicates p value < 0.05; blank cells indicate no significant trend; shaded cells indicates managed catchments.

Catchment	**Mean daily SO_4-S (mg L^{-1} yr^{-1})**	**Mean daily NO_3-N (mg L^{-1} yr^{-1})**	**Mean daily NH_4-N (mg L^{-1} yr^{-1})**	**Mean daily TDP (mg L^{-1} yr^{-1})**	**Mean daily DOC (mg L^{-1} yr^{-1})**	**Mean daily Ca (mg L^{-1} yr^{-1})**
HJA06	-0.01**		$+8\times10^{-5}$**	-3×10^{-4}**		+0.02**
HJA07	-0.01**	-5×10^{-5}**	$+4\times10^{-5}$**	-4×10^{-4}**		+0.01**
HJA08	-2×10^{-2}*		-2×10^{-4}**			
HJA09	-0.01**	-6×10^{-5}**				
HJA10	-0.01**	-6×10^{-5}**				
ELA01	-0.08**	-3.83**		-0.20*		-0.04**
ELA02	-0.09**			-0.27**	-42.86**	
ELA03	-0.09**	-2.08**		-0.09*		-0.04**
MEF02	+0.01*		+0.02**			
MEF04	$+3\times10^{-2}$**	+0.02**	+0.02**	$+4\times10^{-2}$**		
MEF05	+0.01**		+0.01**	$+2\times10^{-2}$**		+0.03**
MEF06	+0.02**	+0.02**	+0.01**	$+2\times10^{-2}$**	+0.86**	
TLW31	-0.03**	-0.03**	-1×10^{-2}**			
TLW32	-0.03**		-1×10^{-2}**			
TLW33	-0.03**				+0.02**	
TLW34	-0.03**		-1×10^{-2}**			
TLW35	-0.03**		-1×10^{-2}*			
TLW38			-1×10^{-2}**	$+2\times10^{-4}$**	+0.33**	
DOR00	+0.04**	-3×10^{-2}**	$+3\times10^{-5}$**		+0.03**	-0.01**
DOR03			-2×10^{-2}**			
DOR05						
DOR06	-0.08*	-0.01**	-0.01**		+0.16**	
BBWM01		-0.01**				-0.03**
BBWM02						-0.03**
HBEF01	-0.03*		+0.01**	-4×10^{-2}**		
HBEF06	-0.04**	-0.01**	-1×10^{-2}**	-5×10^{-5}**		-0.02**
HBEF07	-0.03**		-1×10^{-2}**		-0.01*	-0.02**
HBEF08	-0.03**		-4×10^{-4}**			-0.01**
HBEF09	-0.04**			-2×10^{-4}**		-0.01**
CTW02[1]		-3×10^{-2}**	$+2\times10^{-2}$**			
CTW07[1]		-2×10^{-2}**	-0.02**	-1×10^{-2}**		
CTW17[1]		-2×10^{-2}**		-1×10^{-2}*		+0.02**
CTW18[1]		-2×10^{-2}**	+0.01*	-1×10^{-2}*		+0.02*
SEF77	+0.55**		$+2\times10^{-2}$**	-0.02**	-1.79**	
SEF80	+0.01**	$+3.00\times10^{-2}$*	$+2\times10^{-2}$**	-0.01**		
LEF01	+0.01**			+0.24**		+0.03**
LEF02				+0.15**		
LEF03				+0.23**	-0.06**	
LEF04		-4×10^{-4}**	-2×10^{-2}**			+0.02**
LEF05		-1×10^{-2}**	-2×10^{-2}**	-0.17**	-0.09**	+0.06**
LEF06	+0.01**			+0.07**	-0.03**	

[1]2002 to 2017 at CWT

Appendix E RDA results

Table E.1 showed the analysis results of RDA. Adjusted r^2 value indicates the percentage of variation explained by the global stressors that actually affect the stream responses. There is no clear patterns of the r^2 and adjusted r^2 values among the catchments. The percentage of variance explained by NH_4-N deposition were relatively higher than other global stressors.

Table E.1 RDA results including all six global stressors and six responses; N/A indicate that there were no sufficient data for RDA. Adj r^2 means adjusted r^2. p means p value. % means percentage of variance explained. Temp means temperature. Time means water year.

Catchment	r^2	Adj r^2	p	Temp (%)	Temp (p)	NH4 (%)	NH4 (p)	NO3 (%)	NO3 (p)	SO4 (%)	SO4 (p)	Runoff (%)	Runoff (p)	Time (%)	Time (p)
HJA06	0.93	0.48	0.39	12.22	0.35	9.18	0.45	62.32	0.05	2.43	0.76	2.88	0.74	3.48	0.73
HJA07	0.87	0.07	0.55	10.04	0.60	16.49	0.44	18.07	0.39	7.33	0.72	30.14	0.26	4.59	0.85
HJA08	0.61	-0.18	0.74	8.95	0.63	19.18	0.29	8.45	0.62	3.66	0.92	15.75	0.35	4.58	0.87
HJA09	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
HJA10	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
ELA01	0.64	0.50	0.00	2.43	0.39	34.35	0.00	8.61	0.02	9.30	0.01	2.01	0.48	7.43	0.02
ELA02	0.57	0.38	0.00	1.91	0.65	25.17	0.00	12.08	0.01	3.92	0.27	12.80	0.01	0.91	0.88
ELA03	0.68	0.56	0.00	1.81	0.47	36.08	0.00	9.30	0.01	10.73	0.01	8.56	0.01	1.78	0.47
MEF02	0.61	0.38	0.00	4.37	0.36	23.33	0.00	21.13	0.00	5.30	0.23	2.25	0.76	4.63	0.33
MEF04	0.63	0.39	0.00	7.03	0.15	17.63	0.00	28.39	0.00	1.83	0.84	3.53	0.48	4.87	0.31
MEF05	0.62	0.40	0.00	1.51	0.86	21.26	0.00	22.90	0.00	9.84	0.04	1.74	0.82	5.11	0.28
MEF06	0.72	0.48	0.00	6.87	0.19	22.89	0.00	35.48	0.00	2.73	0.63	0.81	0.95	3.10	0.56
TLW31	0.52	0.32	0.00	5.78	0.14	22.16	0.00	7.02	0.10	6.14	0.11	3.40	0.37	7.30	0.07
TLW32	0.77	0.68	0.00	17.97	0.00	40.71	0.00	5.00	0.06	10.39	0.00	1.81	0.30	1.44	0.38
TLW33	0.62	0.47	0.00	4.39	0.14	32.71	0.00	6.72	0.04	8.67	0.01	5.46	0.06	4.26	0.15
TLW34	0.58	0.41	0.00	6.90	0.06	29.83	0.00	5.47	0.13	7.51	0.03	3.91	0.25	4.32	0.20
TLW35	0.66	0.53	0.00	4.79	0.12	49.14	0.00	4.62	0.13	5.90	0.08	0.63	0.83	1.28	0.61
TLW38	0.46	0.24	0.04	11.16	0.05	22.11	0.00	5.66	0.18	5.45	0.20	0.51	0.96	1.04	0.86
DOR00	0.83	0.72	0.00	7.06	0.05	47.52	0.00	24.98	0.00	1.40	0.48	1.58	0.40	0.45	0.84

DOR03	0.60	-0.19	0.73	2.91	0.92	28.60	0.15	7.28	0.69	12.81	0.44	3.54	0.87	5.16	0.82
DOR05	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
DOR06	0.72	0.43	0.03	5.93	0.33	31.27	0.00	19.75	0.02	7.49	0.22	1.16	0.88	5.68	0.35
BBWM01	0.63	0.39	0.00	3.65	0.47	18.69	0.00	15.17	0.01	6.05	0.22	3.88	0.46	15.77	0.00
BBWM02	0.61	0.36	0.01	3.14	0.60	17.97	0.01	21.28	0.00	4.19	0.44	5.70	0.30	9.04	0.10
HBEF01	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
HBEF06	0.78	0.66	0.00	14.19	0.00	41.08	0.00	9.59	0.01	6.37	0.04	5.20	0.07	1.38	0.56
HBEF07	0.75	0.56	0.00	5.29	0.17	36.61	0.00	6.19	0.13	15.14	0.01	9.75	0.03	1.91	0.66
HBEF08	0.83	0.71	0.00	5.73	0.07	45.88	0.00	3.09	0.23	17.22	0.00	10.49	0.01	0.78	0.79
HBEF09	0.82	0.68	0.00	6.88	0.08	34.17	0.00	1.94	0.42	23.56	0.00	13.16	0.01	1.89	0.46
CWT02	0.91	0.35	0.22	35.13	0.05	16.08	0.24	7.75	0.58	8.36	0.52	15.92	0.23	7.48	0.61
CWT07	0.71	0.13	0.31	12.32	0.30	24.30	0.07	9.43	0.47	11.72	0.35	5.25	0.79	7.91	0.58
CWT17	0.76	0.28	0.20	10.21	0.32	20.42	0.07	15.05	0.16	19.70	0.08	6.75	0.55	3.93	0.80
SEF77	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
SEF80	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
CWT18	0.78	0.35	0.10	35.84	0.00	13.67	0.13	10.03	0.26	12.42	0.17	1.23	0.99	5.27	0.61
LEF01	0.47	0.26	0.00	13.70	0.01	14.77	0.01	3.97	0.36	1.86	0.75	4.44	0.27	8.73	0.05
LEF02	0.39	0.14	0.07	10.98	0.03	17.28	0.01	4.38	0.36	1.75	0.85	1.55	0.86	2.94	0.57
LEF03	0.52	0.26	0.02	10.29	0.08	15.33	0.02	5.24	0.31	3.26	0.58	3.68	0.53	14.31	0.02
LEF04	0.50	0.29	0.01	10.74	0.06	26.00	0.00	3.06	0.43	1.66	0.72	5.92	0.15	2.26	0.59
LEF05	0.93	0.83	0.00	5.89	0.05	38.06	0.00	9.44	0.01	7.67	0.02	5.38	0.05	26.89	0.00
LEF06	0.62	0.45	0.00	8.71	0.02	30.71	0.00	6.22	0.08	1.30	0.73	10.96	0.01	3.88	0.25

Appendix F Bootstrapping results for MARSS models

Tables F.1 to **F.20** showed the bootstrapping results of the best fitted model and no-stressor model at each site across 41 catchments. No N/A or errors were found in these results which indicate that the MARSS models were adequate. Standard errors and confidence interval (CI) showed the accuracy of the modeling results. Most modeling results had small standard errors which indicate that the results for this study were reasonable.

Table F.1 Bootstrapping results of the best fitted no-stressor MARSS models at BBWM; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	ML Est	Std. Err	Low. CI	Up. CI
R.r_BBWM01_NO3	0.131	0.056	0.021	0.241
R.r_BBWM01_NH4	1.770	0.561	0.675	2.874
R.r_BBWM01_DOC	0.744	0.224	0.304	1.184
R.r_BBWM01_TDP	0.964	0.321	0.334	1.594
R.r_BBWM02_NH4	0.130	0.041	0.050	0.211
R.r_BBWM02_DOC	0.950	0.286	0.388	1.511
R.r_BBWM02_TDP	0.981	0.327	0.340	1.621
Q.q_BBWM_NO3	0.066	0.019	0.030	0.102
Q.q_BBWM_Ca	0.243	0.052	0.141	0.345
Q.q_BBWM_SO4	0.299	0.064	0.174	0.424
x0.BBWM01_NO3	1.200	0.362	0.492	1.912
x0.BBWM01_NH4	0.000	0.298	-0.584	0.584
x0.BBWM01_Ca	-0.495	0.493	-1.461	0.471
x0.BBWM01_SO4	-2.720	0.547	-3.787	-1.644
x0.BBWM01_DOC	0.000	0.184	-0.361	0.360
x0.BBWM01_TDP	0.000	0.231	-0.454	0.454
x0.BBWM02_NO3	-0.228	0.256	-0.731	0.274
x0.BBWM02_NH4	0.000	0.081	-0.158	0.158
x0.BBWM02_Ca	-0.495	0.493	-1.461	0.471
x0.BBWM02_SO4	-2.720	0.547	-3.787	-1.644
x0.BBWM02_DOC	0.000	0.208	-0.407	0.407
x0.BBWM02_TDP	0.000	0.233	-0.457	0.457

Table F.2 Bootstrapping results of the best fitted stressor (NH_4-N deposition) MARSS models at BBWM; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.r_BBWM01_NO3	0.132	0.057	0.021	0.243
R.r_BBWM01_NH4	1.615	0.511	0.614	2.617
R.r_BBWM01_DOC	0.660	0.199	0.270	1.050
R.r_BBWM01_TDP	0.417	0.139	0.145	0.690
R.r_BBWM02_NH4	0.119	0.038	0.045	0.192
R.r_BBWM02_DOC	0.802	0.242	0.328	1.276
R.r_BBWM02_TDP	0.437	0.146	0.151	0.722
Q.q_BBWM_NO3	0.063	0.018	0.028	0.098
Q.q_BBWM_Ca	0.238	0.051	0.139	0.337
Q.q_BBWM_SO4	0.296	0.063	0.172	0.420
x0.BBWM01_NO3	1.170	0.359	0.466	1.873
x0.BBWM01_NH4	-0.377	0.391	-1.144	0.390
x0.BBWM01_Ca	-0.432	0.497	-1.405	0.542
x0.BBWM01_SO4	-2.669	0.554	-3.754	-1.583
x0.BBWM01_DOC	0.273	0.238	-0.193	0.739
x0.BBWM01_TDP	0.851	0.233	0.395	1.307
x0.BBWM02_NO3	-0.259	0.255	-0.759	0.242
x0.BBWM02_NH4	-0.103	0.106	-0.311	0.105
x0.BBWM02_Ca	-0.432	0.497	-1.405	0.542
x0.BBWM02_SO4	-2.669	0.554	-3.754	-1.583
x0.BBWM02_DOC	0.361	0.262	-0.153	0.874
x0.BBWM02_TDP	0.848	0.238	0.382	1.315
C.BBWM01_NO3	-0.101	0.123	-0.342	0.140
C.BBWM01_NH4	0.475	0.338	-0.188	1.138
C.BBWM01_Ca	0.073	0.107	-0.137	0.283
C.BBWM01_SO4	0.054	0.120	-0.180	0.288
C.BBWM01_DOC	-0.354	0.211	-0.768	0.060
C.BBWM01_TDP	-0.969	0.200	-1.362	-0.577
C.BBWM02_NO3	-0.035	0.055	-0.143	0.073
C.BBWM02_NH4	0.129	0.092	-0.050	0.309
C.BBWM02_Ca	0.073	0.107	-0.137	0.283
C.BBWM02_SO4	0.054	0.120	-0.180	0.288
C.BBWM02_DOC	-0.468	0.233	-0.924	-0.012
C.BBWM02_TDP	-0.967	0.205	-1.368	-0.565

Table F.3 Bootstrapping results of the best fitted no-stressor MARSS models at CWT; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	ML Est	Std. Err	Low. CI	Up. CI
R.(NO3-1,NO3-1)	0.308	0.163	-0.011	0.628
R.(NH4-1,NH4-1)	0.097	0.072	-0.044	0.237
R.(Ca-1,Ca-1)	0.925	0.327	0.283	1.566
R.(SO4-1,SO4-1)	0.124	0.044	0.038	0.210
R.(DOC-1,DOC-1)	0.705	0.288	0.141	1.270
R.(TDP-1,TDP-1)	0.337	0.229	-0.111	0.785
R.(NO3-2,NO3-2)	0.142	0.096	-0.047	0.331
R.(NH4-2,NH4-2)	0.245	0.124	0.002	0.489
R.(Ca-2,Ca-2)	0.903	0.320	0.277	1.530
R.(SO4-2,SO4-2)	0.240	0.085	0.074	0.406
R.(DOC-2,DOC-2)	1.160	0.472	0.231	2.081
R.(TDP-2,TDP-2)	0.766	0.426	-0.069	1.601
R.(NO3-3,NO3-3)	0.196	0.120	-0.040	0.432
R.(NH4-3,NH4-3)	0.109	0.069	-0.025	0.244
R.(Ca-3,Ca-3)	0.127	0.047	0.035	0.218
R.(SO4-3,SO4-3)	0.798	0.282	0.245	1.351
R.(DOC-3,DOC-3)	0.559	0.228	0.112	1.007
R.(TDP-3,TDP-3)	0.251	0.160	-0.063	0.565
R.(NO3-4,NO3-4)	0.040	0.052	-0.063	0.142
R.(NH4-4,NH4-4)	0.000	0.026	-0.050	0.050
R.(Ca-4,Ca-4)	0.070	0.028	0.015	0.125
R.(SO4-4,SO4-4)	1.140	0.402	0.350	1.927
R.(DOC-4,DOC-4)	0.664	0.271	0.133	1.196
R.(TDP-4,TDP-4)	0.737	0.398	-0.043	1.517
Q.q_NO3	0.183	0.072	0.042	0.324
Q.q_NH4	0.127	0.049	0.031	0.224
Q.q_Ca	0.000	0.002	-0.003	0.003
Q.q_TDP	0.120	0.069	-0.016	0.255
x0.CWT02_NO3	1.550	0.589	0.396	2.704
x0.CWT02_NH4	-0.880	0.438	-1.737	-0.022
x0.CWT02_Ca	0.000	0.240	-0.471	0.471
x0.CWT02_SO4	0.000	0.088	-0.173	0.173
x0.CWT02_DOC	0.000	0.242	-0.475	0.475
x0.CWT02_TDP	0.508	0.994	-1.439	2.455
x0.CWT18_NO3	1.240	0.527	0.205	2.270
x0.CWT18_NH4	-1.520	0.501	-2.505	-0.539
x0.CWT18_Ca	0.000	0.238	-0.466	0.466
x0.CWT18_SO4	0.000	0.122	-0.240	0.240
x0.CWT18_DOC	0.000	0.310	-0.608	0.608

x0.CWT18_TDP	0.559	1.042	-1.483	2.602
x0.CWT07_NO3	1.320	0.550	0.241	2.397
x0.CWT07_NH4	0.286	0.445	-0.585	1.158
x0.CWT07_Ca	0.000	0.089	-0.175	0.175
x0.CWT07_SO4	0.000	0.223	-0.438	0.438
x0.CWT07_DOC	0.000	0.216	-0.423	0.423
x0.CWT07_TDP	0.778	0.980	-1.143	2.699
x0.CWT17_NO3	1.520	0.466	0.607	2.432
x0.CWT17_NH4	-1.060	0.357	-1.754	-0.356
x0.CWT17_Ca	0.000	0.069	-0.136	0.136
x0.CWT17_SO4	0.000	0.267	-0.523	0.523
x0.CWT17_DOC	0.000	0.235	-0.461	0.461
x0.CWT17_TDP	0.762	1.040	-1.276	2.799

Table F.4 Bootstrapping results of the best fitted stressor (runoff) MARSS models at CWT; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	ML Est	Std. Err	Low. CI	Up. CI
R.(NO3-1,NO3-1)	0.312	0.167	-0.014	0.639
R.(NH4-1,NH4-1)	0.057	0.049	-0.039	0.152
R.(Ca-1,Ca-1)	0.889	0.314	0.272	1.505
R.(SO4-1,SO4-1)	0.113	0.040	0.035	0.191
R.(DOC-1,DOC-1)	0.565	0.231	0.113	1.017
R.(TDP-1,TDP-1)	0.475	0.224	0.036	0.913
R.(NO3-2,NO3-2)	0.138	0.096	-0.049	0.326
R.(NH4-2,NH4-2)	0.178	0.093	-0.004	0.360
R.(Ca-2,Ca-2)	0.845	0.299	0.259	1.430
R.(SO4-2,SO4-2)	0.214	0.076	0.066	0.362
R.(DOC-2,DOC-2)	1.060	0.431	0.211	1.902
R.(TDP-2,TDP-2)	0.669	0.299	0.083	1.255
R.(NO3-3,NO3-3)	0.183	0.114	-0.041	0.407
R.(NH4-3,NH4-3)	0.000	0.024	-0.046	0.046
R.(Ca-3,Ca-3)	0.120	0.044	0.033	0.207
R.(SO4-3,SO4-3)	0.351	0.124	0.108	0.594
R.(DOC-3,DOC-3)	0.532	0.217	0.106	0.958
R.(TDP-3,TDP-3)	0.448	0.200	0.055	0.841
R.(NO3-4,NO3-4)	0.041	0.053	-0.062	0.144
R.(NH4-4,NH4-4)	0.000	0.022	-0.044	0.044
R.(Ca-4,Ca-4)	0.050	0.021	0.008	0.092
R.(SO4-4,SO4-4)	0.698	0.247	0.214	1.181
R.(DOC-4,DOC-4)	0.599	0.245	0.120	1.078
R.(TDP-4,TDP-4)	0.915	0.409	0.113	1.717

Q.q_NO3	0.181	0.072	0.040	0.322
Q.q_NH4	0.118	0.041	0.037	0.199
Q.q_Ca	0.000	0.001	-0.003	0.003
x0.CWT02_NO3	1.380	0.675	0.056	2.701
x0.CWT02_NH4	-1.300	0.451	-2.184	-0.416
x0.CWT02_Ca	0.132	0.287	-0.430	0.695
x0.CWT02_SO4	-0.074	0.102	-0.274	0.127
x0.CWT02_DOC	-0.178	0.240	-0.649	0.293
x0.CWT02_TDP	-0.059	0.257	-0.562	0.444
x0.CWT18_NO3	1.090	0.595	-0.078	2.253
x0.CWT18_NH4	-1.990	0.532	-3.028	-0.943
x0.CWT18_Ca	0.169	0.280	-0.380	0.717
x0.CWT18_SO4	-0.112	0.141	-0.388	0.164
x0.CWT18_DOC	-0.150	0.329	-0.794	0.494
x0.CWT18_TDP	-0.327	0.294	-0.903	0.248
x0.CWT07_NO3	1.520	0.618	0.310	2.733
x0.CWT07_NH4	1.070	0.378	0.326	1.809
x0.CWT07_Ca	-0.056	0.109	-0.269	0.157
x0.CWT07_SO4	-0.465	0.180	-0.819	-0.112
x0.CWT07_DOC	-0.078	0.233	-0.535	0.379
x0.CWT07_TDP	-0.206	0.241	-0.677	0.266
x0.CWT17_NO3	1.530	0.518	0.516	2.546
x0.CWT17_NH4	-1.050	0.377	-1.791	-0.315
x0.CWT17_Ca	0.100	0.068	-0.034	0.233
x0.CWT17_SO4	-0.462	0.254	-0.961	0.037
x0.CWT17_DOC	-0.121	0.247	-0.606	0.363
x0.CWT17_TDP	-0.305	0.344	-0.979	0.368
C.CWT02_NO3	-0.129	0.259	-0.636	0.379
C.CWT02_NH4	-0.261	0.145	-0.546	0.023
C.CWT02_Ca	0.233	0.289	-0.333	0.799
C.CWT02_SO4	-0.130	0.103	-0.331	0.072
C.CWT02_DOC	-0.443	0.257	-0.946	0.060
C.CWT02_TDP	-0.126	0.244	-0.603	0.352
C.CWT18_NO3	-0.109	0.204	-0.509	0.292
C.CWT18_NH4	-0.319	0.198	-0.707	0.069
C.CWT18_Ca	0.297	0.281	-0.255	0.848
C.CWT18_SO4	-0.198	0.142	-0.475	0.080
C.CWT18_DOC	-0.373	0.351	-1.061	0.315
C.CWT18_TDP	-0.678	0.289	-1.245	-0.112
C.CWT07_NO3	0.142	0.218	-0.286	0.570
C.CWT07_NH4	0.557	0.105	0.351	0.764
C.CWT07_Ca	-0.099	0.116	-0.327	0.129
C.CWT07_SO4	-0.819	0.181	-1.175	-0.464

C.CWT07_DOC	-0.195	0.249	-0.683	0.293
C.CWT07_TDP	-0.426	0.237	-0.890	0.038
C.CWT17_NO3	0.010	0.156	-0.295	0.315
C.CWT17_NH4	0.002	0.103	-0.200	0.203
C.CWT17_Ca	0.175	0.069	0.040	0.310
C.CWT17_SO4	-0.813	0.256	-1.314	-0.312
C.CWT17_DOC	-0.302	0.264	-0.820	0.216
C.CWT17_TDP	-0.633	0.338	-1.296	0.030

Table F.5 Bootstrapping results of the best fitted no-stressor MARSS models at DOR; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.(NO3-1,NO3-1)	0.027	0.029	-0.029	0.083
R.(NH4-1,NH4-1)	0.000	0.016	-0.031	0.031
R.(Ca-1,Ca-1)	0.016	0.007	0.001	0.030
R.(SO4-1,SO4-1)	0.001	0.019	-0.036	0.039
R.(DOC-1,DOC-1)	0.014	0.006	0.003	0.024
R.(TDP-1,TDP-1)	0.015	0.005	0.005	0.025
R.(NO3-2,NO3-2)	0.288	0.183	-0.071	0.646
R.(NH4-2,NH4-2)	0.094	0.073	-0.049	0.237
R.(Ca-2,Ca-2)	0.974	0.451	0.091	1.858
R.(SO4-2,SO4-2)	0.866	0.307	0.264	1.467
R.(DOC-2,DOC-2)	0.179	0.058	0.065	0.294
R.(TDP-2,TDP-2)	0.191	0.058	0.078	0.304
R.(NO3-3,NO3-3)	0.421	0.328	-0.222	1.064
R.(NH4-3,NH4-3)	0.435	0.329	-0.209	1.080
R.(Ca-3,Ca-3)	1.480	0.879	-0.243	3.204
R.(SO4-3,SO4-3)	0.822	0.294	0.245	1.398
R.(DOC-3,DOC-3)	0.353	0.112	0.134	0.572
R.(TDP-3,TDP-3)	0.616	0.186	0.252	0.980
R.(NO3-4,NO3-4)	0.769	0.360	0.063	1.475
R.(NH4-4,NH4-4)	0.596	0.284	0.040	1.153
R.(Ca-4,Ca-4)	0.759	0.309	0.154	1.363
R.(SO4-4,SO4-4)	0.898	0.319	0.273	1.523
R.(DOC-4,DOC-4)	0.133	0.042	0.050	0.216
R.(TDP-4,TDP-4)	0.352	0.106	0.144	0.560
Q.q_DOR_NO3	0.098	0.045	0.008	0.187
Q.q_DOR_NH4	0.086	0.035	0.017	0.155
Q.q_DOR_Ca	0.002	0.003	-0.003	0.008
Q.q_DOR_SO4	0.106	0.042	0.023	0.188
Q.q_DOR_DOC	0.004	0.002	-0.001	0.008

Q.q_DOR_TDP	0.000	0.000	0.000	0.000
x0.DOR00_NO3	0.835	0.346	0.158	1.513
x0.DOR00_NH4	0.581	0.294	0.005	1.156
x0.DOR00_Ca	0.057	0.149	-0.236	0.349
x0.DOR00_SO4	-0.247	0.327	-0.888	0.394
x0.DOR00_DOC	-0.163	0.095	-0.349	0.023
x0.DOR00_TDP	0.000	0.026	-0.051	0.051
x0.DOR03_NO3	0.011	1.180	-2.302	2.324
x0.DOR03_NH4	0.472	1.086	-1.655	2.600
x0.DOR03_Ca	-0.004	0.368	-0.725	0.718
x0.DOR03_SO4	0.490	0.600	-0.685	1.666
x0.DOR03_DOC	-0.061	0.165	-0.385	0.264
x0.DOR03_TDP	0.000	0.093	-0.183	0.183
x0.DOR05_NO3	-0.230	1.348	-2.873	2.412
x0.DOR05_NH4	-0.280	1.275	-2.778	2.218
x0.DOR05_Ca	-0.008	0.542	-1.071	1.055
x0.DOR05_SO4	-0.316	0.593	-1.479	0.847
x0.DOR05_DOC	0.019	0.196	-0.365	0.404
x0.DOR05_TDP	0.000	0.167	-0.328	0.328
x0.DOR06_NO3	0.381	1.098	-1.771	2.533
x0.DOR06_NH4	0.626	1.025	-1.383	2.636
x0.DOR06_Ca	-0.004	0.303	-0.597	0.590
x0.DOR06_SO4	0.438	0.605	-0.747	1.623
x0.DOR06_DOC	-0.208	0.155	-0.511	0.095
x0.DOR06_TDP	0.000	0.126	-0.248	0.248

Table F.6 Bootstrapping results of the best fitted no-stressor MARSS models at ELA; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	ML Est	Std. Err	Low. CI	Up. CI
R.r_ELA1_NO3	0.081	0.039	0.006	0.157
R.r_ELA1_NH4	0.777	0.234	0.318	1.236
R.r_ELA1_Ca	0.042	0.021	0.000	0.084
R.r_ELA1_SO4	0.107	0.084	-0.057	0.272
R.r_ELA1_DOC	0.167	0.052	0.064	0.270
R.r_ELA1_TDP	0.429	0.129	0.176	0.683
R.r_ELA2_NO3	0.175	0.051	0.074	0.275
R.r_ELA2_NH4	0.968	0.206	0.563	1.372
R.r_ELA2_Ca	0.275	0.067	0.143	0.406
R.r_ELA2_SO4	0.270	0.103	0.068	0.472
R.r_ELA2_DOC	0.150	0.035	0.081	0.219
R.r_ELA2_TDP	0.503	0.107	0.293	0.713

Q.q_ELA_NO3	0.053	0.025	0.004	0.102
Q.q_ELA_Ca	0.028	0.015	-0.001	0.057
Q.q_ELA_SO4	0.243	0.096	0.056	0.431
Q.q_ELA_DOC	0.000	0.001	-0.002	0.002
x0.ELA01_NO3	1.040	0.311	0.433	1.653
x0.ELA01_NH4	0.000	0.188	-0.368	0.368
x0.ELA01_Ca	0.089	0.226	-0.353	0.531
x0.ELA01_SO4	1.480	0.569	0.368	2.599
x0.ELA01_DOC	0.000	0.089	-0.173	0.173
x0.ELA01_TDP	0.000	0.140	-0.274	0.274
x0.ELA02_NO3	0.196	0.355	-0.499	0.891
x0.ELA02_NH4	0.000	0.210	-0.411	0.411
x0.ELA02_Ca	0.649	0.321	0.020	1.278
x0.ELA02_SO4	1.700	0.637	0.454	2.950
x0.ELA02_DOC	0.000	0.083	-0.162	0.162
x0.ELA02_TDP	0.000	0.151	-0.296	0.296
x0.ELA03_NO3	1.200	0.355	0.508	1.898
x0.ELA03_NH4	0.000	0.210	-0.411	0.411
x0.ELA03_Ca	0.620	0.321	-0.009	1.248
x0.ELA03_SO4	1.310	0.637	0.064	2.560
x0.ELA03_DOC	0.000	0.083	-0.162	0.162
x0.ELA03_TDP	0.000	0.151	-0.296	0.296

Table F.7 Bootstrapping results of the best fitted stressor (temperature) MARSS models at ELA; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.r_ELA1_NO3	0.092	0.038	0.018	0.166
R.r_ELA1_NH4	0.668	0.201	0.273	1.062
R.r_ELA1_Ca	0.041	0.018	0.005	0.077
R.r_ELA1_SO4	0.001	0.062	-0.120	0.122
R.r_ELA1_DOC	0.165	0.052	0.063	0.268
R.r_ELA1_TDP	0.328	0.099	0.134	0.521
R.r_ELA2_NO3	0.126	0.038	0.053	0.200
R.r_ELA2_NH4	0.743	0.158	0.432	1.053
R.r_ELA2_Ca	0.237	0.057	0.126	0.348
R.r_ELA2_SO4	0.117	0.077	-0.034	0.267
R.r_ELA2_DOC	0.149	0.035	0.079	0.218
R.r_ELA2_TDP	0.500	0.107	0.291	0.709
Q.q_ELA_NO3	0.034	0.018	-0.001	0.068
Q.q_ELA_Ca	0.014	0.009	-0.004	0.033
Q.q_ELA_SO4	0.334	0.114	0.110	0.559

Q.q_ELA_DOC	0.000	0.001	-0.003	0.003
x0.ELA01_NO3	1.020	0.285	0.460	1.579
x0.ELA01_NH4	0.455	0.297	-0.127	1.037
x0.ELA01_Ca	-0.014	0.188	-0.382	0.353
x0.ELA01_SO4	1.717	0.584	0.573	2.861
x0.ELA01_DOC	0.063	0.148	-0.227	0.352
x0.ELA01_TDP	-0.440	0.208	-0.848	-0.033
x0.ELA02_NO3	0.442	0.306	-0.158	1.041
x0.ELA02_NH4	0.428	0.313	-0.186	1.042
x0.ELA02_Ca	1.034	0.300	0.446	1.622
x0.ELA02_SO4	1.863	0.661	0.568	3.158
x0.ELA02_DOC	-0.031	0.144	-0.313	0.251
x0.ELA02_TDP	-0.085	0.257	-0.589	0.418
x0.ELA03_NO3	1.516	0.306	0.917	2.116
x0.ELA03_NH4	0.821	0.313	0.207	1.434
x0.ELA03_Ca	0.731	0.300	0.143	1.320
x0.ELA03_SO4	1.448	0.661	0.154	2.743
x0.ELA03_DOC	0.056	0.144	-0.227	0.339
x0.ELA03_TDP	0.061	0.257	-0.442	0.565
C.ELA01_NO3	0.057	0.077	-0.094	0.209
C.ELA01_NH4	0.227	0.120	-0.008	0.462
C.ELA01_Ca	-0.106	0.051	-0.206	-0.007
C.ELA01_SO4	0.370	0.129	0.117	0.623
C.ELA01_DOC	0.031	0.060	-0.086	0.148
C.ELA01_TDP	-0.220	0.084	-0.384	-0.055
C.ELA02_NO3	0.224	0.084	0.059	0.389
C.ELA02_NH4	0.213	0.126	-0.034	0.461
C.ELA02_Ca	0.288	0.088	0.115	0.461
C.ELA02_SO4	0.435	0.157	0.128	0.743
C.ELA02_DOC	-0.016	0.059	-0.131	0.100
C.ELA02_TDP	-0.043	0.104	-0.246	0.161
C.ELA03_NO3	0.298	0.085	0.131	0.464
C.ELA03_NH4	0.409	0.126	0.161	0.657
C.ELA03_Ca	0.126	0.088	-0.047	0.299
C.ELA03_SO4	0.163	0.156	-0.142	0.467
C.ELA03_DOC	0.028	0.058	-0.086	0.142
C.ELA03_TDP	0.031	0.104	-0.173	0.234

Table F.8 Bootstrapping results of the best fitted no-stressor MARSS models at HBEF; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.r1_HBEF_NO3	0.002	0.196	-0.383	0.387
R.r1_HBEF_NH4	0.283	0.127	0.034	0.532
R.r1_HBEF_Ca	0.000	0.134	-0.262	0.262
R.r1_HBEF_SO4	0.034	0.068	-0.099	0.166
R.r1_HBEF_DOC	0.801	0.725	-0.621	2.220
R.r1_HBEF_TDP	0.004	0.067	-0.126	0.135
R.r2_HBEF_NO3	0.132	0.251	-0.359	0.623
R.r2_HBEF_NH4	0.003	0.002	-0.002	0.008
R.r2_HBEF_Ca	0.000	0.020	-0.040	0.040
R.r2_HBEF_SO4	0.000	0.031	-0.060	0.060
R.r2_HBEF_DOC	0.016	0.005	0.005	0.026
R.r2_HBEF_TDP	0.000	0.034	-0.066	0.067
R.r3_HBEF_NO3	0.000	0.082	-0.161	0.162
R.r3_HBEF_NH4	0.006	0.004	-0.001	0.013
R.r3_HBEF_Ca	0.020	0.019	-0.017	0.057
R.r3_HBEF_SO4	0.000	0.026	-0.051	0.051
R.r3_HBEF_DOC	0.015	0.005	0.004	0.025
R.r3_HBEF_TDP	0.002	0.178	-0.347	0.351
R.r4_HBEF_NO3	0.001	0.055	-0.107	0.108
R.r4_HBEF_NH4	0.004	0.003	-0.002	0.010
R.r4_HBEF_Ca	0.007	0.028	-0.048	0.062
R.r4_HBEF_SO4	0.000	0.018	-0.035	0.035
R.r4_HBEF_DOC	0.024	0.009	0.007	0.042
R.r4_HBEF_TDP	0.000	0.058	-0.112	0.113
R.r5_HBEF_NO3	0.001	0.102	-0.199	0.200
R.r5_HBEF_NH4	0.001	0.000	0.000	0.002
R.r5_HBEF_Ca	0.055	0.043	-0.030	0.140
R.r5_HBEF_SO4	1.130	0.411	0.320	1.930
R.r5_HBEF_DOC	0.042	0.015	0.012	0.072
R.r5_HBEF_TDP	0.000	0.084	-0.165	0.166
Q.q1_HBEF_NO3	0.909	0.471	-0.014	1.830
Q.q1_HBEF_NH4	0.113	0.092	-0.067	0.293
Q.q1_HBEF_ca	0.624	0.322	-0.007	1.250
Q.q1_HBEF_SO4	0.239	0.137	-0.029	0.506
Q.q1_HBEF_DOC	0.000	0.026	-0.051	0.051
Q.q1_HBEF_TDP	0.307	0.158	-0.003	0.616
Q.q2_HBEF_NO3	0.899	0.507	-0.094	1.890
Q.q2_HBEF_NH4	0.006	0.004	-0.001	0.013
Q.q2_HBEF_ca	0.096	0.049	0.000	0.192

Q.q2_HBEF_SO4	0.138	0.073	-0.005	0.281
Q.q2_HBEF_DOC	0.000	0.000	0.000	0.000
Q.q2_HBEF_TDP	0.161	0.082	0.000	0.322
Q.q3_HBEF_NO3	0.328	0.195	-0.055	0.711
Q.q3_HBEF_NH4	0.004	0.003	-0.003	0.010
Q.q3_HBEF_ca	0.038	0.027	-0.015	0.090
Q.q3_HBEF_SO4	0.100	0.061	-0.020	0.220
Q.q3_HBEF_TDP	0.717	0.424	-0.113	1.550
Q.q4_HBEF_NO3	0.213	0.128	-0.039	0.464
Q.q4_HBEF_NH4	0.003	0.003	-0.002	0.009
Q.q4_HBEF_ca	0.101	0.062	-0.020	0.221
Q.q4_HBEF_SO4	0.071	0.043	-0.012	0.154
Q.q4_HBEF_TDP	0.234	0.138	-0.036	0.503
Q.q5_HBEF_NO3	0.385	0.237	-0.079	0.849
Q.q5_HBEF_NH4	0.000	0.000	0.000	0.000
Q.q5_HBEF_ca	0.068	0.052	-0.034	0.170
Q.q5_HBEF_TDP	0.343	0.201	-0.052	0.738
x0.HBEF01_NO3	0.698	0.954	-1.170	2.570
x0.HBEF01_NH4	-1.790	0.494	-2.760	-0.822
x0.HBEF01_Ca	0.673	0.790	-0.876	2.220
x0.HBEF01_SO4	1.400	0.518	0.387	2.420
x0.HBEF01_DOC	0.001	0.574	-1.120	1.130
x0.HBEF01_TDP	1.770	0.558	0.677	2.860
x0.HBEF06_NO3	1.810	1.010	-0.170	3.780
x0.HBEF06_NH4	0.296	0.089	0.123	0.470
x0.HBEF06_Ca	1.630	0.310	1.020	2.240
x0.HBEF06_SO4	1.750	0.372	1.020	2.470
x0.HBEF06_DOC	0.000	0.036	-0.070	0.070
x0.HBEF06_TDP	1.240	0.401	0.458	2.030
x0.HBEF07_NO3	0.197	1.620	-2.980	3.370
x0.HBEF07_NH4	0.206	0.180	-0.147	0.558
x0.HBEF07_Ca	0.467	0.561	-0.633	1.570
x0.HBEF07_SO4	1.150	0.895	-0.603	2.900
x0.HBEF07_DOC	0.000	0.031	-0.061	0.061
x0.HBEF07_TDP	0.398	2.400	-4.300	5.090
x0.HBEF08_NO3	0.079	1.300	-2.480	2.630
x0.HBEF08_NH4	0.220	0.170	-0.113	0.554
x0.HBEF08_Ca	0.621	0.901	-1.140	2.390
x0.HBEF08_SO4	1.030	0.754	-0.445	2.510
x0.HBEF08_DOC	0.000	0.040	-0.079	0.079
x0.HBEF08_TDP	0.516	1.370	-2.170	3.200
x0.HBEF09_NO3	-0.573	1.760	-4.010	2.870
x0.HBEF09_NH4	0.000	0.011	-0.022	0.022

x0.HBEF09_Ca	0.558	0.762	-0.935	2.050
x0.HBEF09_SO4	0.000	0.274	-0.537	0.537
x0.HBEF09_DOC	0.000	0.053	-0.104	0.104
x0.HBEF09_TDP	0.751	1.660	-2.490	4.000

Table F.9 Bootstrapping results of the best fitted stressor (water year) MARSS models at HBEF; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.r1_HBEF_NO3	0.002	0.196	-0.382	0.385
R.r1_HBEF_NH4	0.280	0.120	0.045	0.516
R.r1_HBEF_Ca	0.000	0.130	-0.255	0.256
R.r1_HBEF_SO4	0.041	0.065	-0.085	0.168
R.r1_HBEF_DOC	0.556	0.548	-0.518	1.630
R.r1_HBEF_TDP	0.005	0.066	-0.124	0.135
R.r2_HBEF_NO3	0.120	0.247	-0.364	0.604
R.r2_HBEF_NH4	0.003	0.002	-0.002	0.008
R.r2_HBEF_Ca	0.000	0.020	-0.040	0.040
R.r2_HBEF_SO4	0.000	0.029	-0.057	0.058
R.r2_HBEF_DOC	0.012	0.005	0.003	0.020
R.r2_HBEF_TDP	0.000	0.034	-0.066	0.067
R.r3_HBEF_NO3	0.002	0.071	-0.137	0.140
R.r3_HBEF_NH4	0.007	0.003	0.001	0.013
R.r3_HBEF_Ca	0.038	0.014	0.011	0.064
R.r3_HBEF_SO4	0.016	0.019	-0.020	0.053
R.r3_HBEF_DOC	0.011	0.004	0.003	0.018
R.r3_HBEF_TDP	0.010	0.161	-0.305	0.325
R.r4_HBEF_NO3	0.041	0.046	-0.049	0.130
R.r4_HBEF_NH4	0.005	0.002	0.000	0.009
R.r4_HBEF_Ca	0.057	0.026	0.007	0.107
R.r4_HBEF_SO4	0.000	0.015	-0.029	0.029
R.r4_HBEF_DOC	0.024	0.009	0.007	0.041
R.r4_HBEF_TDP	0.001	0.055	-0.107	0.108
R.r5_HBEF_NO3	0.005	0.082	-0.155	0.165
R.r5_HBEF_NH4	0.001	0.000	0.000	0.002
R.r5_HBEF_Ca	0.078	0.028	0.022	0.133
R.r5_HBEF_SO4	0.140	0.051	0.040	0.239
R.r5_HBEF_DOC	0.040	0.015	0.011	0.068
R.r5_HBEF_TDP	0.003	0.075	-0.144	0.149
Q.q1_HBEF_NO3	0.907	0.469	-0.013	1.830
Q.q1_HBEF_NH4	0.080	0.073	-0.063	0.223
Q.q1_HBEF_ca	0.612	0.315	-0.004	1.230

Q.q1_HBEF_SO4	0.216	0.125	-0.029	0.460
Q.q1_HBEF_DOC	0.000	0.021	-0.041	0.041
Q.q1_HBEF_TDP	0.303	0.156	-0.004	0.609
Q.q2_HBEF_NO3	0.912	0.508	-0.084	1.910
Q.q2_HBEF_NH4	0.005	0.003	-0.001	0.012
Q.q2_HBEF_ca	0.096	0.049	0.000	0.192
Q.q2_HBEF_SO4	0.134	0.070	-0.003	0.272
Q.q2_HBEF_DOC	0.000	0.000	0.000	0.000
Q.q2_HBEF_TDP	0.160	0.082	-0.001	0.321
Q.q3_HBEF_NO3	0.284	0.168	-0.044	0.613
Q.q3_HBEF_NH4	0.001	0.001	-0.001	0.003
Q.q3_HBEF_SO4	0.043	0.030	-0.015	0.102
Q.q3_HBEF_TDP	0.637	0.377	-0.102	1.380
Q.q4_HBEF_NO3	0.103	0.072	-0.038	0.244
Q.q4_HBEF_NH4	0.001	0.001	-0.001	0.004
Q.q4_HBEF_ca	0.000	0.001	-0.002	0.002
Q.q4_HBEF_SO4	0.061	0.036	-0.009	0.130
Q.q4_HBEF_TDP	0.222	0.131	-0.034	0.479
Q.q5_HBEF_NO3	0.314	0.189	-0.057	0.685
Q.q5_HBEF_NH4	0.000	0.000	0.000	0.000
Q.q5_HBEF_TDP	0.296	0.176	-0.049	0.640
x0.HBEF01_NO3	0.610	1.020	-1.390	2.610
x0.HBEF01_NH4	-2.130	0.522	-3.160	-1.110
x0.HBEF01_Ca	0.861	0.837	-0.779	2.500
x0.HBEF01_SO4	1.210	0.542	0.145	2.270
x0.HBEF01_DOC	-0.676	0.723	-2.090	0.740
x0.HBEF01_TDP	1.850	0.594	0.688	3.020
x0.HBEF06_NO3	1.640	1.090	-0.488	3.780
x0.HBEF06_NH4	0.316	0.096	0.127	0.504
x0.HBEF06_Ca	1.650	0.331	1.000	2.300
x0.HBEF06_SO4	1.640	0.393	0.871	2.410
x0.HBEF06_DOC	-0.165	0.075	-0.312	-0.017
x0.HBEF06_TDP	1.280	0.429	0.436	2.120
x0.HBEF07_NO3	-1.870	2.060	-5.920	2.170
x0.HBEF07_NH4	-0.155	0.153	-0.456	0.145
x0.HBEF07_Ca	-0.974	0.123	-1.220	-0.732
x0.HBEF07_SO4	-0.727	0.834	-2.360	0.907
x0.HBEF07_DOC	-0.143	0.065	-0.271	-0.015
x0.HBEF07_TDP	2.990	3.090	-3.060	9.050
x0.HBEF08_NO3	-1.960	1.300	-4.500	0.586
x0.HBEF08_NH4	-0.080	0.170	-0.412	0.253
x0.HBEF08_Ca	-1.160	0.152	-1.460	-0.865
x0.HBEF08_SO4	-0.017	0.951	-1.880	1.850

x0.HBEF08_DOC	-0.036	0.099	-0.229	0.158
x0.HBEF08_TDP	1.590	1.820	-1.980	5.170
x0.HBEF09_NO3	-3.130	2.180	-7.400	1.150
x0.HBEF09_NH4	-0.035	0.019	-0.073	0.004
x0.HBEF09_Ca	-1.140	0.177	-1.480	-0.790
x0.HBEF09_SO4	-2.240	0.238	-2.700	-1.770
x0.HBEF09_DOC	-0.104	0.127	-0.353	0.145
x0.HBEF09_TDP	-1.370	2.110	-5.500	2.760
C.HBEF01_NO3	-0.054	0.223	-0.490	0.382
C.HBEF01_NH4	-0.132	0.082	-0.293	0.030
C.HBEF01_Ca	0.117	0.183	-0.242	0.475
C.HBEF01_SO4	-0.099	0.111	-0.317	0.118
C.HBEF01_DOC	-0.234	0.224	-0.674	0.206
C.HBEF01_TDP	0.050	0.129	-0.202	0.302
C.HBEF06_NO3	-0.085	0.223	-0.522	0.352
C.HBEF06_NH4	0.008	0.018	-0.027	0.043
C.HBEF06_Ca	0.014	0.071	-0.125	0.153
C.HBEF06_SO4	-0.063	0.084	-0.228	0.102
C.HBEF06_DOC	-0.024	0.010	-0.044	-0.004
C.HBEF06_TDP	0.019	0.092	-0.161	0.199
C.HBEF07_NO3	-0.236	0.160	-0.550	0.079
C.HBEF07_NH4	-0.035	0.014	-0.062	-0.008
C.HBEF07_Ca	-0.144	0.017	-0.177	-0.111
C.HBEF07_SO4	-0.197	0.065	-0.325	-0.069
C.HBEF07_DOC	-0.021	0.009	-0.038	-0.004
C.HBEF07_TDP	0.296	0.240	-0.174	0.767
C.HBEF08_NO3	-0.225	0.102	-0.426	-0.024
C.HBEF08_NH4	-0.030	0.014	-0.057	-0.003
C.HBEF08_Ca	-0.172	0.021	-0.213	-0.132
C.HBEF08_SO4	-0.120	0.074	-0.264	0.025
C.HBEF08_DOC	-0.005	0.013	-0.031	0.021
C.HBEF08_TDP	0.123	0.142	-0.155	0.400
C.HBEF09_NO3	-0.291	0.170	-0.625	0.043
C.HBEF09_NH4	-0.005	0.003	-0.010	0.000
C.HBEF09_Ca	-0.168	0.024	-0.215	-0.121
C.HBEF09_SO4	-0.331	0.032	-0.393	-0.268
C.HBEF09_DOC	-0.015	0.017	-0.049	0.018
C.HBEF09_TDP	-0.241	0.164	-0.563	0.080

Table F.10 Bootstrapping results of the best fitted no-stressor MARSS models at HJA; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.(NO3-1,NO3-1)	0.000	0.002	-0.004	0.004
R.(NH4-1,NH4-1)	0.738	0.225	0.298	1.178
R.(Ca-1,Ca-1)	0.075	0.026	0.025	0.125
R.(SO4-1,SO4-1)	0.000	0.009	-0.017	0.017
R.(DOC-1,DOC-1)	0.040	0.021	-0.002	0.082
R.(TDP-1,TDP-1)	0.004	0.024	-0.042	0.050
R.(NO3-2,NO3-2)	0.000	0.001	-0.002	0.002
R.(NH4-2,NH4-2)	0.386	0.120	0.151	0.622
R.(Ca-2,Ca-2)	0.266	0.089	0.091	0.441
R.(SO4-2,SO4-2)	0.000	0.008	-0.016	0.016
R.(DOC-2,DOC-2)	0.039	0.021	-0.003	0.081
R.(TDP-2,TDP-2)	0.081	0.053	-0.023	0.184
R.(NO3-3,NO3-3)	2.080	0.758	0.597	3.570
R.(NH4-3,NH4-3)	1.300	0.394	0.530	2.072
R.(Ca-3,Ca-3)	0.474	0.153	0.173	0.774
R.(SO4-3,SO4-3)	0.098	0.042	0.015	0.181
R.(DOC-3,DOC-3)	0.039	0.019	0.002	0.077
R.(TDP-3,TDP-3)	0.125	0.067	-0.007	0.257
R.(NO3-4,NO3-4)	1.280	0.398	0.497	2.059
R.(NH4-4,NH4-4)	0.958	0.290	0.389	1.527
R.(Ca-4,Ca-4)	0.184	0.063	0.061	0.308
R.(SO4-4,SO4-4)	0.290	0.107	0.081	0.500
R.(DOC-4,DOC-4)	0.087	0.040	0.009	0.165
R.(TDP-4,TDP-4)	0.228	0.105	0.023	0.433
R.(NO3-5,NO3-5)	0.228	0.090	0.051	0.405
R.(NH4-5,NH4-5)	0.899	0.273	0.364	1.434
R.(Ca-5,Ca-5)	0.123	0.043	0.038	0.207
R.(SO4-5,SO4-5)	0.299	0.107	0.090	0.508
R.(DOC-5,DOC-5)	0.181	0.081	0.022	0.341
R.(TDP-5,TDP-5)	0.391	0.152	0.093	0.688
Q.q_HJA_NO3	0.008	0.003	0.002	0.015
Q.q_HJA_NH4	0.000	0.003	-0.005	0.005
Q.q_HJA_Ca	0.009	0.006	-0.002	0.021
Q.q_HJA_SO4	0.052	0.015	0.022	0.082
Q.q_HJA_DOC	0.000	0.000	-0.001	0.001
Q.q_HJA_TDP	0.134	0.041	0.053	0.215
x0.HJA06_NO3	0.000	0.092	-0.180	0.180
x0.HJA06_NH4	0.000	0.189	-0.371	0.370
x0.HJA06_Ca	-0.547	0.177	-0.893	-0.200

x0.HJA06_SO4	1.400	0.227	0.950	1.841
x0.HJA06_DOC	0.000	0.077	-0.151	0.151
x0.HJA06_TDP	1.390	0.371	0.658	2.113
x0.HJA07_NO3	1.420	0.092	1.240	1.600
x0.HJA07_NH4	0.000	0.135	-0.266	0.265
x0.HJA07_Ca	-0.189	0.233	-0.646	0.267
x0.HJA07_SO4	1.720	0.227	1.270	2.161
x0.HJA07_DOC	0.000	0.075	-0.147	0.147
x0.HJA07_TDP	1.280	0.437	0.425	2.137
x0.HJA10_NO3	0.067	0.422	-0.761	0.895
x0.HJA10_NH4	0.000	0.244	-0.477	0.478
x0.HJA10_Ca	0.022	0.267	-0.500	0.545
x0.HJA10_SO4	1.050	0.319	0.427	1.676
x0.HJA10_DOC	0.000	0.063	-0.123	0.123
x0.HJA10_TDP	0.870	0.461	-0.034	1.774
x0.HJA08_NO3	0.076	0.338	-0.586	0.738
x0.HJA08_NH4	0.001	0.209	-0.410	0.412
x0.HJA08_Ca	-0.013	0.215	-0.434	0.407
x0.HJA08_SO4	0.811	0.388	0.050	1.573
x0.HJA08_DOC	0.000	0.096	-0.189	0.189
x0.HJA08_TDP	0.524	0.504	-0.464	1.511
x0.HJA09_NO3	0.100	0.221	-0.333	0.532
x0.HJA09_NH4	0.000	0.203	-0.397	0.397
x0.HJA09_Ca	0.007	0.196	-0.378	0.392
x0.HJA09_SO4	1.180	0.391	0.412	1.944
x0.HJA09_DOC	0.000	0.135	-0.264	0.264
x0.HJA09_TDP	1.050	0.553	-0.028	2.138

Table F.11 Bootstrapping results of the best fitted stressor (NO_3-N deposition) MARSS models at HJA; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.(NO3-1,NO3-1)	0.000	0.002	-0.004	0.004
R.(NH4-1,NH4-1)	0.586	0.181	0.231	0.941
R.(Ca-1,Ca-1)	0.075	0.026	0.024	0.125
R.(SO4-1,SO4-1)	0.000	0.009	-0.017	0.017
R.(DOC-1,DOC-1)	0.028	0.016	-0.003	0.059
R.(TDP-1,TDP-1)	0.000	0.023	-0.046	0.046
R.(NO3-2,NO3-2)	0.000	0.001	-0.002	0.002
R.(NH4-2,NH4-2)	0.342	0.110	0.126	0.558
R.(Ca-2,Ca-2)	0.266	0.089	0.092	0.441
R.(SO4-2,SO4-2)	0.000	0.008	-0.015	0.016

R.(DOC-2,DOC-2)	0.027	0.016	-0.003	0.058
R.(TDP-2,TDP-2)	0.062	0.047	-0.031	0.155
R.(NO3-3,NO3-3)	2.080	0.758	0.597	3.570
R.(NH4-3,NH4-3)	1.300	0.394	0.528	2.073
R.(Ca-3,Ca-3)	0.268	0.089	0.094	0.442
R.(SO4-3,SO4-3)	0.078	0.035	0.010	0.147
R.(DOC-3,DOC-3)	0.036	0.018	0.001	0.070
R.(TDP-3,TDP-3)	0.109	0.062	-0.014	0.231
R.(NO3-4,NO3-4)	1.160	0.363	0.447	1.870
R.(NH4-4,NH4-4)	0.867	0.264	0.349	1.386
R.(Ca-4,Ca-4)	0.150	0.052	0.048	0.252
R.(SO4-4,SO4-4)	0.287	0.106	0.080	0.494
R.(DOC-4,DOC-4)	0.074	0.034	0.008	0.141
R.(TDP-4,TDP-4)	0.181	0.091	0.003	0.358
R.(NO3-5,NO3-5)	0.228	0.090	0.051	0.405
R.(NH4-5,NH4-5)	0.899	0.274	0.362	1.436
R.(Ca-5,Ca-5)	0.065	0.024	0.018	0.113
R.(SO4-5,SO4-5)	0.264	0.096	0.077	0.451
R.(DOC-5,DOC-5)	0.166	0.075	0.020	0.312
R.(TDP-5,TDP-5)	0.391	0.154	0.089	0.694
Q.q_HJA_NO3	0.008	0.003	0.002	0.015
Q.q_HJA_NH4	0.000	0.003	-0.007	0.007
Q.q_HJA_Ca	0.009	0.006	-0.002	0.020
Q.q_HJA_SO4	0.049	0.015	0.020	0.078
Q.q_HJA_DOC	0.000	0.000	-0.001	0.001
Q.q_HJA_TDP	0.141	0.043	0.057	0.225
x0.HJA06_NO3	0.000	0.091	-0.178	0.178
x0.HJA06_NH4	-0.562	0.300	-1.150	0.027
x0.HJA06_Ca	-0.583	0.185	-0.945	-0.220
x0.HJA06_SO4	1.410	0.223	0.977	1.849
x0.HJA06_DOC	-0.126	0.092	-0.306	0.053
x0.HJA06_TDP	1.380	0.377	0.640	2.117
x0.HJA07_NO3	1.420	0.091	1.250	1.603
x0.HJA07_NH4	-0.282	0.249	-0.769	0.205
x0.HJA07_Ca	-0.189	0.258	-0.694	0.317
x0.HJA07_SO4	1.730	0.223	1.290	2.163
x0.HJA07_DOC	-0.116	0.087	-0.287	0.054
x0.HJA07_TDP	1.260	0.435	0.409	2.113
x0.HJA10_NO3	0.070	0.459	-0.830	0.971
x0.HJA10_NH4	-0.011	0.300	-0.598	0.577
x0.HJA10_Ca	0.212	0.239	-0.256	0.680
x0.HJA10_SO4	1.150	0.304	0.553	1.743
x0.HJA10_DOC	0.070	0.109	-0.144	0.284

x0.HJA10_TDP	0.868	0.465	-0.043	1.779
x0.HJA08_NO3	-0.089	0.345	-0.764	0.587
x0.HJA08_NH4	-0.080	0.209	-0.490	0.330
x0.HJA08_Ca	-0.146	0.216	-0.569	0.277
x0.HJA08_SO4	0.733	0.393	-0.037	1.502
x0.HJA08_DOC	-0.004	0.090	-0.181	0.172
x0.HJA08_TDP	0.448	0.497	-0.526	1.421
x0.HJA09_NO3	0.096	0.223	-0.341	0.533
x0.HJA09_NH4	-0.011	0.249	-0.500	0.478
x0.HJA09_Ca	0.043	0.173	-0.295	0.382
x0.HJA09_SO4	1.260	0.377	0.518	1.995
x0.HJA09_DOC	0.150	0.204	-0.250	0.550
x0.HJA09_TDP	1.070	0.564	-0.032	2.178
C.HJA06_NO3	0.000	0.589	-1.150	1.154
C.HJA06_NH4	-8.230	3.787	-15.700	-0.808
C.HJA06_Ca	-1.060	1.650	-4.290	2.175
C.HJA06_SO4	1.540	1.531	-1.460	4.544
C.HJA06_DOC	-1.620	0.897	-3.380	0.134
C.HJA06_TDP	-1.010	2.450	-5.820	3.789
C.HJA07_NO3	0.074	0.093	-0.109	0.257
C.HJA07_NH4	-0.713	0.527	-1.750	0.321
C.HJA07_Ca	0.004	0.418	-0.816	0.824
C.HJA07_SO4	0.203	0.217	-0.223	0.629
C.HJA07_DOC	-0.254	0.138	-0.525	0.016
C.HJA07_TDP	-0.467	0.491	-1.430	0.495
C.HJA10_NO3	-0.008	0.349	-0.693	0.676
C.HJA10_NH4	0.015	0.233	-0.442	0.473
C.HJA10_Ca	-0.464	0.118	-0.696	-0.233
C.HJA10_SO4	-0.191	0.107	-0.401	0.020
C.HJA10_DOC	-0.108	0.123	-0.350	0.134
C.HJA10_TDP	0.097	0.156	-0.209	0.403
C.HJA08_NO3	-0.280	0.180	-0.633	0.072
C.HJA08_NH4	-0.205	0.150	-0.500	0.089
C.HJA08_Ca	-0.149	0.074	-0.294	-0.003
C.HJA08_SO4	-0.089	0.116	-0.317	0.139
C.HJA08_DOC	-0.229	0.175	-0.573	0.115
C.HJA08_TDP	-0.265	0.130	-0.520	-0.010
C.HJA09_NO3	0.006	0.092	-0.175	0.187
C.HJA09_NH4	0.011	0.144	-0.271	0.293
C.HJA09_Ca	-0.206	0.052	-0.308	-0.104
C.HJA09_SO4	-0.188	0.110	-0.404	0.028
C.HJA09_DOC	-0.172	0.179	-0.523	0.180
C.HJA09_TDP	-0.027	0.155	-0.330	0.276

Table F.12 Bootstrapping results of the best fitted no-stressor MARSS models at LEF; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.(NO3-1,NO3-1)	0.011	0.072	-0.130	0.152
R.(NH4-1,NH4-1)	0.011	0.072	-0.130	0.152
R.(Ca-1,Ca-1)	0.363	0.113	0.142	0.584
R.(SO4-1,SO4-1)	0.645	0.214	0.225	1.064
R.(DOC-1,DOC-1)	0.153	0.114	-0.071	0.377
R.(TDP-1,TDP-1)	0.497	0.189	0.126	0.869
R.(NO3-2,NO3-2)	0.002	0.066	-0.127	0.132
R.(NH4-2,NH4-2)	0.002	0.066	-0.127	0.132
R.(Ca-2,Ca-2)	0.353	0.110	0.138	0.567
R.(SO4-2,SO4-2)	0.502	0.167	0.176	0.829
R.(DOC-2,DOC-2)	0.002	0.058	-0.111	0.115
R.(TDP-2,TDP-2)	0.396	0.157	0.089	0.703
R.(NO3-3,NO3-3)	0.002	0.070	-0.135	0.138
R.(NH4-3,NH4-3)	0.002	0.070	-0.135	0.138
R.(Ca-3,Ca-3)	0.288	0.099	0.093	0.482
R.(SO4-3,SO4-3)	0.674	0.247	0.190	1.158
R.(DOC-3,DOC-3)	0.026	0.070	-0.111	0.163
R.(TDP-3,TDP-3)	0.547	0.229	0.098	0.995
R.(NO3-4,NO3-4)	0.778	0.344	0.104	1.451
R.(NH4-4,NH4-4)	0.776	0.343	0.104	1.449
R.(Ca-4,Ca-4)	0.011	0.004	0.003	0.019
R.(SO4-4,SO4-4)	0.191	0.071	0.051	0.331
R.(DOC-4,DOC-4)	0.288	0.164	-0.034	0.610
R.(TDP-4,TDP-4)	0.341	0.139	0.068	0.615
R.(NO3-5,NO3-5)	0.033	0.084	-0.131	0.198
R.(NH4-5,NH4-5)	0.034	0.084	-0.131	0.199
R.(Ca-5,Ca-5)	0.505	0.155	0.200	0.809
R.(SO4-5,SO4-5)	0.075	0.031	0.014	0.136
R.(DOC-5,DOC-5)	0.282	0.160	-0.032	0.595
R.(TDP-5,TDP-5)	0.017	0.037	-0.055	0.089
R.(NO3-6,NO3-6)	0.000	0.070	-0.137	0.137
R.(NH4-6,NH4-6)	0.000	0.070	-0.137	0.137
R.(Ca-6,Ca-6)	0.027	0.009	0.009	0.044
R.(SO4-6,SO4-6)	0.159	0.060	0.041	0.277
R.(DOC-6,DOC-6)	0.000	0.072	-0.142	0.142
R.(TDP-6,TDP-6)	0.288	0.119	0.055	0.522
Q.q_LEF_NO3	0.463	0.105	0.258	0.669
Q.q_LEF_NH4	0.463	0.105	0.258	0.668
Q.q_LEF_Ca	0.002	0.001	-0.001	0.004

Q.q_LEF_SO4	0.032	0.014	0.005	0.059
Q.q_LEF_DOC	0.403	0.096	0.214	0.592
Q.q_LEF_TDP	0.133	0.043	0.048	0.218
x0.LEF01_NO3	0.400	0.689	-0.950	1.750
x0.LEF01_NH4	0.399	0.689	-0.950	1.749
x0.LEF01_Ca	-0.066	0.165	-0.391	0.258
x0.LEF01_SO4	-0.053	0.402	-0.840	0.734
x0.LEF01_DOC	-0.285	0.722	-1.700	1.130
x0.LEF01_TDP	-1.633	0.576	-2.762	-0.504
x0.LEF02_NO3	1.041	0.682	-0.297	2.378
x0.LEF02_NH4	1.037	0.682	-0.300	2.374
x0.LEF02_Ca	-0.023	0.164	-0.344	0.298
x0.LEF02_SO4	0.074	0.380	-0.671	0.819
x0.LEF02_DOC	-1.286	0.636	-2.533	-0.039
x0.LEF02_TDP	-1.519	0.552	-2.601	-0.436
x0.LEF03_NO3	1.019	0.682	-0.318	2.355
x0.LEF03_NH4	1.019	0.682	-0.317	2.355
x0.LEF03_Ca	-0.022	0.159	-0.333	0.289
x0.LEF03_SO4	0.157	0.406	-0.638	0.953
x0.LEF03_DOC	-1.404	0.654	-2.686	-0.123
x0.LEF03_TDP	-1.263	0.587	-2.413	-0.114
x0.LEF04_NO3	0.785	0.936	-1.048	2.619
x0.LEF04_NH4	0.786	0.935	-1.047	2.619
x0.LEF04_Ca	-0.072	0.070	-0.210	0.065
x0.LEF04_SO4	-0.002	0.310	-0.610	0.606
x0.LEF04_DOC	-0.409	0.773	-1.924	1.106
x0.LEF04_TDP	-1.122	0.538	-2.177	-0.068
x0.LEF05_NO3	0.494	0.703	-0.884	1.872
x0.LEF05_NH4	0.494	0.703	-0.885	1.872
x0.LEF05_Ca	-0.031	0.186	-0.395	0.334
x0.LEF05_SO4	-0.534	0.260	-1.044	-0.023
x0.LEF05_DOC	-0.300	0.771	-1.810	1.211
x0.LEF05_TDP	1.159	1.269	-1.328	3.645
x0.LEF06_NO3	0.833	0.681	-0.501	2.168
x0.LEF06_NH4	0.833	0.681	-0.501	2.167
x0.LEF06_Ca	0.047	0.085	-0.120	0.214
x0.LEF06_SO4	-0.292	0.299	-0.878	0.294
x0.LEF06_DOC	0.308	0.898	-1.451	2.067
x0.LEF06_TDP	-1.521	0.523	-2.546	-0.497

Table F.13 Bootstrapping results of the best fitted stressor (DIN deposition) MARSS models at LEF; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	ML Est	Std. Err	Low. CI	Up. CI
R.(NO3-1,NO3-1)	0.018	0.071	-0.122	0.158
R.(NH4-1,NH4-1)	0.018	0.071	-0.122	0.158
R.(Ca-1,Ca-1)	0.334	0.103	0.132	0.537
R.(SO4-1,SO4-1)	0.596	0.201	0.202	0.990
R.(DOC-1,DOC-1)	0.382	0.116	0.156	0.609
R.(TDP-1,TDP-1)	0.335	0.145	0.052	0.619
R.(NO3-2,NO3-2)	0.012	0.067	-0.118	0.143
R.(NH4-2,NH4-2)	0.012	0.066	-0.118	0.142
R.(Ca-2,Ca-2)	0.312	0.097	0.122	0.502
R.(SO4-2,SO4-2)	0.450	0.153	0.151	0.749
R.(DOC-2,DOC-2)	0.218	0.066	0.088	0.348
R.(TDP-2,TDP-2)	0.255	0.118	0.023	0.487
R.(NO3-3,NO3-3)	0.009	0.069	-0.127	0.144
R.(NH4-3,NH4-3)	0.009	0.069	-0.127	0.144
R.(Ca-3,Ca-3)	0.274	0.094	0.090	0.459
R.(SO4-3,SO4-3)	0.602	0.226	0.160	1.044
R.(DOC-3,DOC-3)	0.316	0.105	0.109	0.522
R.(TDP-3,TDP-3)	0.336	0.160	0.023	0.649
R.(NO3-4,NO3-4)	0.806	0.350	0.120	1.491
R.(NH4-4,NH4-4)	0.804	0.349	0.120	1.488
R.(Ca-4,Ca-4)	0.011	0.004	0.003	0.018
R.(SO4-4,SO4-4)	0.173	0.068	0.040	0.305
R.(DOC-4,DOC-4)	0.565	0.171	0.231	0.899
R.(TDP-4,TDP-4)	0.260	0.120	0.025	0.495
R.(NO3-5,NO3-5)	0.039	0.082	-0.122	0.199
R.(NH4-5,NH4-5)	0.039	0.082	-0.122	0.200
R.(Ca-5,Ca-5)	0.496	0.153	0.197	0.795
R.(SO4-5,SO4-5)	0.069	0.031	0.009	0.130
R.(DOC-5,DOC-5)	1.645	0.496	0.673	2.617
R.(TDP-5,TDP-5)	0.001	0.039	-0.076	0.078
R.(NO3-6,NO3-6)	0.000	0.066	-0.129	0.129
R.(NH4-6,NH4-6)	0.000	0.066	-0.129	0.129
R.(Ca-6,Ca-6)	0.024	0.008	0.008	0.040
R.(SO4-6,SO4-6)	0.151	0.059	0.034	0.267
R.(DOC-6,DOC-6)	0.079	0.026	0.027	0.130
R.(TDP-6,TDP-6)	0.162	0.084	-0.003	0.327
Q.q_LEF_NO3	0.437	0.100	0.241	0.633
Q.q_LEF_NH4	0.437	0.100	0.241	0.633
Q.q_LEF_Ca	0.001	0.001	-0.001	0.003

Q.q_LEF_SO4	0.039	0.016	0.007	0.071
Q.q_LEF_DOC	0.000	0.001	-0.002	0.002
Q.q_LEF_TDP	0.181	0.053	0.078	0.285
x0.LEF01_NO3	0.533	0.684	-0.807	1.873
x0.LEF01_NH4	0.532	0.684	-0.808	1.872
x0.LEF01_Ca	-0.259	0.224	-0.698	0.181
x0.LEF01_SO4	-0.389	0.559	-1.484	0.707
x0.LEF01_DOC	-0.901	0.204	-1.301	-0.501
x0.LEF01_TDP	-2.655	0.668	-3.964	-1.345
x0.LEF02_NO3	1.135	0.679	-0.197	2.466
x0.LEF02_NH4	1.130	0.679	-0.201	2.461
x0.LEF02_Ca	-0.276	0.219	-0.705	0.153
x0.LEF02_SO4	-0.252	0.517	-1.266	0.762
x0.LEF02_DOC	-0.831	0.154	-1.134	-0.529
x0.LEF02_TDP	-2.488	0.627	-3.717	-1.259
x0.LEF03_NO3	1.161	0.681	-0.173	2.496
x0.LEF03_NH4	1.161	0.681	-0.173	2.496
x0.LEF03_Ca	-0.153	0.219	-0.582	0.275
x0.LEF03_SO4	-0.253	0.584	-1.398	0.892
x0.LEF03_DOC	-1.075	0.199	-1.465	-0.684
x0.LEF03_TDP	-2.433	0.695	-3.795	-1.070
x0.LEF04_NO3	0.860	1.036	-1.170	2.891
x0.LEF04_NH4	0.861	1.036	-1.168	2.891
x0.LEF04_Ca	-0.113	0.084	-0.278	0.051
x0.LEF04_SO4	-0.272	0.392	-1.041	0.497
x0.LEF04_DOC	-0.520	0.245	-0.999	-0.040
x0.LEF04_TDP	-1.699	0.630	-2.933	-0.465
x0.LEF05_NO3	0.463	0.700	-0.908	1.834
x0.LEF05_NH4	0.463	0.700	-0.909	1.835
x0.LEF05_Ca	0.142	0.263	-0.374	0.659
x0.LEF05_SO4	-0.602	0.306	-1.203	-0.002
x0.LEF05_DOC	-0.443	0.417	-1.259	0.374
x0.LEF05_TDP	1.153	1.480	-1.747	4.053
x0.LEF06_NO3	0.905	0.669	-0.407	2.216
x0.LEF06_NH4	0.905	0.669	-0.407	2.216
x0.LEF06_Ca	-0.100	0.105	-0.307	0.106
x0.LEF06_SO4	-0.385	0.376	-1.123	0.353
x0.LEF06_DOC	-0.370	0.094	-0.553	-0.186
x0.LEF06_TDP	-2.312	0.571	-3.431	-1.192
C.LEF01_NO3	0.167	0.150	-0.127	0.461
C.LEF01_NH4	0.166	0.150	-0.128	0.460
C.LEF01_Ca	-0.138	0.112	-0.357	0.081
C.LEF01_SO4	-0.169	0.184	-0.530	0.192

C.LEF01_DOC	-0.688	0.116	-0.916	-0.460
C.LEF01_TDP	-0.380	0.183	-0.739	-0.022
C.LEF02_NO3	0.121	0.148	-0.170	0.412
C.LEF02_NH4	0.120	0.148	-0.170	0.411
C.LEF02_Ca	-0.174	0.108	-0.386	0.038
C.LEF02_SO4	-0.173	0.166	-0.498	0.153
C.LEF02_DOC	-0.635	0.088	-0.807	-0.462
C.LEF02_TDP	-0.368	0.168	-0.697	-0.038
C.LEF03_NO3	0.185	0.182	-0.171	0.541
C.LEF03_NH4	0.185	0.182	-0.171	0.541
C.LEF03_Ca	-0.090	0.106	-0.298	0.118
C.LEF03_SO4	-0.216	0.203	-0.614	0.181
C.LEF03_DOC	-0.792	0.110	-1.007	-0.577
C.LEF03_TDP	-0.478	0.217	-0.903	-0.053
C.LEF04_NO3	0.051	0.285	-0.507	0.608
C.LEF04_NH4	0.050	0.284	-0.507	0.608
C.LEF04_Ca	-0.022	0.026	-0.073	0.030
C.LEF04_SO4	-0.132	0.116	-0.359	0.096
C.LEF04_DOC	-0.397	0.140	-0.672	-0.121
C.LEF04_TDP	-0.222	0.169	-0.554	0.109
C.LEF05_NO3	-0.042	0.157	-0.349	0.265
C.LEF05_NH4	-0.042	0.157	-0.350	0.266
C.LEF05_Ca	0.118	0.135	-0.147	0.383
C.LEF05_SO4	-0.013	0.084	-0.177	0.151
C.LEF05_DOC	-0.338	0.239	-0.807	0.131
C.LEF05_TDP	-0.052	0.122	-0.292	0.187
C.LEF06_NO3	0.100	0.144	-0.182	0.382
C.LEF06_NH4	0.100	0.144	-0.182	0.382
C.LEF06_Ca	-0.074	0.036	-0.144	-0.003
C.LEF06_SO4	-0.040	0.109	-0.255	0.174
C.LEF06_DOC	-0.276	0.053	-0.380	-0.173
C.LEF06_TDP	-0.323	0.148	-0.612	-0.033

Table F.14 Bootstrapping results of the best fitted no-stressor MARSS models at MEF; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**low. CI**	**Up. CI**
R.r_MEF_NO3	0.789	0.137	0.520	1.059
R.r_MEF_NH4	0.370	0.078	0.217	0.523
R.r_MEF_Ca	0.894	0.151	0.598	1.191
R.r_MEF_SO4	0.674	0.139	0.400	0.947
R.r_MEF_DOC	0.364	0.079	0.209	0.518

R.r_MEF_TDP	0.586	0.110	0.370	0.801
Q.q_MEF_NO3	0.037	0.025	-0.013	0.087
Q.q_MEF_NH4	0.087	0.042	0.004	0.170
Q.q_MEF_Ca	0.000	0.006	-0.011	0.011
Q.q_MEF_SO4	0.086	0.050	-0.013	0.185
Q.q_MEF_DOC	0.055	0.031	-0.006	0.116
Q.q_MEF_TDP	0.069	0.037	-0.004	0.142
x0.MEF02_NO3	0.202	0.437	-0.654	1.059
x0.MEF02_NH4	-0.590	0.478	-1.526	0.347
x0.MEF02_Ca	0.000	0.217	-0.426	0.425
x0.MEF02_SO4	0.280	0.543	-0.786	1.345
x0.MEF02_DOC	-0.184	0.581	-1.323	0.955
x0.MEF02_TDP	0.079	0.489	-0.879	1.037
x0.MEF05_NO3	-0.242	0.439	-1.102	0.617
x0.MEF05_NH4	-0.744	0.478	-1.681	0.192
x0.MEF05_Ca	0.000	0.208	-0.408	0.408
x0.MEF05_SO4	-0.180	0.543	-1.245	0.884
x0.MEF05_DOC	-0.037	0.582	-1.177	1.103
x0.MEF05_TDP	-0.728	0.489	-1.686	0.230
x0.MEF04_NO3	-0.664	0.437	-1.521	0.193
x0.MEF04_NH4	-0.523	0.478	-1.459	0.414
x0.MEF04_Ca	0.000	0.210	-0.411	0.411
x0.MEF04_SO4	-0.065	0.555	-1.153	1.024
x0.MEF04_DOC	0.243	0.582	-0.898	1.383
x0.MEF04_TDP	-0.475	0.489	-1.433	0.483
x0.MEF06_NO3	-0.459	0.437	-1.317	0.398
x0.MEF06_NH4	-0.520	0.478	-1.456	0.417
x0.MEF06_Ca	0.000	0.227	-0.444	0.444
x0.MEF06_SO4	0.080	0.543	-0.985	1.145
x0.MEF06_DOC	-0.189	0.582	-1.330	0.953
x0.MEF06_TDP	-0.422	0.489	-1.379	0.536

Table F.15 Bootstrapping results of the best fitted stressor (temperature) MARSS models at MEF; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.r_MEF_NO3	0.919	0.155	0.615	1.223
R.r_MEF_NH4	0.386	0.073	0.243	0.528
R.r_MEF_Ca	0.841	0.155	0.538	1.144
R.r_MEF_SO4	0.538	0.113	0.317	0.758
R.r_MEF_DOC	0.376	0.074	0.231	0.522
R.r_MEF_TDP	0.706	0.120	0.470	0.942

Q.q_MEF_NO3	0.000	0.006	-0.011	0.012
Q.q_MEF_NH4	0.041	0.024	-0.006	0.087
Q.q_MEF_Ca	0.000	0.008	-0.015	0.015
Q.q_MEF_SO4	0.000	0.006	-0.012	0.012
Q.q_MEF_DOC	0.000	0.003	-0.006	0.006
Q.q_MEF_TDP	0.000	0.005	-0.009	0.009
x0.MEF02_NO3	0.091	0.269	-0.436	0.618
x0.MEF02_NH4	-0.400	0.409	-1.200	0.401
x0.MEF02_Ca	0.230	0.305	-0.368	0.828
x0.MEF02_SO4	0.496	0.221	0.064	0.928
x0.MEF02_DOC	0.294	0.189	-0.076	0.665
x0.MEF02_TDP	0.052	0.255	-0.448	0.551
x0.MEF05_NO3	0.092	0.264	-0.425	0.610
x0.MEF05_NH4	-0.530	0.409	-1.331	0.272
x0.MEF05_Ca	0.239	0.253	-0.258	0.735
x0.MEF05_SO4	0.336	0.205	-0.066	0.738
x0.MEF05_DOC	0.288	0.189	-0.083	0.658
x0.MEF05_TDP	0.445	0.231	-0.007	0.897
x0.MEF04_NO3	0.214	0.304	-0.381	0.809
x0.MEF04_NH4	-0.269	0.409	-1.071	0.533
x0.MEF04_Ca	-0.003	0.288	-0.569	0.562
x0.MEF04_SO4	0.331	0.233	-0.127	0.788
x0.MEF04_DOC	0.174	0.264	-0.343	0.691
x0.MEF04_TDP	0.458	0.231	0.006	0.911
x0.MEF06_NO3	0.336	0.320	-0.290	0.962
x0.MEF06_NH4	-0.152	0.410	-0.956	0.651
x0.MEF06_Ca	-0.166	0.299	-0.751	0.420
x0.MEF06_SO4	0.762	0.242	0.288	1.235
x0.MEF06_DOC	0.709	0.216	0.285	1.133
x0.MEF06_TDP	0.287	0.270	-0.241	0.815
C.MEF02_NO3	0.068	0.126	-0.179	0.315
C.MEF02_NH4	0.144	0.114	-0.079	0.367
C.MEF02_Ca	0.174	0.148	-0.117	0.464
C.MEF02_SO4	0.406	0.103	0.205	0.607
C.MEF02_DOC	0.206	0.082	0.046	0.366
C.MEF02_TDP	0.039	0.115	-0.186	0.264
C.MEF05_NO3	0.070	0.126	-0.176	0.316
C.MEF05_NH4	0.062	0.114	-0.161	0.285
C.MEF05_Ca	0.182	0.120	-0.053	0.416
C.MEF05_SO4	0.276	0.097	0.085	0.467
C.MEF05_DOC	0.201	0.083	0.038	0.364
C.MEF05_TDP	0.338	0.109	0.125	0.551
C.MEF04_NO3	0.165	0.146	-0.121	0.451

C.MEF04_NH4	0.275	0.119	0.043	0.507
C.MEF04_Ca	-0.001	0.127	-0.250	0.248
C.MEF04_SO4	0.266	0.113	0.045	0.488
C.MEF04_DOC	0.121	0.102	-0.078	0.321
C.MEF04_TDP	0.348	0.109	0.135	0.561
C.MEF06_NO3	0.218	0.150	-0.075	0.512
C.MEF06_NH4	0.242	0.116	0.015	0.470
C.MEF06_Ca	-0.107	0.128	-0.358	0.145
C.MEF06_SO4	0.523	0.104	0.319	0.728
C.MEF06_DOC	0.411	0.090	0.235	0.587
C.MEF06_TDP	0.186	0.120	-0.050	0.421

Table F.16 Bootstrapping results of the best fitted no-stressor MARSS models at SEF; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.r_SEF_NO3	0.044	0.055	-0.064	0.151
R.r_SEF_NH4	0.958	0.204	0.558	1.358
R.r_SEF_Ca	0.117	0.025	0.068	0.166
R.r_SEF_SO4	0.062	0.018	0.027	0.096
R.r_SEF_DOC	0.697	0.263	0.181	1.213
R.r_SEF_TDP	0.930	0.340	0.264	1.596
Q.q_SEF77_NO3	0.438	0.179	0.088	0.788
Q.q_SEF77_SO4	0.144	0.069	0.008	0.279
Q.q_SEF80_NO3	0.208	0.112	-0.011	0.428
x0.SEF77_NO3	-1.040	0.691	-2.393	0.317
x0.SEF77_NH4	0.000	0.209	-0.409	0.409
x0.SEF77_Ca	0.000	0.073	-0.143	0.143
x0.SEF77_SO4	-1.260	0.436	-2.111	-0.402
x0.SEF77_DOC	0.000	0.315	-0.618	0.618
x0.SEF77_TDP	0.000	0.341	-0.668	0.668
x0.SEF80_NO3	-0.855	0.495	-1.826	0.116
x0.SEF80_NH4	0.000	0.209	-0.409	0.409
x0.SEF80_Ca	0.000	0.073	-0.143	0.143
x0.SEF80_SO4	0.000	0.053	-0.104	0.104
x0.SEF80_DOC	0.000	0.315	-0.618	0.618
x0.SEF80_TDP	0.000	0.365	-0.714	0.714

Table F.17 Bootstrapping results of the best fitted stressor (water year) MARSS models at SEF; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.r_SEF_NO3	0.101	0.051	0.001	0.200
R.r_SEF_NH4	0.654	0.139	0.381	0.927
R.r_SEF_Ca	0.102	0.022	0.059	0.145
R.r_SEF_SO4	0.035	0.010	0.015	0.056
R.r_SEF_DOC	0.396	0.150	0.103	0.690
R.r_SEF_TDP	0.254	0.093	0.072	0.436
Q.q_SEF77_NO3	0.263	0.131	0.006	0.520
Q.q_SEF77_SO4	0.145	0.061	0.026	0.264
Q.q_SEF80_NO3	0.101	0.067	-0.029	0.232
x0.SEF77_NO3	-1.497	0.636	-2.744	-0.250
x0.SEF77_NH4	-1.722	0.418	-2.541	-0.903
x0.SEF77_Ca	0.202	0.165	-0.122	0.525
x0.SEF77_SO4	-1.002	0.452	-1.888	-0.115
x0.SEF77_DOC	-1.221	0.458	-2.120	-0.323
x0.SEF77_TDP	-1.603	0.354	-2.297	-0.910
x0.SEF80_NO3	-1.444	0.451	-2.327	-0.560
x0.SEF80_NH4	0.059	0.418	-0.760	0.878
x0.SEF80_Ca	0.324	0.165	0.000	0.647
x0.SEF80_SO4	0.394	0.097	0.204	0.585
x0.SEF80_DOC	-0.160	0.458	-1.058	0.739
x0.SEF80_TDP	-1.035	0.367	-1.754	-0.316
C.SEF77_NO3	-0.211	0.123	-0.452	0.031
C.SEF77_NH4	-0.275	0.061	-0.394	-0.156
C.SEF77_Ca	0.032	0.024	-0.015	0.079
C.SEF77_SO4	0.114	0.090	-0.063	0.291
C.SEF77_DOC	-0.297	0.095	-0.483	-0.111
C.SEF77_TDP	-0.346	0.066	-0.476	-0.217
C.SEF80_NO3	-0.199	0.080	-0.356	-0.042
C.SEF80_NH4	0.009	0.061	-0.110	0.128
C.SEF80_Ca	0.052	0.024	0.005	0.099
C.SEF80_SO4	0.063	0.014	0.035	0.091
C.SEF80_DOC	-0.039	0.095	-0.225	0.147
C.SEF80_TDP	-0.252	0.076	-0.400	-0.103

Table F.18 Bootstrapping results of the best fitted no-stressor MARSS models at TLW; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.(NO3-1,NO3-1)	0.097	0.029	0.040	0.154
R.(NH4-1,NH4-1)	0.460	0.173	0.122	0.799
R.(Ca-1,Ca-1)	0.073	0.023	0.027	0.119
R.(SO4-1,SO4-1)	0.043	0.013	0.018	0.069
R.(DOC-1,DOC-1)	0.028	0.012	0.004	0.053
R.(TDP-1,TDP-1)	0.202	0.063	0.078	0.326
R.(NO3-2,NO3-2)	0.060	0.018	0.024	0.095
R.(NH4-2,NH4-2)	0.591	0.222	0.156	1.027
R.(Ca-2,Ca-2)	0.033	0.010	0.012	0.053
R.(SO4-2,SO4-2)	0.000	0.008	-0.016	0.016
R.(DOC-2,DOC-2)	0.024	0.011	0.003	0.045
R.(TDP-2,TDP-2)	0.142	0.044	0.054	0.229
R.(NO3-3,NO3-3)	0.212	0.130	-0.042	0.466
R.(NH4-3,NH4-3)	0.492	0.191	0.118	0.866
R.(Ca-3,Ca-3)	0.447	0.137	0.178	0.717
R.(SO4-3,SO4-3)	2.570	0.823	0.955	4.181
R.(DOC-3,DOC-3)	0.035	0.014	0.008	0.061
R.(TDP-3,TDP-3)	0.036	0.012	0.013	0.059
R.(NO3-4,NO3-4)	0.001	0.037	-0.072	0.073
R.(NH4-4,NH4-4)	0.548	0.204	0.148	0.948
R.(Ca-4,Ca-4)	0.402	0.123	0.160	0.644
R.(SO4-4,SO4-4)	0.788	0.253	0.292	1.283
R.(DOC-4,DOC-4)	0.808	0.254	0.311	1.306
R.(TDP-4,TDP-4)	1.040	0.316	0.418	1.657
R.(NO3-5,NO3-5)	0.001	0.045	-0.086	0.089
R.(NH4-5,NH4-5)	0.593	0.221	0.159	1.026
R.(Ca-5,Ca-5)	0.252	0.078	0.099	0.404
R.(SO4-5,SO4-5)	0.087	0.034	0.021	0.153
R.(DOC-5,DOC-5)	0.167	0.055	0.059	0.276
R.(TDP-5,TDP-5)	0.887	0.270	0.357	1.417
R.(NO3-6,NO3-6)	0.000	0.052	-0.103	0.103
R.(NH4-6,NH4-6)	0.616	0.231	0.164	1.069
R.(Ca-6,Ca-6)	0.078	0.025	0.029	0.126
R.(SO4-6,SO4-6)	0.055	0.025	0.006	0.104
R.(DOC-6,DOC-6)	0.247	0.082	0.086	0.408
R.(TDP-6,TDP-6)	1.010	0.307	0.407	1.612
Q.q_TLW_NH4	0.108	0.045	0.020	0.196
Q.q_TLW_Ca	0.001	0.001	-0.001	0.003
Q.q_TLW_DOC	0.012	0.005	0.002	0.021

Q.q_TLW_TDP	0.001	0.001	-0.001	0.003
Q.q_TLW_SO4	0.041	0.014	0.014	0.068
Q.q_TLW_NO3	0.275	0.080	0.119	0.432
x0.TLW32_NO3	0.000	0.066	-0.130	0.130
x0.TLW32_NH4	1.380	0.532	0.338	2.423
x0.TLW32_Ca	-0.002	0.095	-0.187	0.184
x0.TLW32_SO4	0.000	0.044	-0.087	0.087
x0.TLW32_DOC	0.188	0.158	-0.122	0.499
x0.TLW32_TDP	0.004	0.127	-0.245	0.253
x0.TLW35_NO3	0.000	0.052	-0.102	0.102
x0.TLW35_NH4	0.866	0.559	-0.229	1.960
x0.TLW35_Ca	0.108	0.078	-0.045	0.261
x0.TLW35_SO4	0.448	0.202	0.051	0.844
x0.TLW35_DOC	0.212	0.154	-0.089	0.514
x0.TLW35_TDP	0.027	0.115	-0.198	0.253
x0.TLW38_NO3	-0.501	0.645	-1.764	0.763
x0.TLW38_NH4	0.736	0.539	-0.320	1.792
x0.TLW38_Ca	-0.022	0.165	-0.346	0.302
x0.TLW38_SO4	-0.112	0.590	-1.269	1.044
x0.TLW38_DOC	-0.502	0.164	-0.824	-0.180
x0.TLW38_TDP	-0.116	0.081	-0.275	0.043
x0.TLW31_NO3	0.227	0.525	-0.802	1.257
x0.TLW31_NH4	1.350	0.550	0.274	2.431
x0.TLW31_Ca	0.003	0.159	-0.309	0.315
x0.TLW31_SO4	1.010	0.449	0.131	1.889
x0.TLW31_DOC	-0.048	0.325	-0.685	0.589
x0.TLW31_TDP	-0.002	0.234	-0.462	0.457
x0.TLW33_NO3	-0.318	0.526	-1.348	0.712
x0.TLW33_NH4	0.859	0.559	-0.236	1.954
x0.TLW33_Ca	-0.004	0.135	-0.269	0.261
x0.TLW33_SO4	1.510	0.289	0.948	2.080
x0.TLW33_DOC	-0.123	0.225	-0.565	0.318
x0.TLW33_TDP	0.017	0.219	-0.413	0.446
x0.TLW34_NO3	-0.254	0.525	-1.282	0.775
x0.TLW34_NH4	0.856	0.563	-0.248	1.960
x0.TLW34_Ca	-0.041	0.096	-0.230	0.148
x0.TLW34_SO4	1.470	0.269	0.948	2.001
x0.TLW34_DOC	0.040	0.246	-0.442	0.521
x0.TLW34_TDP	-0.007	0.231	-0.461	0.446

Table F.19 Bootstrapping results of the best fitted stressor (water year) MARSS models at SEF; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.r_SEF_NO3	0.101	0.051	0.001	0.200
R.r_SEF_NH4	0.654	0.139	0.381	0.927
R.r_SEF_Ca	0.102	0.022	0.059	0.145
R.r_SEF_SO4	0.035	0.010	0.015	0.056
R.r_SEF_DOC	0.396	0.150	0.103	0.690
R.r_SEF_TDP	0.254	0.093	0.072	0.436
Q.q_SEF77_NO3	0.263	0.131	0.006	0.520
Q.q_SEF77_SO4	0.145	0.061	0.026	0.264
Q.q_SEF80_NO3	0.101	0.067	-0.029	0.232
x0.SEF77_NO3	-1.497	0.636	-2.744	-0.250
x0.SEF77_NH4	-1.722	0.418	-2.541	-0.903
x0.SEF77_Ca	0.202	0.165	-0.122	0.525
x0.SEF77_SO4	-1.002	0.452	-1.888	-0.115
x0.SEF77_DOC	-1.221	0.458	-2.120	-0.323
x0.SEF77_TDP	-1.603	0.354	-2.297	-0.910
x0.SEF80_NO3	-1.444	0.451	-2.327	-0.560
x0.SEF80_NH4	0.059	0.418	-0.760	0.878
x0.SEF80_Ca	0.324	0.165	0.000	0.647
x0.SEF80_SO4	0.394	0.097	0.204	0.585
x0.SEF80_DOC	-0.160	0.458	-1.058	0.739
x0.SEF80_TDP	-1.035	0.367	-1.754	-0.316
C.SEF77_NO3	-0.211	0.123	-0.452	0.031
C.SEF77_NH4	-0.275	0.061	-0.394	-0.156
C.SEF77_Ca	0.032	0.024	-0.015	0.079
C.SEF77_SO4	0.114	0.090	-0.063	0.291
C.SEF77_DOC	-0.297	0.095	-0.483	-0.111
C.SEF77_TDP	-0.346	0.066	-0.476	-0.217
C.SEF80_NO3	-0.199	0.080	-0.356	-0.042
C.SEF80_NH4	0.009	0.061	-0.110	0.128
C.SEF80_Ca	0.052	0.024	0.005	0.099
C.SEF80_SO4	0.063	0.014	0.035	0.091
C.SEF80_DOC	-0.039	0.095	-0.225	0.147
C.SEF80_TDP	-0.252	0.076	-0.400	-0.103

Table F.20 Bootstrapping results of the best fitted no-stressor MARSS models at TLW; x0 is the initial estimations for the stream response; ML Est means modeling estimations; Std. Err means standard error; CI means confidence interval.

Matrix	**ML Est**	**Std. Err**	**Low. CI**	**Up. CI**
R.(NO3-1,NO3-1)	0.097	0.029	0.040	0.154
R.(NH4-1,NH4-1)	0.460	0.173	0.122	0.799
R.(Ca-1,Ca-1)	0.073	0.023	0.027	0.119
R.(SO4-1,SO4-1)	0.043	0.013	0.018	0.069
R.(DOC-1,DOC-1)	0.028	0.012	0.004	0.053
R.(TDP-1,TDP-1)	0.202	0.063	0.078	0.326
R.(NO3-2,NO3-2)	0.060	0.018	0.024	0.095
R.(NH4-2,NH4-2)	0.591	0.222	0.156	1.027
R.(Ca-2,Ca-2)	0.033	0.010	0.012	0.053
R.(SO4-2,SO4-2)	0.000	0.008	-0.016	0.016
R.(DOC-2,DOC-2)	0.024	0.011	0.003	0.045
R.(TDP-2,TDP-2)	0.142	0.044	0.054	0.229
R.(NO3-3,NO3-3)	0.212	0.130	-0.042	0.466
R.(NH4-3,NH4-3)	0.492	0.191	0.118	0.866
R.(Ca-3,Ca-3)	0.447	0.137	0.178	0.717
R.(SO4-3,SO4-3)	2.570	0.823	0.955	4.181
R.(DOC-3,DOC-3)	0.035	0.014	0.008	0.061
R.(TDP-3,TDP-3)	0.036	0.012	0.013	0.059
R.(NO3-4,NO3-4)	0.001	0.037	-0.072	0.073
R.(NH4-4,NH4-4)	0.548	0.204	0.148	0.948
R.(Ca-4,Ca-4)	0.402	0.123	0.160	0.644
R.(SO4-4,SO4-4)	0.788	0.253	0.292	1.283
R.(DOC-4,DOC-4)	0.808	0.254	0.311	1.306
R.(TDP-4,TDP-4)	1.040	0.316	0.418	1.657
R.(NO3-5,NO3-5)	0.001	0.045	-0.086	0.089
R.(NH4-5,NH4-5)	0.593	0.221	0.159	1.026
R.(Ca-5,Ca-5)	0.252	0.078	0.099	0.404
R.(SO4-5,SO4-5)	0.087	0.034	0.021	0.153
R.(DOC-5,DOC-5)	0.167	0.055	0.059	0.276
R.(TDP-5,TDP-5)	0.887	0.270	0.357	1.417
R.(NO3-6,NO3-6)	0.000	0.052	-0.103	0.103
R.(NH4-6,NH4-6)	0.616	0.231	0.164	1.069
R.(Ca-6,Ca-6)	0.078	0.025	0.029	0.126
R.(SO4-6,SO4-6)	0.055	0.025	0.006	0.104
R.(DOC-6,DOC-6)	0.247	0.082	0.086	0.408
R.(TDP-6,TDP-6)	1.010	0.307	0.407	1.612
Q.q_TLW_NH4	0.108	0.045	0.020	0.196
Q.q_TLW_Ca	0.001	0.001	-0.001	0.003
Q.q_TLW_DOC	0.012	0.005	0.002	0.021

Q.q_TLW_TDP	0.001	0.001	-0.001	0.003
Q.q_TLW_SO4	0.041	0.014	0.014	0.068
Q.q_TLW_NO3	0.275	0.080	0.119	0.432
x0.TLW32_NO3	0.000	0.066	-0.130	0.130
x0.TLW32_NH4	1.380	0.532	0.338	2.423
x0.TLW32_Ca	-0.002	0.095	-0.187	0.184
x0.TLW32_SO4	0.000	0.044	-0.087	0.087
x0.TLW32_DOC	0.188	0.158	-0.122	0.499
x0.TLW32_TDP	0.004	0.127	-0.245	0.253
x0.TLW35_NO3	0.000	0.052	-0.102	0.102
x0.TLW35_NH4	0.866	0.559	-0.229	1.960
x0.TLW35_Ca	0.108	0.078	-0.045	0.261
x0.TLW35_SO4	0.448	0.202	0.051	0.844
x0.TLW35_DOC	0.212	0.154	-0.089	0.514
x0.TLW35_TDP	0.027	0.115	-0.198	0.253
x0.TLW38_NO3	-0.501	0.645	-1.764	0.763
x0.TLW38_NH4	0.736	0.539	-0.320	1.792
x0.TLW38_Ca	-0.022	0.165	-0.346	0.302
x0.TLW38_SO4	-0.112	0.590	-1.269	1.044
x0.TLW38_DOC	-0.502	0.164	-0.824	-0.180
x0.TLW38_TDP	-0.116	0.081	-0.275	0.043
x0.TLW31_NO3	0.227	0.525	-0.802	1.257
x0.TLW31_NH4	1.350	0.550	0.274	2.431
x0.TLW31_Ca	0.003	0.159	-0.309	0.315
x0.TLW31_SO4	1.010	0.449	0.131	1.889
x0.TLW31_DOC	-0.048	0.325	-0.685	0.589
x0.TLW31_TDP	-0.002	0.234	-0.462	0.457
x0.TLW33_NO3	-0.318	0.526	-1.348	0.712
x0.TLW33_NH4	0.859	0.559	-0.236	1.954
x0.TLW33_Ca	-0.004	0.135	-0.269	0.261
x0.TLW33_SO4	1.510	0.289	0.948	2.080
x0.TLW33_DOC	-0.123	0.225	-0.565	0.318
x0.TLW33_TDP	0.017	0.219	-0.413	0.446
x0.TLW34_NO3	-0.254	0.525	-1.282	0.775
x0.TLW34_NH4	0.856	0.563	-0.248	1.960
x0.TLW34_Ca	-0.041	0.096	-0.230	0.148
x0.TLW34_SO4	1.470	0.269	0.948	2.001
x0.TLW34_DOC	0.040	0.246	-0.442	0.521
x0.TLW34_TDP	-0.007	0.231	-0.461	0.446

Appendix G AIC_c results of MARSS models

Table G.1 to **G.10** showed that the state space model had lower ΔAIC_c values and higher AIC_c weights than the identity model. Combination of *Q* and *R* matrix varied at each site.

Table G.1 The top MARSS model with different combination *Z, Q, R* matrix of at HJA; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	***Q***	***R***	**Stressor**	**ΔAIC_c**	**AIC_c weight**
2	2	1	No stressor	0.00	1.00
2	1	1	No stressor	79.59	0.00
2	1	2	No stressor	214.26	0.00
2	2	2	No stressor	228.46	0.00
1	2	1	NO_3-N deposition	248.12	0.00
1	2	2	No stressor	276.09	0.00
1	1	1	NO_3-N deposition	288.84	0.00
1	1	2	No stressor	320.15	0.00

Table G.2 The top MARSS model with different combination *Z, Q, R* matrix of at ELA; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	***Q***	***R***	**Stressor**	**ΔAIC_c**	**AIC_c weight**
2	--	1	Temperature	0.00	1.00
2	--	2	Temperature	36.88	0.00
1	2	1	Temperature	110.72	0.00
1	2	2	Temperature	111.07	0.00
1	1	1	Temperature	124.01	0.00
1	1	2	Temperature	127.98	0.00

Table G.3 The top MARSS model with different combination *Z, Q, R* matrix of at MEF; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	***Q***	***R***	**Stressor**	**ΔAIC_c**	**AIC_c weight**
2	2	2	Temperature	0.00	0.98
2	1	2	Temperature	7.98	0.02
2	1	1	Temperature	23.73	0.00
2	2	1	Temperature	25.40	0.00
1	2	2	Temperature	40.60	0.00
1	2	1	Temperature	71.65	0.00
1	1	2	Temperature	84.97	0.00
1	1	1	Temperature	113.75	0.00

Table G.4 The top MARSS model with different combination *Z, Q, R* matrix of at TLW; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	*Q*	*R*	Stressor	ΔAIC_c	AIC_c weight
2	1	1	Temperature	0.00	0.68
2	2	1	Temperature	1.52	0.32
1	2	1	No stressor	101.82	0.00
1	1	1	No stressor	114.62	0.00
1	1	2	Runoff	150.98	0.00
2	1	2	Runoff	243.22	0.00
2	2	2	Runoff	328.14	0.00
1	2	2	No stressor	417.51	0.00

Table G.5 The top MARSS model with different combination *Z, Q, R* matrix of at DOR; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	*Q*	*R*	Stressor	ΔAIC_c	AIC_c weight
2	--	1	Runoff	0.00	1.00
1	2	1	No stressor	65.48	0.00
1	1	1	No stressor	79.95	0.00
1	1	2	SO_4-S deposition	159.47	0.00
2	--	2	No stressor	164.24	0.00
1	2	2	NO_3-N deposition	195.63	0.00

Table G.6 The top MARSS model with different combination *Z, Q, R* matrix of at BBWM; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	*Q*	*R*	Stressor	ΔAIC_c	AIC_c weight
--	2	1	NH_4-N deposition	0.00	0.95
--	1	2	NH_4-N deposition	6.24	0.04
--	1	1	NH_4-N deposition	9.88	0.01
--	2	2	NH_4-N deposition	30.51	0.00

Table G.7 The top MARSS model with different combination *Z, Q, R* matrix of at HBEF; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	*Q*	*R*	Stressor	ΔAIC_c	AIC_c weight
2	1	2	No stressor	0.00	1.00
2	1	1	Water year	11.53	0.00
2	2	1	Runoff	14.68	0.00
1	1	1	Water year	38.29	0.00
2	2	2	No stressor	103.22	0.00
1	2	1	Water year	137.51	0.00
1	1	2	Water year	183.40	0.00
1	2	2	Water year	484.06	0.00

Table G.8 The top MARSS model with different combination *Z, Q, R* matrix of at CWT; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	***Q***	***R***	**Stressor**	**ΔAIC_c**	**AIC_c weight**
2	1	2	No stressor	0.00	0.64
2	2	1	No stressor	1.14	0.36
2	1	1	No stressor	18.94	0.00
2	2	2	Temperature	23.78	0.00
1	2	1	Runoff	34.37	0.00
1	1	2	Runoff	44.78	0.00
1	2	2	Runoff	50.70	0.00
1	1	1	No stressor	71.45	0.00

Table G.9 The top MARSS model with different combination *Z, Q, R* matrix of at SEF; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	***Q***	***R***	**Stressor**	**ΔAIC_c**	**AIC_c weight**
--	1	2	Water year	0.00	1.00
--	1	1	Water year	19.39	0.00
--	2	2	NO_3-N deposition	25.59	0.00
--	2	1	NO_3-N deposition	42.71	0.00

Table G.10 The top MARSS model with different combination *Z, Q, R* matrix of at LEF; AIC_c weights were calculated on ΔAIC_c which have a range from 0 to 1; The best model is the one that has an AIC_c weight of 1; "--" means the matrix is not applicable.

Z	***Q***	***R***	**Stressor**	**ΔAIC_c**	**AIC_c weight**
2	1	1	No stressor	0.00	0.85
2	1	2	No stressor	8.39	0.20
2	2	1	NO_3-N deposition	64.52	0.00
2	2	2	No stressor	101.79	0.00
1	2	1	SO_4-S deposition	477.59	0.00
1	1	1	SO_4-S deposition	477.59	0.00
1	2	2	No stressor	541.30	0.00
1	1	2	No stressor	541.30	0.00

Appendix H Process errors from MARSS models for early warning signal detections

Table H.1 to **H.41** contain the process errors (i.e., the response residuals) from the best fitted MARSS models in 41 catchments from 1989 to 2009. The response residuals in 2010 cannot be modeled due the algorithm of the models.

Table H.1 Process errors from the stressor (NH_4-N deposition) models in BBWM01.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	-8.23E-02	0.00E+00	0.00E+00	0.00E+00	-2.78E-17	0.00E+00
1990	-1.13E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1991	-2.66E-01	-6.94E-18	1.73E-18	0.00E+00	-6.94E-18	-2.78E-17
1992	-2.37E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1993	-1.89E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1994	-7.55E-02	0.00E+00	4.34E-19	1.04E-17	-1.04E-17	1.39E-17
1995	-1.19E-01	1.39E-17	0.00E+00	6.94E-18	0.00E+00	-1.39E-17
1996	3.79E-03	0.00E+00	-3.47E-18	0.00E+00	0.00E+00	0.00E+00
1997	-6.49E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1998	7.91E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1999	-9.12E-02	0.00E+00	0.00E+00	1.39E-17	0.00E+00	0.00E+00
2000	-1.10E-01	5.55E-17	-6.94E-18	5.55E-17	5.55E-17	-1.11E-16
2001	5.71E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2002	-8.80E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2003	-1.52E-01	0.00E+00	0.00E+00	0.00E+00	-2.78E-17	0.00E+00
2004	1.22E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2005	7.71E-02	5.55E-17	6.94E-18	5.55E-17	0.00E+00	0.00E+00
2006	-5.62E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2007	-2.47E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2008	-3.25E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2009	-1.76E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Table H.2 Process errors from the stressor (NH_4-N deposition) models in BBWM02.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	-2.50E-02	-1.39E-17	0.00E+00	5.81E-01	0.00E+00	-1.11E-16
1990	4.49E-01	0.00E+00	0.00E+00	6.29E-01	0.00E+00	0.00E+00
1991	-5.29E-04	-1.73E-18	1.73E-18	6.28E-01	-1.04E-17	6.94E-18
1992	4.87E-02	0.00E+00	0.00E+00	5.02E-01	0.00E+00	0.00E+00
1993	-9.85E-02	0.00E+00	0.00E+00	5.84E-01	0.00E+00	0.00E+00
1994	2.12E-01	1.73E-18	4.34E-19	1.84E-01	-1.04E-17	6.94E-18
1995	-2.45E-01	-3.47E-18	0.00E+00	6.73E-02	-1.39E-17	0.00E+00
1996	-3.89E-02	6.94E-18	-3.47E-18	-2.34E-01	-1.39E-17	0.00E+00

1997	5.13E-02	0.00E+00	0.00E+00	7.50E-02	0.00E+00	0.00E+00
1998	3.68E-01	0.00E+00	0.00E+00	1.18E-02	0.00E+00	0.00E+00
1999	-2.60E-01	3.47E-18	0.00E+00	-1.31E-02	0.00E+00	0.00E+00
2000	-1.90E-01	0.00E+00	-6.94E-18	1.44E-01	5.55E-17	-1.11E-16
2001	7.98E-02	0.00E+00	0.00E+00	2.70E-01	0.00E+00	0.00E+00
2002	-4.21E-01	0.00E+00	0.00E+00	-4.15E-01	0.00E+00	0.00E+00
2003	-1.63E-01	0.00E+00	0.00E+00	-5.72E-01	0.00E+00	0.00E+00
2004	4.09E-01	0.00E+00	0.00E+00	-5.11E-01	0.00E+00	0.00E+00
2005	2.54E-01	0.00E+00	6.94E-18	-5.61E-01	5.55E-17	-1.11E-16
2006	3.79E-02	0.00E+00	0.00E+00	6.58E-01	0.00E+00	0.00E+00
2007	-1.75E-01	0.00E+00	0.00E+00	2.30E-01	0.00E+00	0.00E+00
2008	-1.87E-01	0.00E+00	0.00E+00	-1.23E-01	0.00E+00	0.00E+00
2009	1.43E-02	0.00E+00	0.00E+00	-7.07E-02	-5.55E-17	0.00E+00

Table H.3 Process errors from the stressor (runoff) models in CWT02.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
2002	2.00E+03	-1.56E-01	3.73E-01	1.73E-18	-5.81E-05	-5.00E-07
2003	2.00E+03	-5.33E-01	5.94E-02	0.00E+00	-4.88E-05	-5.00E-07
2004	2.00E+03	3.85E-02	2.82E-01	0.00E+00	-5.42E-05	-5.00E-07
2005	2.01E+03	4.36E-02	2.18E-01	2.78E-17	-1.68E-05	-5.00E-07
2006	2.01E+03	-2.83E-01	3.57E-01	0.00E+00	-3.74E-05	5.33E-05
2007	2.01E+03	-4.19E-01	-2.89E-01	0.00E+00	-2.12E-05	4.62E-05
2008	2.01E+03	-3.05E-01	-3.34E-02	2.78E-17	-3.12E-05	4.16E-05
2009	2.01E+03	-2.64E-02	8.32E-04	0.00E+00	-6.19E-06	4.07E-05
2010	2.01E+03	-9.67E-02	4.39E-01	0.00E+00	-8.25E-06	8.09E-05
2011	2.01E+03	7.45E-02	-1.29E-02	-1.39E-17	-1.31E-06	5.23E-05
2012	2.01E+03	-4.07E-01	-5.98E-02	0.00E+00	-3.69E-06	5.78E-05
2013	2.01E+03	-2.61E-01	6.34E-02	0.00E+00	-1.65E-05	-1.19E-06
2014	2.01E+03	-1.34E-01	2.51E-01	0.00E+00	1.72E-06	-3.22E-06
2015	2.02E+03	-1.42E-01	3.12E-01	0.00E+00	-7.19E-06	2.61E-05
2016	2.02E+03	-6.16E-02	4.90E-01	0.00E+00	-2.04E-05	-7.74E-06

Table H.4 Process errors from the stressor (runoff) models in CWT18.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
2002	2.00E+03	-3.01E-01	2.13E-01	0.00E+00	-3.69E-05	-3.16E-07
2003	2.00E+03	-4.03E-01	2.87E-01	0.00E+00	-3.71E-05	-3.16E-07
2004	2.00E+03	2.21E-01	5.19E-01	0.00E+00	-4.35E-05	-3.16E-07
2005	2.01E+03	4.07E-02	2.36E-01	-2.78E-17	-3.20E-05	-3.16E-07
2006	2.01E+03	-2.84E-01	3.45E-01	0.00E+00	-4.36E-05	4.98E-05
2007	2.01E+03	-4.92E-01	6.05E-02	0.00E+00	-2.40E-05	4.75E-05
2008	2.01E+03	-2.54E-01	3.63E-01	0.00E+00	-2.86E-05	5.06E-05
2009	2.01E+03	1.75E-01	1.31E-01	0.00E+00	-2.01E-05	5.68E-05

2010	2.01E+03	2.13E-01	3.21E-01	0.00E+00	-2.32E-05	7.41E-05
2011	2.01E+03	-1.08E-02	1.03E-01	0.00E+00	-3.57E-05	5.54E-05
2012	2.01E+03	-7.00E-01	-1.80E-01	0.00E+00	-3.25E-06	4.10E-05
2013	2.01E+03	-3.32E-01	-2.83E-02	0.00E+00	-7.60E-06	2.26E-05
2014	2.01E+03	8.08E-02	1.62E-01	0.00E+00	1.28E-05	3.45E-05
2015	2.02E+03	9.99E-02	3.74E-01	-5.55E-17	-3.49E-06	5.46E-05
2016	2.02E+03	3.04E-01	2.69E-01	0.00E+00	-9.97E-06	3.70E-05

Table H.5 Process errors from the stressor (runoff) models in CWT07.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
2002	2.00E+03	-3.03E-01	-2.11E-01	-2.60E-18	-2.25E-05	-7.93E-08
2003	2.00E+03	-5.84E-01	2.95E-01	0.00E+00	-1.31E-05	-7.93E-08
2004	2.00E+03	1.73E-01	1.27E-01	0.00E+00	4.71E-07	-7.93E-08
2005	2.01E+03	4.57E-02	-1.18E-02	1.39E-17	2.31E-05	-7.93E-08
2006	2.01E+03	-1.38E-01	-4.37E-01	0.00E+00	1.86E-05	4.77E-05
2007	2.01E+03	-5.17E-01	-5.70E-01	0.00E+00	1.36E-05	3.73E-05
2008	2.01E+03	-1.97E-01	7.92E-02	1.39E-17	-6.51E-07	4.04E-05
2009	2.01E+03	-1.31E-02	-1.93E-03	0.00E+00	1.25E-05	4.96E-05
2010	2.01E+03	-1.62E-01	-4.89E-01	0.00E+00	1.81E-05	7.12E-05
2011	2.01E+03	-2.22E-01	-4.26E-02	-6.94E-18	2.08E-05	4.23E-05
2012	2.01E+03	-1.37E-02	-4.57E-01	0.00E+00	8.19E-06	4.57E-05
2013	2.01E+03	-4.21E-01	-3.31E-01	0.00E+00	-6.43E-06	-2.40E-05
2014	2.01E+03	-1.32E-01	-6.24E-02	0.00E+00	1.16E-05	-1.05E-05
2015	2.02E+03	-3.38E-01	-4.79E-01	0.00E+00	1.15E-05	3.16E-05
2016	2.02E+03	-8.46E-02	5.37E-02	0.00E+00	2.99E-06	-3.45E-06

Table H.6 Process errors from the stressor (runoff) models in CWT17.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
2002	2.00E+03	-2.70E-01	5.26E-01	-6.94E-18	-2.76E-05	-5.19E-08
2003	2.00E+03	-6.93E-01	4.14E-01	-1.04E-17	-3.27E-05	-5.19E-08
2004	2.00E+03	3.61E-01	2.92E-01	0.00E+00	-2.51E-05	-5.19E-08
2005	2.01E+03	8.21E-02	3.00E-01	2.78E-17	-1.32E-05	-5.19E-08
2006	2.01E+03	-2.50E-01	3.10E-01	0.00E+00	-1.24E-05	5.41E-05
2007	2.01E+03	-6.71E-01	-6.13E-01	0.00E+00	-1.55E-05	5.85E-05
2008	2.01E+03	-4.23E-01	-1.39E-01	0.00E+00	-2.30E-05	7.50E-05
2009	2.01E+03	-8.55E-03	-7.24E-02	0.00E+00	-1.72E-05	8.86E-05
2010	2.01E+03	-1.15E-02	3.89E-01	0.00E+00	-1.34E-05	9.32E-05
2011	2.01E+03	1.26E-01	-1.29E-02	0.00E+00	-9.09E-06	8.20E-05
2012	2.01E+03	-3.89E-01	-6.24E-01	0.00E+00	5.64E-07	5.46E-05
2013	2.01E+03	-1.38E-01	-4.97E-02	0.00E+00	-5.57E-07	-5.42E-06
2014	2.01E+03	-1.09E-01	3.71E-01	0.00E+00	6.94E-06	1.86E-05
2015	2.02E+03	-7.86E-01	-8.28E-03	-2.78E-17	6.75E-06	4.63E-05
2016	2.02E+03	-6.19E-02	1.33E-01	0.00E+00	2.43E-06	2.04E-05

Table H.7 Process errors from the no-stressor models in DOR00.

Year	NO_3-N	NH_4-N	Ca	SO4$_4$-S	DOC	TDP
1989	-9.53E-02	-2.17E-02	-1.96E-15	3.55E-02	1.73E-02	0.00E+00
1990	-1.87E-01	-2.84E-02	-1.96E-15	2.65E-02	2.46E-02	0.00E+00
1991	-2.10E-01	-5.69E-01	-1.96E-15	-4.23E-01	4.24E-02	0.00E+00
1992	-2.34E-01	1.47E-01	-1.96E-15	-3.15E-01	3.88E-02	0.00E+00
1993	3.21E-01	-3.84E-01	-1.96E-15	-5.48E-01	2.49E-02	0.00E+00
1994	-2.23E-01	-3.93E-01	-1.96E-15	1.10E+00	1.89E-02	0.00E+00
1995	-1.30E-02	3.10E-01	-2.96E-02	6.66E-01	2.09E-02	0.00E+00
1996	2.55E-02	2.52E-01	-1.68E-02	5.26E-02	-4.21E-02	0.00E+00
1997	3.38E-02	2.12E-01	2.42E-02	3.26E-02	-5.93E-02	0.00E+00
1998	4.42E-02	1.83E-01	2.75E-02	-1.22E-01	6.45E-04	0.00E+00
1999	9.66E-02	1.61E-01	6.15E-03	1.34E-01	4.06E-02	0.00E+00
2000	3.82E-01	5.26E-01	-1.21E-03	-2.69E-01	4.45E-02	0.00E+00
2001	-5.40E-01	-4.52E-01	-9.90E-03	1.96E-01	6.94E-03	0.00E+00
2002	-8.45E-01	-6.87E-01	-3.92E-03	-1.65E-01	1.45E-03	0.00E+00
2003	-1.61E-01	-1.41E-01	-1.46E-02	7.14E-02	3.76E-02	0.00E+00
2004	-3.53E-02	-1.58E-01	-2.54E-02	9.89E-02	1.24E-02	0.00E+00
2005	-1.07E-02	4.70E-02	-3.13E-02	-1.61E-01	1.47E-02	0.00E+00
2006	2.78E-02	0.00E+00	-4.16E-02	6.36E-02	1.58E-02	0.00E+00
2007	3.63E-02	0.00E+00	-3.90E-02	7.57E-02	2.14E-02	0.00E+00
2008	4.76E-02	0.00E+00	-4.45E-02	-7.01E-02	2.29E-02	0.00E+00
2009	3.34E-01	3.33E-01	-2.25E-02	5.38E-02	-1.63E-02	0.00E+00

Table H.8 Process errors from the no-stressor models in DOR03.

Year	NO_3-N	NH_4-N	Ca	SO4$_4$-S	DOC	TDP
1989	4.50E-02	3.56E-02	2.08E-02	9.41E-01	0.00E+00	-5.85E-06
1990	-2.87E-02	4.41E-02	-3.61E-02	-7.28E-02	-8.67E-19	-5.82E-05
1991	-8.30E-02	3.28E-02	-8.22E-02	-1.13E+00	0.00E+00	-9.76E-05
1992	-5.54E-02	1.93E-02	-6.67E-02	-7.91E-01	0.00E+00	-9.41E-05
1993	-4.18E-03	1.84E-02	-4.70E-02	-4.58E-01	0.00E+00	-9.37E-05
1994	3.27E-02	1.68E-04	-7.20E-02	7.80E-01	0.00E+00	-1.29E-04
1995	1.39E-01	2.09E-02	-2.25E-02	8.22E-01	3.47E-18	-8.73E-05
1996	7.73E-02	1.63E-02	-3.49E-02	-1.62E-01	-3.47E-18	-1.10E-04
1997	-8.09E-02	-1.72E-03	-3.76E-02	3.77E-01	0.00E+00	-1.40E-04
1998	-2.92E-02	1.85E-02	-6.62E-02	-5.76E-01	0.00E+00	-1.36E-04
1999	-2.92E-02	2.30E-02	-9.79E-02	-1.38E+00	0.00E+00	-1.20E-04
2000	2.59E-02	1.16E-02	-7.77E-02	-3.94E-01	0.00E+00	-8.63E-05
2001	7.01E-02	1.02E-02	-3.23E-02	1.93E-01	0.00E+00	-7.98E-05
2002	-6.92E-03	6.78E-03	9.40E-03	6.20E-01	0.00E+00	-7.50E-05
2003	-2.82E-02	3.66E-03	-2.11E-02	-2.26E-01	0.00E+00	-7.28E-05

2004	-8.86E-03	2.52E-02	-3.63E-02	-3.02E-01	0.00E+00	-2.75E-05
2005	1.21E-01	4.64E-02	4.33E-03	-9.24E-02	0.00E+00	-7.81E-07
2006	-7.72E-02	1.75E-02	-2.32E-02	5.72E-01	0.00E+00	-5.75E-05
2007	-1.50E-01	2.06E-02	-8.65E-02	-6.50E-01	-1.73E-18	-7.78E-05
2008	-6.71E-02	1.43E-03	-6.15E-02	-1.84E-01	0.00E+00	-5.03E-05
2009	4.13E-03	5.32E-03	-4.19E-02	-7.57E-01	0.00E+00	-2.90E-05

Table H.9 Process errors from the no-stressor models in DOR05.

Year	NO_3-N	NH_4-N	Ca	$SO4_4$-S	DOC	TDP
1989	2.78E-17	-1.12E-05	3.36E-15	1.71E-01	-3.21E-03	0.00E+00
1990	2.78E-17	-1.12E-05	3.36E-15	2.07E-01	1.53E-03	0.00E+00
1991	2.78E-17	-1.12E-05	3.36E-15	9.04E-02	-2.41E-03	0.00E+00
1992	2.78E-17	-1.12E-05	3.36E-15	1.24E-01	-9.39E-03	0.00E+00
1993	2.78E-17	-1.12E-05	3.36E-15	1.92E-01	-1.09E-02	0.00E+00
1994	2.78E-17	-1.12E-05	3.36E-15	-1.46E-02	-8.63E-03	0.00E+00
1995	2.78E-17	-1.12E-05	3.36E-15	-5.24E-02	-1.15E-02	0.00E+00
1996	2.78E-17	-1.12E-05	3.36E-15	-1.08E-01	-3.70E-04	0.00E+00
1997	2.78E-17	-1.12E-05	3.36E-15	6.32E-03	-3.44E-03	0.00E+00
1998	2.78E-17	-1.12E-05	3.36E-15	-7.22E-02	-9.37E-03	0.00E+00
1999	2.78E-17	-1.12E-05	3.36E-15	-1.58E-01	-2.58E-03	0.00E+00
2000	2.78E-17	-1.12E-05	3.36E-15	-1.98E-01	6.33E-03	0.00E+00
2001	2.78E-17	-1.12E-05	3.36E-15	-6.44E-02	-1.46E-04	0.00E+00
2002	2.78E-17	-1.12E-05	3.36E-15	-1.12E-01	1.01E-02	0.00E+00
2003	2.78E-17	-1.12E-05	3.36E-15	-1.01E-01	1.11E-02	0.00E+00
2004	2.78E-17	-1.12E-05	3.36E-15	-2.09E-02	1.10E-02	0.00E+00
2005	1.17E-01	1.92E-01	1.63E-03	-4.23E-02	1.72E-02	0.00E+00
2006	2.28E-01	1.40E-01	3.76E-03	1.83E-01	1.22E-02	0.00E+00
2007	4.31E-03	9.73E-02	5.66E-03	2.35E-01	1.78E-02	0.00E+00
2008	-1.27E-02	-1.21E-02	2.91E-03	7.94E-02	1.36E-02	0.00E+00
2009	-1.01E-01	-1.05E-01	9.83E-04	-3.81E-02	8.59E-03	0.00E+00

Table H.10 Process errors from the no-stressor models in DOR06.

Year	NO_3-N	NH_4-N	Ca	$SO4_4$-S	DOC	TDP
1989	0.00E+00	1.06E-05	4.90E-16	1.67E-01	-1.12E-02	0.00E+00
1990	0.00E+00	1.06E-05	4.90E-16	2.32E-02	-7.47E-03	0.00E+00
1991	-5.55E-17	1.06E-05	4.90E-16	-1.20E-02	5.24E-03	0.00E+00
1992	-5.55E-17	1.06E-05	4.90E-16	-1.26E-01	1.68E-02	0.00E+00
1993	0.00E+00	1.06E-05	4.90E-16	-1.39E-01	2.44E-02	0.00E+00
1994	-5.55E-17	1.06E-05	4.90E-16	-1.89E-01	2.87E-02	0.00E+00
1995	0.00E+00	1.06E-05	4.90E-16	-1.90E-01	3.94E-02	0.00E+00
1996	-5.55E-17	1.06E-05	4.90E-16	-1.78E-01	4.11E-02	0.00E+00
1997	0.00E+00	1.06E-05	4.90E-16	-1.39E-01	3.83E-02	0.00E+00

1998	1.03E-01	7.72E-02	2.65E-03	-6.96E-02	3.79E-02	0.00E+00
1999	1.17E-01	-1.51E-02	4.97E-03	4.89E-02	2.72E-02	0.00E+00
2000	1.04E-01	-1.88E-01	6.29E-03	2.25E-01	1.76E-02	0.00E+00
2001	-5.29E-02	-3.39E-01	3.82E-03	1.44E-01	8.56E-03	0.00E+00
2002	-1.76E-01	-1.71E-01	-6.06E-04	-3.17E-02	3.17E-02	0.00E+00
2003	-3.05E-01	-9.73E-02	-6.46E-03	-1.74E-01	4.03E-02	0.00E+00
2004	-3.30E-01	-3.01E-02	-5.26E-03	-1.11E-01	3.43E-02	0.00E+00
2005	-1.82E-01	-6.85E-02	-3.09E-03	6.10E-02	2.42E-02	0.00E+00
2006	-1.27E-01	-1.66E-01	-4.33E-03	2.33E-02	1.58E-02	0.00E+00
2007	-1.60E-01	-1.49E-01	-3.59E-03	-8.41E-03	1.29E-02	0.00E+00
2008	-2.32E-01	-1.26E-01	-2.69E-03	6.22E-03	1.33E-02	0.00E+00
2009	-1.47E-01	-3.24E-02	-3.59E-03	-8.34E-02	1.44E-02	0.00E+00

Table H.11 Process errors from the stressor (temperature) models in ELA01.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	-9.57E-02	-2.13E-02	1.89E-02	2.83E-02	0.00E+00	-2.61E-05
1990	-9.36E-02	-1.93E-02	-4.51E-02	3.61E-01	-3.47E-18	-5.07E-05
1991	-2.29E-01	-3.91E-02	-1.35E-01	-5.51E-01	0.00E+00	-5.38E-05
1992	-1.76E-01	-3.86E-02	-2.29E-02	-7.03E-01	0.00E+00	-1.45E-05
1993	-1.46E-01	-5.04E-02	1.89E-03	-4.66E-02	0.00E+00	-1.75E-05
1994	4.24E-03	-1.26E-02	-2.98E-02	1.04E-01	0.00E+00	2.98E-05
1995	8.22E-03	-1.51E-02	3.94E-02	7.31E-01	-6.94E-18	3.82E-05
1996	3.21E-02	-3.55E-02	5.28E-02	-5.62E-01	-6.94E-18	2.59E-05
1997	-4.98E-02	-5.73E-02	-2.68E-02	6.95E-01	0.00E+00	-1.16E-05
1998	-1.49E-01	-5.14E-02	1.53E-02	-8.84E-01	0.00E+00	-4.81E-05
1999	-5.64E-02	-4.66E-02	-4.19E-02	-7.53E-01	0.00E+00	-9.35E-05
2000	-1.54E-02	-6.30E-02	-1.09E-02	-4.75E-01	0.00E+00	-9.51E-05
2001	-3.93E-02	-7.38E-02	-3.24E-02	4.19E-01	0.00E+00	-1.18E-04
2002	-6.73E-02	-7.52E-02	-1.05E-02	6.88E-01	0.00E+00	-1.21E-04
2003	-1.61E-01	-7.45E-02	-7.92E-02	-1.31E-01	0.00E+00	-1.06E-04
2004	-9.51E-02	-4.39E-02	-9.74E-02	-6.48E-01	0.00E+00	-5.26E-05
2005	-8.02E-02	-1.38E-02	-2.26E-02	-1.63E-02	0.00E+00	8.37E-06
2006	-2.09E-01	-2.00E-02	6.31E-02	6.20E-01	3.47E-18	-1.45E-05
2007	6.71E-02	-1.58E-02	4.26E-02	-5.75E-01	-3.47E-18	-3.85E-05
2008	7.24E-02	2.32E-03	4.80E-02	1.07E-01	0.00E+00	-2.73E-05
2009	1.57E-02	8.44E-03	1.09E-01	-8.73E-01	0.00E+00	1.97E-05

Table H.12 Process errors from the stressor (temperature) models in ELA02.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	4.50E-02	3.56E-02	2.08E-02	9.41E-01	0.00E+00	-5.85E-06
1990	-2.87E-02	4.41E-02	-3.61E-02	-7.28E-02	-8.67E-19	-5.82E-05
1991	-8.30E-02	3.28E-02	-8.22E-02	-1.13E+00	0.00E+00	-9.76E-05

1992	-5.54E-02	1.93E-02	-6.67E-02	-7.91E-01	0.00E+00	-9.41E-05
1993	-4.18E-03	1.84E-02	-4.70E-02	-4.58E-01	0.00E+00	-9.37E-05
1994	3.27E-02	1.68E-04	-7.20E-02	7.80E-01	0.00E+00	-1.29E-04
1995	1.39E-01	2.09E-02	-2.25E-02	8.22E-01	3.47E-18	-8.73E-05
1996	7.73E-02	1.63E-02	-3.49E-02	-1.62E-01	-3.47E-18	-1.10E-04
1997	-8.09E-02	-1.72E-03	-3.76E-02	3.77E-01	0.00E+00	-1.40E-04
1998	-2.92E-02	1.85E-02	-6.62E-02	-5.76E-01	0.00E+00	-1.36E-04
1999	-2.92E-02	2.30E-02	-9.79E-02	-1.38E+00	0.00E+00	-1.20E-04
2000	2.59E-02	1.16E-02	-7.77E-02	-3.94E-01	0.00E+00	-8.63E-05
2001	7.01E-02	1.02E-02	-3.23E-02	1.93E-01	0.00E+00	-7.98E-05
2002	-6.92E-03	6.78E-03	9.40E-03	6.20E-01	0.00E+00	-7.50E-05
2003	-2.82E-02	3.66E-03	-2.11E-02	-2.26E-01	0.00E+00	-7.28E-05
2004	-8.86E-03	2.52E-02	-3.63E-02	-3.02E-01	0.00E+00	-2.75E-05
2005	1.21E-01	4.64E-02	4.33E-03	-9.24E-02	0.00E+00	-7.81E-07
2006	-7.72E-02	1.75E-02	-2.32E-02	5.72E-01	0.00E+00	-5.75E-05
2007	-1.50E-01	2.06E-02	-8.65E-02	-6.50E-01	-1.73E-18	-7.78E-05
2008	-6.71E-02	1.43E-03	-6.15E-02	-1.84E-01	0.00E+00	-5.03E-05
2009	4.13E-03	5.32E-03	-4.19E-02	-7.57E-01	0.00E+00	-2.90E-05

Table H.13 Process errors from the stressor (temperature) models in ELA03.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	-4.59E-02	1.94E-02	-1.47E-02	1.28E-01	0.00E+00	-2.26E-05
1990	-1.18E-01	-9.57E-03	-5.60E-02	-1.89E-01	0.00E+00	-4.59E-05
1991	-1.17E-01	-1.81E-02	-7.69E-02	-3.06E-01	0.00E+00	-5.74E-05
1992	-4.55E-02	-1.86E-02	-6.49E-02	-3.36E-01	0.00E+00	-4.99E-05
1993	-8.62E-02	-1.80E-02	-5.64E-02	-2.79E-01	0.00E+00	-5.65E-05
1994	-7.96E-02	-4.46E-03	-4.54E-02	2.16E-01	0.00E+00	-8.02E-05
1995	-1.80E-02	-5.50E-03	-2.11E-02	1.66E-01	0.00E+00	-5.68E-05
1996	-8.26E-02	-1.11E-02	-3.70E-02	9.64E-04	6.94E-18	-6.71E-05
1997	-8.71E-02	-2.17E-02	-4.11E-02	1.45E-01	0.00E+00	-7.39E-05
1998	-2.30E-01	-1.33E-02	-7.43E-02	-6.76E-01	0.00E+00	-6.86E-05
1999	-9.66E-02	-1.33E-02	-8.39E-02	-6.03E-01	0.00E+00	-9.10E-05
2000	-6.86E-02	-2.90E-02	-6.59E-02	-3.66E-01	0.00E+00	-6.95E-05
2001	-4.71E-02	-2.97E-02	-4.13E-02	1.32E-01	0.00E+00	-5.01E-05
2002	-2.95E-02	-2.53E-02	-1.83E-02	2.87E-01	0.00E+00	-3.26E-05
2003	-2.26E-01	-3.34E-02	-1.33E-02	2.46E-02	0.00E+00	-1.45E-05
2004	-1.61E-01	-1.90E-02	-2.13E-02	-3.13E-02	0.00E+00	2.47E-06
2005	4.14E-03	-4.82E-03	-4.75E-03	1.56E-01	0.00E+00	-7.35E-06
2006	-7.28E-02	4.62E-03	-9.25E-03	1.29E-01	-1.73E-18	-3.88E-05
2007	-1.21E-01	5.36E-03	-3.16E-02	-2.07E-01	-3.47E-18	-7.43E-05
2008	-8.42E-02	-9.64E-03	-1.83E-02	-1.39E-01	0.00E+00	-5.46E-05
2009	-5.12E-02	1.20E-04	-1.21E-02	-2.93E-01	-6.94E-18	-3.33E-05

Table H.14 Process errors from the stressor (temperature) models in HBEF01.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	8.91E-01	1.10E-01	-3.60E-01	-4.24E-01	-1.88E-06	-1.80E-01
1990	-2.17E-01	2.02E-01	3.85E-01	-3.16E-01	-1.88E-06	3.87E-01
1991	-1.33E+00	9.66E-02	-4.16E-02	1.30E-02	-1.88E-06	-5.84E-01
1992	-1.43E+00	2.50E-01	-8.57E-01	-2.64E-01	-1.88E-06	-8.30E-01
1993	-5.25E-01	1.82E-01	-8.22E-02	-3.18E-02	-1.88E-06	-8.99E-01
1994	1.32E+00	1.75E-01	2.32E-01	-2.83E-01	-1.88E-06	2.10E-02
1995	6.42E-03	-1.62E-02	-2.37E-01	-4.18E-01	-1.88E-06	1.50E-01
1996	-6.44E-01	8.26E-02	-6.67E-01	-6.65E-01	-1.88E-06	-2.33E-01
1997	3.06E-01	-1.68E-01	4.11E-02	-1.37E-01	-1.88E-06	5.05E-01
1998	2.48E+00	2.59E-01	9.89E-01	-4.27E-01	-1.88E-06	1.44E-01
1999	-4.45E-01	1.69E-01	2.88E+00	9.58E-01	-1.88E-06	1.50E+00
2000	-1.00E+00	1.36E-01	-9.19E-02	5.77E-01	-1.88E-06	-8.14E-01
2001	-9.81E-01	1.06E-01	-1.18E+00	-5.21E-01	-1.88E-06	-2.65E-01
2002	3.44E-01	1.25E-01	-7.67E-01	2.57E-01	-1.88E-06	-4.27E-02
2003	-3.06E-03	1.21E-01	2.34E-01	-2.78E-01	-1.88E-06	-7.15E-01
2004	-5.70E-01	1.26E-01	-4.11E-01	-2.05E-01	-1.88E-06	-6.56E-02
2005	-1.04E-01	1.21E-01	-1.71E-01	-2.01E-01	-1.88E-06	-7.37E-01
2006	1.68E+00	1.28E-01	-5.74E-02	-3.13E-01	-5.46E-05	-6.96E-02
2007	-6.58E-01	1.27E-01	-2.09E-01	1.51E-01	-1.81E-05	-6.59E-02
2008	-1.25E-01	1.13E-01	-3.48E-01	-5.69E-01	2.42E-05	-7.35E-02
2009	-8.08E-01	7.59E-02	4.56E-01	-3.90E-01	1.82E-05	-7.97E-02

Table H.15 Process errors from the stressor (temperature) models in HBEF06.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	5.48E-01	2.80E-02	-2.27E-01	-6.96E-01	3.57E-07	2.99E-02
1990	-6.74E-01	2.53E-02	-4.08E-01	-2.22E-01	3.57E-07	6.27E-01
1991	-1.27E+00	2.16E-02	5.18E-03	9.78E-02	3.57E-07	-6.89E-01
1992	-1.02E+00	3.34E-02	-2.56E-01	-2.71E-01	3.57E-07	-8.89E-01
1993	-7.32E-01	-1.43E-01	8.72E-02	9.26E-02	2.25E-06	-2.78E-01
1994	7.25E-01	-9.42E-02	4.63E-02	-1.41E-01	5.03E-06	-1.95E-01
1995	-5.37E-02	-7.78E-02	-7.01E-01	-5.39E-01	6.79E-06	2.81E-01
1996	-3.87E-01	-4.37E-02	-3.91E-01	-4.76E-01	8.18E-06	-5.08E-01
1997	2.95E-01	4.29E-02	3.32E-01	1.37E-01	8.60E-06	5.21E-01
1998	2.30E+00	-1.27E-01	4.37E-01	-7.30E-01	1.03E-05	2.32E-01
1999	-7.62E-01	-4.66E-02	-4.67E-01	2.43E-01	6.80E-06	5.22E-01
2000	-9.65E-01	1.81E-02	-9.09E-02	2.57E-01	4.32E-06	-5.27E-01
2001	-1.12E+00	-4.75E-02	5.63E-02	7.02E-02	5.68E-06	-1.20E-01
2002	-2.43E-01	-2.27E-02	-2.42E-01	1.34E-01	2.51E-06	-5.60E-01
2003	8.22E-01	-9.35E-03	-4.62E-01	-6.66E-01	6.11E-06	-1.01E-01

2004	-3.62E-01	-1.10E-02	5.66E-02	1.13E-01	-9.55E-07	-1.77E-02
2005	-1.36E-01	-9.58E-03	-3.28E-01	-3.77E-01	-2.43E-06	-4.29E-01
2006	9.89E-01	-1.00E-02	-1.06E-01	-1.65E-02	-1.70E-07	-2.35E-02
2007	-1.01E+00	-1.08E-02	2.15E-01	5.62E-02	1.75E-06	-2.55E-02
2008	-4.44E-01	-1.11E-02	-4.14E-01	-5.53E-01	4.46E-06	-2.85E-02
2009	-6.65E-01	-9.23E-03	-1.32E-01	-4.11E-01	2.24E-06	-3.14E-02

Table H.16 Process errors from the stressor (temperature) models in HBEF07.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	8.47E-07	0.00E+00	5.55E-17	-1.67E-16	-6.94E-18	4.63E-07
1990	8.47E-07	0.00E+00	0.00E+00	-1.67E-16	0.00E+00	4.63E-07
1991	8.47E-07	-6.94E-18	0.00E+00	-2.22E-16	0.00E+00	4.63E-07
1992	8.47E-07	-6.94E-18	0.00E+00	-1.11E-16	0.00E+00	4.63E-07
1993	8.47E-07	-2.08E-17	0.00E+00	-1.67E-16	0.00E+00	4.63E-07
1994	8.47E-07	-1.04E-17	1.39E-17	-2.50E-16	0.00E+00	4.63E-07
1995	8.47E-07	1.04E-17	0.00E+00	-1.94E-16	0.00E+00	4.63E-07
1996	-7.41E-01	-1.29E-02	-1.39E-17	-3.99E-01	3.47E-18	-4.91E-01
1997	3.46E-01	-8.78E-03	-1.39E-17	-1.74E-01	8.67E-19	1.42E-01
1998	5.86E-01	-2.24E-02	-2.26E-17	-1.56E-01	-1.95E-18	6.61E-01
1999	3.01E-01	-1.97E-02	2.26E-17	2.87E-02	1.95E-18	6.51E-01
2000	-6.60E-01	-1.07E-02	1.39E-17	1.35E-01	-8.67E-19	-9.45E-01
2001	-5.78E-01	-3.12E-02	1.39E-17	1.13E-01	-3.47E-18	-3.05E-01
2002	7.78E-01	-1.67E-02	0.00E+00	9.34E-02	0.00E+00	1.19E-01
2003	1.52E-01	-4.82E-03	0.00E+00	-2.86E-01	0.00E+00	-1.14E+00
2004	5.80E-01	3.28E-03	0.00E+00	-6.55E-02	0.00E+00	-4.40E-01
2005	3.15E-01	7.88E-03	-2.78E-17	-2.04E-01	0.00E+00	-9.64E-01
2006	6.57E-01	8.87E-03	0.00E+00	8.02E-02	0.00E+00	-3.99E-01
2007	-7.73E-01	5.68E-03	0.00E+00	1.62E-01	0.00E+00	-2.73E-01
2008	-4.92E-01	-2.84E-03	5.55E-17	-3.95E-02	6.94E-18	2.12E+00
2009	-1.02E-01	-2.81E-03	2.78E-17	-7.54E-02	-6.94E-18	-2.67E-02

Table H.17 Process errors from the stressor (temperature) models in HBEF08.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	-3.33E-16	-1.39E-17	-7.47E-07	5.55E-17	-1.73E-18	1.78E-07
1990	0.00E+00	-1.39E-17	-7.47E-07	8.33E-17	8.67E-19	1.78E-07
1991	-1.11E-16	-1.39E-17	-7.47E-07	1.11E-16	0.00E+00	1.78E-07
1992	-8.33E-17	-1.73E-17	-7.47E-07	6.94E-17	0.00E+00	1.78E-07
1993	-1.11E-16	-3.47E-18	-7.47E-07	-2.78E-17	0.00E+00	1.78E-07
1994	-8.33E-17	-1.04E-17	-7.47E-07	5.55E-17	-4.34E-19	1.78E-07
1995	-9.71E-17	-3.12E-17	-7.47E-07	1.39E-17	-4.34E-19	1.78E-07
1996	-1.68E-01	-2.82E-02	-7.34E-06	-6.25E-01	-4.34E-19	-3.75E-01

1997	1.10E-01	-1.47E-02	-1.65E-06	-4.53E-02	0.00E+00	1.34E-01
1998	2.48E-01	-5.29E-02	2.61E-06	-9.60E-02	0.00E+00	2.44E-01
1999	3.45E-01	-2.33E-02	5.73E-06	7.72E-02	0.00E+00	-9.45E-03
2000	-2.05E-01	-1.32E-02	3.53E-06	6.10E-02	0.00E+00	-2.13E-01
2001	-3.21E-01	-2.76E-02	3.46E-06	1.97E-01	4.34E-19	-2.59E-01
2002	2.00E-01	-1.37E-02	-3.80E-06	2.41E-02	4.34E-19	1.91E-01
2003	1.25E-01	5.28E-04	-1.33E-05	-5.01E-01	4.34E-19	-1.86E-01
2004	3.18E-01	6.84E-03	-6.76E-06	-2.54E-01	0.00E+00	-8.17E-01
2005	3.28E-01	1.25E-02	-1.84E-06	-1.42E-01	0.00E+00	-6.23E-01
2006	3.62E-01	1.26E-02	4.51E-06	-1.52E-02	0.00E+00	-1.46E-01
2007	-4.04E-01	5.97E-03	2.24E-06	3.39E-01	-8.67E-19	-1.59E-01
2008	-2.24E-01	-1.10E-02	-3.03E-06	2.09E-02	1.73E-18	1.34E+00
2009	-1.43E-01	-1.27E-02	6.53E-07	-7.41E-02	0.00E+00	-1.17E-01

Table H.18 Process errors from the stressor (temperature) models in HBEF09.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	-4.87E-07	-8.67E-19	0.00E+00	-1.11E-16	0.00E+00	6.90E-07
1990	-4.87E-07	0.00E+00	2.78E-17	5.55E-17	0.00E+00	6.90E-07
1991	-4.87E-07	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.90E-07
1992	-4.87E-07	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.90E-07
1993	-4.87E-07	0.00E+00	0.00E+00	0.00E+00	0.00E+00	6.90E-07
1994	-4.87E-07	4.34E-19	-1.39E-17	2.78E-17	-1.73E-18	6.90E-07
1995	-4.87E-07	-8.67E-19	1.39E-17	-2.78E-17	1.73E-18	6.90E-07
1996	-5.77E-02	0.00E+00	-1.39E-17	0.00E+00	2.60E-18	-1.58E-01
1997	-3.28E-01	0.00E+00	6.94E-18	-1.39E-17	-2.60E-18	-7.33E-02
1998	8.93E-01	-5.42E-19	-1.56E-17	3.47E-17	-8.67E-19	6.72E-01
1999	8.40E-01	5.42E-19	1.56E-17	-3.47E-17	8.67E-19	-5.04E-02
2000	-3.61E-01	0.00E+00	-6.94E-18	1.39E-17	2.60E-18	-5.60E-01
2001	-6.35E-01	0.00E+00	1.39E-17	0.00E+00	8.67E-19	6.64E-01
2002	6.41E-01	0.00E+00	-1.39E-17	2.78E-17	1.73E-18	-2.13E-01
2003	5.72E-02	0.00E+00	1.39E-17	-2.78E-17	0.00E+00	2.32E-01
2004	1.04E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	-8.54E-01
2005	3.69E-01	0.00E+00	0.00E+00	0.00E+00	-3.47E-18	-1.35E+00
2006	1.98E-01	8.67E-19	0.00E+00	0.00E+00	-3.47E-18	2.70E-01
2007	-7.49E-01	0.00E+00	-2.78E-17	-5.55E-17	0.00E+00	3.22E-01
2008	2.91E-02	8.67E-19	0.00E+00	1.11E-16	0.00E+00	4.71E-01
2009	-4.30E-01	0.00E+00	-5.55E-17	-1.11E-16	3.47E-18	2.82E-01

Table H.19 Process errors from the stressor (NO_3-N deposition) models in HJA10.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	0.00E+00	6.94E-18	9.93E-03	0.00E+00	-2.78E-17	0.00E+00

1990	-5.55E-17	0.00E+00	9.54E-03	-1.39E-17	-2.78E-17	0.00E+00
1991	6.94E-18	6.94E-18	5.65E-03	-6.94E-18	-5.55E-17	1.73E-17
1992	5.55E-17	0.00E+00	2.95E-03	6.94E-18	2.78E-17	-2.08E-17
1993	1.39E-17	-3.47E-18	-3.55E-03	1.04E-17	4.16E-17	-1.39E-17
1994	-4.86E-17	8.67E-18	-2.27E-02	0.00E+00	-1.04E-17	0.00E+00
1995	2.78E-17	0.00E+00	-2.52E-02	0.00E+00	0.00E+00	-1.39E-17
1996	0.00E+00	0.00E+00	-1.52E-02	6.94E-18	0.00E+00	2.78E-17
1997	0.00E+00	0.00E+00	3.98E-03	-3.47E-18	-2.08E-17	0.00E+00
1998	0.00E+00	0.00E+00	1.99E-03	0.00E+00	2.78E-17	0.00E+00
1999	0.00E+00	0.00E+00	1.83E-02	0.00E+00	0.00E+00	0.00E+00
2000	-5.55E-17	0.00E+00	3.12E-02	0.00E+00	0.00E+00	0.00E+00
2001	-2.78E-17	0.00E+00	1.44E-02	0.00E+00	0.00E+00	-2.78E-17
2002	8.33E-17	0.00E+00	2.04E-02	6.94E-18	1.39E-17	0.00E+00
2003	5.55E-17	1.39E-17	1.54E-02	6.94E-18	0.00E+00	-2.78E-17
2004	-5.55E-17	1.39E-17	2.07E-02	-1.39E-17	0.00E+00	0.00E+00
2005	-5.55E-17	0.00E+00	-5.62E-03	6.94E-18	0.00E+00	-6.94E-18
2006	1.04E-17	1.34E-17	4.41E-04	-1.13E-17	8.67E-19	2.34E-17
2007	4.16E-17	0.00E+00	1.15E-02	-3.47E-18	0.00E+00	-6.94E-18
2008	3.12E-17	-8.67E-19	1.49E-02	-5.20E-18	1.73E-18	-1.39E-17
2009	0.00E+00	6.94E-18	1.21E-02	0.00E+00	0.00E+00	0.00E+00

Table H.20 Process errors from the stressor (NO_3-N deposition) models in HJA08.

Year	**NO_3-N**	**NH_4-N**	**Ca**	**SO_4-S**	**DOC**	**TDP**
1989	-9.91E-11	7.37E-07	7.05E-03	2.78E-17	2.78E-17	-7.13E-02
1990	5.04E-10	1.89E-05	3.86E-03	0.00E+00	-2.78E-17	9.24E-02
1991	1.06E-09	2.35E-05	2.33E-03	0.00E+00	2.78E-17	1.33E-01
1992	1.88E-11	-5.49E-06	1.21E-02	0.00E+00	0.00E+00	-1.58E-02
1993	-1.68E-10	-2.33E-06	6.33E-03	-2.78E-17	1.39E-17	2.74E-02
1994	-9.00E-10	3.34E-06	-1.50E-02	0.00E+00	0.00E+00	-3.40E-02
1995	-8.22E-10	1.35E-05	-1.38E-02	6.94E-18	-3.47E-18	-8.85E-03
1996	-1.21E-09	-4.60E-05	-9.23E-03	0.00E+00	0.00E+00	8.56E-02
1997	-1.81E-09	-5.17E-05	3.00E-02	-2.78E-17	0.00E+00	1.85E-02
1998	-2.82E-09	-6.69E-05	1.06E-02	0.00E+00	0.00E+00	-2.24E-02
1999	-2.39E-09	-7.14E-05	3.21E-02	-2.08E-17	-1.04E-17	4.50E-02
2000	-2.42E-09	-8.90E-05	4.72E-02	-2.08E-17	-3.47E-18	5.10E-02
2001	-1.99E-09	-7.31E-05	1.60E-02	0.00E+00	0.00E+00	-2.38E-01
2002	-1.54E-09	-5.47E-05	1.16E-02	0.00E+00	0.00E+00	6.86E-02
2003	-1.07E-09	-6.19E-05	1.39E-02	0.00E+00	0.00E+00	2.39E-01
2004	-5.96E-10	-5.99E-05	0.015813	-3.47E-18	0.00E+00	1.32E-01
2005	-5.78E-10	-5.75E-05	-0.02407	0.00E+00	0.00E+00	-1.05E-02
2006	-1.10E-10	-7.70E-05	-0.00999	0.00E+00	0.00E+00	8.02E-02
2007	3.91E-10	-6.28E-05	0.015712	3.47E-18	0.00E+00	-5.77E-02

2008	8.90E-10	-2.36E-05	0.002158	0.00E+00	0.00E+00	-1.35E-01
2009	1.42E-09	1.93E-05	0.005299	0.00E+00	0.00E+00	-7.08E-02

Table H.21 Process errors from the stressor (NO_3-N deposition) models in HJA09.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	-1.80E-09	-1.43E-05	1.81E-02	-2.06E-01	5.55E-17	-2.02E-01
1990	-3.64E-09	-4.13E-05	1.69E-02	-2.33E-01	0.00E+00	-1.12E-01
1991	-5.17E-09	-5.90E-05	1.05E-02	-1.47E-01	-2.78E-17	-6.73E-02
1992	-3.97E-09	-5.50E-05	7.07E-03	-1.17E-01	0.00E+00	-6.93E-02
1993	-2.71E-09	-4.40E-05	-3.38E-03	-8.17E-02	6.94E-17	-1.11E-01
1994	-1.50E-09	-1.28E-05	-3.97E-02	-1.63E-01	1.11E-16	-5.20E-02
1995	-2.68E-10	-1.53E-06	-4.41E-02	-1.66E-01	-1.11E-16	-1.23E-01
1996	-4.54E-09	-2.71E-05	-2.57E-02	-2.44E-01	5.55E-17	-1.04E-01
1997	-3.58E-09	-2.12E-05	9.20E-03	-1.15E-01	2.78E-17	-1.35E-01
1998	-2.69E-09	-5.18E-05	1.75E-03	-1.11E-01	0.00E+00	-5.67E-02
1999	-1.91E-09	-3.68E-05	3.08E-02	-4.46E-02	0.00E+00	-7.24E-03
2000	-1.91E-09	-1.10E-05	5.36E-02	3.50E-02	0.00E+00	-5.70E-02
2001	-1.54E-09	-2.22E-05	1.83E-02	-1.08E-01	0.00E+00	6.16E-02
2002	-1.54E-09	6.46E-06	2.91E-02	-8.29E-02	0.00E+00	1.56E-01
2003	-1.54E-09	1.34E-05	1.85E-02	1.33E-02	0.00E+00	2.43E-01
2004	-1.54E-09	-2.74E-05	0.029672	-9.08E-04	0.00E+00	1.73E-01
2005	-1.25E-09	-3.80E-05	-0.02107	-5.86E-02	0.00E+00	2.08E-01
2006	-9.09E-10	-6.40E-05	-0.00766	5.33E-03	0.00E+00	2.33E-01
2007	-9.09E-10	-4.54E-05	0.015167	-1.08E-03	-1.39E-17	6.80E-02
2008	-9.09E-10	-4.11E-05	0.023607	2.37E-02	-6.94E-18	5.78E-03
2009	-5.22E-10	-3.07E-06	0.020366	1.62E-02	2.78E-17	-1.37E-01

Table H.22 Process errors from the stressor (NO_3-N deposition) models in HJA06.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	0.00E+00	1.90E-06	1.54E-02	-1.27E-01	2.78E-17	-1.66E-01
1990	0.00E+00	-4.04E-06	2.14E-02	-5.78E-02	2.78E-17	-6.37E-02
1991	0.00E+00	-3.06E-06	3.16E-02	-1.73E-01	0.00E+00	-2.69E-01
1992	0.00E+00	-1.69E-05	2.79E-02	-4.55E-02	0.00E+00	-6.17E-03
1993	0.00E+00	-1.89E-05	3.34E-02	-1.46E-01	1.39E-17	-1.73E-01
1994	0.00E+00	-2.75E-05	3.23E-02	-1.07E-01	-1.39E-17	-9.60E-02
1995	0.00E+00	-3.34E-05	3.26E-02	-1.35E-01	0.00E+00	-9.97E-02
1996	0.00E+00	-4.04E-05	3.11E-02	-9.16E-02	0.00E+00	1.85E-02
1997	0.00E+00	-3.77E-05	3.71E-02	-1.39E-01	-1.39E-17	-6.30E-02
1998	0.00E+00	-3.25E-05	4.50E-02	-1.49E-01	1.39E-17	-1.08E-01
1999	0.00E+00	-2.39E-05	5.61E-02	-2.02E-01	-6.94E-18	-2.23E-01
2000	0.00E+00	-1.91E-05	6.53E-02	-2.05E-01	0.00E+00	-2.27E-01

2001	0.00E+00	-1.51E-05	7.62E-02	-2.55E-01	0.00E+00	-2.67E-01
2002	0.00E+00	-1.69E-05	8.55E-02	-2.83E-01	0.00E+00	-1.26E-01
2003	0.00E+00	-2.45E-05	9.42E-02	4.65E-01	0.00E+00	4.84E-01
2004	0.00E+00	-8.10E-05	8.86E-02	-4.81E-01	-3.47E-18	3.67E-01
2005	0.00E+00	-9.17E-05	1.63E-02	-2.72E-01	0.00E+00	-5.01E-02
2006	0.00E+00	-1.26E-04	3.28E-02	-3.62E-02	0.00E+00	3.25E-01
2007	0.00E+00	-5.94E-05	8.44E-02	2.67E-03	1.73E-18	1.77E-01
2008	0.00E+00	-3.48E-05	1.39E-02	-3.07E-02	0.00E+00	-1.27E-01
2009	0.00E+00	2.64E-05	2.96E-02	2.02E-02	0.00E+00	-3.50E-01

Table H.23 Process errors from the stressor (NO_3-N deposition) models in HJA07.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	2.78E-17	6.94E-18	3.40E-03	-5.55E-17	1.39E-17	-1.11E-16
1990	5.55E-17	0.00E+00	6.80E-03	0.00E+00	0.00E+00	0.00E+00
1991	-1.11E-16	0.00E+00	9.33E-03	-1.11E-16	5.55E-17	-1.11E-16
1992	0.00E+00	0.00E+00	1.25E-02	0.00E+00	0.00E+00	0.00E+00
1993	0.00E+00	6.94E-18	1.47E-02	0.00E+00	0.00E+00	2.78E-17
1994	0.00E+00	0.00E+00	1.71E-02	0.00E+00	0.00E+00	0.00E+00
1995	-2.78E-17	3.47E-18	1.93E-02	-1.39E-17	-6.94E-18	1.39E-17
1996	0.00E+00	0.00E+00	2.15E-02	0.00E+00	0.00E+00	0.00E+00
1997	2.78E-17	-6.94E-18	2.32E-02	5.55E-17	-1.39E-17	0.00E+00
1998	0.00E+00	-6.94E-18	2.48E-02	5.55E-17	0.00E+00	0.00E+00
1999	4.16E-17	0.00E+00	2.63E-02	2.78E-17	-1.39E-17	-1.39E-17
2000	-2.78E-17	-1.04E-17	2.84E-02	-6.94E-17	-6.94E-18	-4.16E-17
2001	5.55E-17	-1.39E-17	3.07E-02	5.55E-17	0.00E+00	2.78E-17
2002	0.00E+00	0.00E+00	3.38E-02	5.55E-17	0.00E+00	2.78E-17
2003	0.00E+00	-6.94E-18	3.78E-02	-2.78E-17	0.00E+00	2.78E-17
2004	0.00E+00	3.47E-18	4.79E-02	1.39E-17	0.00E+00	-6.94E-18
2005	-2.78E-17	-6.94E-18	1.01E-03	-2.78E-17	0.00E+00	-2.78E-17
2006	0.00E+00	0.00E+00	2.57E-02	0.00E+00	0.00E+00	0.00E+00
2007	3.47E-18	8.67E-19	5.27E-02	0.00E+00	0.00E+00	3.47E-18
2008	0.00E+00	0.00E+00	4.20E-02	0.00E+00	0.00E+00	0.00E+00
2009	0.00E+00	0.00E+00	2.74E-02	0.00E+00	0.00E+00	0.00E+00

Table H.24 Process errors from the stressor (SO_4-S deposition) models in LEF01.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	5.51E-01	5.52E-01	7.74E-03	-3.01E-03	0.00E+00	6.07E-01
1990	-9.72E-01	-9.74E-01	1.03E-02	-8.08E-03	2.22E-16	3.15E-01
1991	-7.98E-02	-7.95E-02	1.36E-02	-7.78E-03	0.00E+00	1.43E-01
1992	-1.01E+00	-1.01E+00	1.56E-02	-3.36E-02	-2.78E-17	8.32E-02
1993	-9.43E-01	-9.40E-01	1.53E-02	-4.03E-02	1.11E-16	-2.77E-02
1994	6.85E-01	6.82E-01	1.20E-02	-5.59E-02	-1.39E-17	1.77E-03

1995	4.23E-01	4.21E-01	1.13E-02	-5.42E-02	0.00E+00	3.18E-01
1996	1.33E+00	1.33E+00	9.58E-03	-7.53E-02	0.00E+00	2.19E-01
1997	-1.93E-01	-1.93E-01	1.03E-02	4.97E-02	1.11E-16	1.56E-01
1998	6.81E-01	6.82E-01	1.78E-02	4.12E-02	0.00E+00	1.50E-01
1999	1.66E-02	1.62E-02	2.19E-02	2.20E-01	1.39E-17	5.35E-01
2000	-2.54E-01	-2.55E-01	2.08E-02	1.68E-01	0.00E+00	2.41E-01
2001	1.90E-01	1.90E-01	1.63E-02	1.16E-01	0.00E+00	2.98E-03
2002	-1.39E-01	-1.39E-01	1.63E-02	1.00E-01	0.00E+00	2.77E-02
2003	-5.15E-01	-5.16E-01	1.60E-02	8.15E-02	0.00E+00	-4.19E-02
2004	2.91E-01	2.91E-01	0.016117	6.38E-02	2.08E-17	2.19E-02
2005	-2.31E-01	-2.32E-01	0.015487	4.78E-02	1.11E-16	2.11E-02
2006	3.81E-01	3.81E-01	0.00999	1.21E-02	0.00E+00	-1.25E-01
2007	7.29E-02	7.26E-02	0.00727	3.12E-03	0.00E+00	-9.93E-02
2008	-2.82E-01	-2.81E-01	0.00436	9.30E-03	0.00E+00	4.01E-02
2009	-2.41E-01	-2.40E-01	-0.00092	6.96E-03	1.11E-16	4.69E-02

Table H.25 Process errors from the stressor (SO_4-S deposition) models in LEF02.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	2.41E-01	2.49E-01	6.32E-03	-8.05E-03	0.00E+00	6.69E-01
1990	-6.54E-01	-6.60E-01	3.47E-03	-3.06E-02	-2.22E-16	3.40E-01
1991	-3.62E-01	-3.61E-01	8.38E-03	-4.96E-02	0.00E+00	1.34E-01
1992	-1.18E+00	-1.18E+00	8.09E-03	-1.07E-01	-4.16E-17	-2.48E-02
1993	-1.35E+00	-1.35E+00	4.14E-03	-1.01E-01	5.55E-17	-1.31E-01
1994	9.62E-01	9.61E-01	5.21E-03	-6.46E-02	-4.16E-17	-5.04E-02
1995	6.02E-01	6.03E-01	3.59E-03	-7.26E-02	0.00E+00	3.77E-01
1996	1.22E+00	1.22E+00	-6.95E-04	-9.90E-02	0.00E+00	2.20E-01
1997	3.44E-02	3.27E-02	-1.35E-03	2.67E-02	0.00E+00	1.45E-01
1998	5.34E-01	5.35E-01	2.83E-03	1.93E-02	0.00E+00	1.30E-01
1999	-6.80E-01	-6.81E-01	3.73E-03	2.27E-01	0.00E+00	4.55E-01
2000	-4.87E-01	-4.87E-01	6.35E-03	1.82E-01	0.00E+00	1.49E-01
2001	6.14E-01	6.15E-01	7.25E-03	1.68E-01	0.00E+00	3.52E-02
2002	1.28E-01	1.28E-01	9.90E-03	1.50E-01	0.00E+00	4.93E-02
2003	-3.94E-01	-3.95E-01	1.48E-02	1.10E-01	0.00E+00	-3.78E-02
2004	-1.14E-01	-1.13E-01	1.63E-02	7.06E-02	6.94E-18	4.55E-02
2005	-3.10E-01	-3.10E-01	1.60E-02	5.45E-02	0.00E+00	1.91E-02
2006	2.89E-01	2.89E-01	1.28E-02	7.67E-03	0.00E+00	-1.54E-01
2007	7.50E-02	7.46E-02	1.27E-02	2.76E-03	0.00E+00	-4.05E-02
2008	-1.60E-01	-1.60E-01	1.02E-02	1.99E-02	0.00E+00	7.26E-02
2009	-1.22E-01	-1.22E-01	3.57E-03	1.51E-02	1.11E-16	8.05E-02

Table H.26 Process errors from the stressor (SO_4-S deposition) models in LEF03.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	5.36E-01	5.36E-01	7.56E-03	-4.02E-03	0.00E+00	5.19E-01
1990	-5.06E-01	-5.06E-01	5.68E-03	-3.95E-02	0.00E+00	1.84E-01
1991	-7.53E-01	-7.53E-01	7.92E-03	-4.41E-02	0.00E+00	6.15E-02
1992	-9.48E-01	-9.48E-01	5.38E-03	-6.66E-02	2.78E-17	-8.38E-03
1993	-1.50E+00	-1.50E+00	7.97E-03	-4.39E-02	5.55E-17	-2.40E-02
1994	7.59E-01	7.59E-01	6.10E-03	-5.75E-02	0.00E+00	8.66E-02
1995	4.35E-01	4.35E-01	4.39E-03	-6.02E-02	0.00E+00	3.35E-01
1996	1.31E+00	1.31E+00	2.88E-05	-6.31E-02	0.00E+00	3.09E-01
1997	1.08E-01	1.08E-01	2.04E-03	2.74E-03	2.22E-16	1.53E-01
1998	4.09E-01	4.10E-01	9.62E-03	1.60E-02	0.00E+00	1.37E-01
1999	-6.78E-01	-6.78E-01	1.05E-02	1.95E-01	0.00E+00	4.79E-01
2000	-3.12E-01	-3.12E-01	8.82E-03	1.50E-01	5.55E-17	2.14E-01
2001	4.81E-01	4.81E-01	5.79E-03	1.07E-01	0.00E+00	8.83E-03
2002	-1.87E-01	-1.87E-01	6.39E-03	9.58E-02	0.00E+00	3.21E-02
2003	-4.27E-01	-4.27E-01	9.34E-03	8.47E-02	0.00E+00	-2.51E-02
2004	-1.13E-01	-1.13E-01	7.65E-03	5.67E-02	-6.94E-18	2.82E-02
2005	-3.34E-01	-3.34E-01	7.10E-03	4.41E-02	0.00E+00	6.26E-02
2006	0.00E+00	-1.11E-16	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2007	0.00E+00	-2.78E-17	0.00E+00	-2.78E-17	0.00E+00	-5.55E-17
2008	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	-5.55E-17
2009	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Table H.27 Process errors from the stressor (SO_4-S deposition) models in LEF04.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	2.40E-01	2.41E-01	2.08E-03	1.15E-01	0.00E+00	6.78E-01
1990	-9.05E-02	-9.10E-02	-2.67E-04	3.00E-02	0.00E+00	9.96E-02
1991	-3.47E-01	-3.48E-01	6.35E-03	-6.12E-02	0.00E+00	2.82E-02
1992	-4.60E-01	-4.61E-01	3.86E-03	-1.34E-01	-2.43E-17	-1.88E-01
1993	-6.51E-01	-6.52E-01	1.10E-02	-4.74E-02	2.78E-17	-2.06E-01
1994	-9.58E-01	-9.59E-01	7.36E-03	-1.03E-01	4.16E-17	1.13E-01
1995	4.68E-01	4.68E-01	-5.92E-03	-8.74E-02	0.00E+00	3.94E-01
1996	6.20E-01	6.21E-01	-4.50E-03	-5.49E-02	0.00E+00	3.35E-01
1997	2.63E-01	2.64E-01	-1.23E-02	2.49E-01	0.00E+00	3.03E-01
1998	2.56E-01	2.56E-01	3.68E-02	1.22E-01	0.00E+00	1.23E-01
1999	1.20E-01	1.20E-01	2.72E-02	6.54E-02	-1.39E-17	2.00E-01
2000	-4.60E-02	-4.61E-02	1.14E-02	5.12E-02	0.00E+00	1.58E-02
2001	4.02E-02	4.03E-02	-6.15E-03	2.33E-02	0.00E+00	6.76E-02
2002	-1.36E-01	-1.36E-01	1.12E-02	2.03E-02	0.00E+00	1.94E-02
2003	-1.60E-01	-1.60E-01	4.42E-02	3.92E-02	0.00E+00	-1.56E-01
2004	-9.91E-02	-9.91E-02	2.64E-02	2.46E-02	6.94E-18	-1.86E-01

2005	-1.34E-01	-1.34E-01	4.78E-02	1.57E-02	0.00E+00	-2.07E-01
2006	6.81E-02	6.83E-02	2.72E-02	-1.93E-02	0.00E+00	-9.29E-02
2007	2.74E-02	2.75E-02	1.02E-02	-4.32E-02	0.00E+00	-6.26E-03
2008	-7.61E-02	-7.62E-02	4.46E-04	-3.03E-03	0.00E+00	5.75E-02
2009	-1.33E-01	-1.33E-01	2.99E-03	-2.64E-03	-5.55E-17	1.30E-02

Table H.28 Process errors from the stressor (SO_4-S deposition) models in LEF05.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	2.54E-01	2.54E-01	-8.23E-04	1.87E-01	0.00E+00	1.03E-07
1990	1.87E-01	1.87E-01	-2.61E-03	2.35E-01	-1.11E-16	1.03E-07
1991	-4.59E-01	-4.60E-01	-6.00E-03	2.19E-01	0.00E+00	1.03E-07
1992	-1.96E+00	-1.96E+00	-6.47E-03	7.11E-02	2.78E-17	1.03E-07
1993	7.14E-01	7.14E-01	-1.04E-02	1.49E-01	0.00E+00	1.03E-07
1994	-8.34E-02	-8.24E-02	-6.62E-03	-2.24E-02	1.39E-17	1.03E-07
1995	6.67E-01	6.66E-01	-2.71E-03	1.42E-01	0.00E+00	1.03E-07
1996	6.34E-02	6.39E-02	2.63E-03	-3.67E-02	0.00E+00	1.03E-07
1997	2.15E-01	2.15E-01	8.82E-03	-8.92E-02	1.11E-16	1.03E-07
1998	2.21E-01	2.21E-01	1.24E-02	-9.86E-02	0.00E+00	1.03E-07
1999	1.52E-01	1.52E-01	1.33E-02	-5.13E-02	0.00E+00	1.03E-07
2000	-2.03E-01	-2.02E-01	1.25E-02	-2.03E-02	2.78E-17	-3.62E-01
2001	-1.12E-01	-1.13E-01	1.16E-02	7.29E-03	0.00E+00	3.06E-02
2002	-2.42E-01	-2.42E-01	9.91E-03	-2.68E-02	0.00E+00	4.64E-02
2003	-6.10E-02	-6.11E-02	9.17E-03	2.37E-02	2.78E-17	-9.80E-01
2004	-3.88E-03	-3.89E-03	8.33E-03	-1.10E-02	-3.47E-18	-1.69E-03
2005	8.79E-02	8.76E-02	7.50E-03	2.57E-02	-1.11E-16	-2.32E-01
2006	-1.53E-01	-1.53E-01	7.15E-03	-1.38E-01	0.00E+00	-2.63E-01
2007	-7.73E-01	-7.71E-01	5.17E-03	-3.56E-01	0.00E+00	-2.55E-01
2008	1.33E-01	1.32E-01	2.43E-03	-3.71E-02	0.00E+00	-3.32E-01
2009	-2.13E-01	-2.13E-01	6.35E-04	-4.51E-02	0.00E+00	3.82E-01

Table H.29 Process errors from the stressor (SO_4-S deposition) models in LEF06.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	6.18E-01	6.18E-01	9.28E-03	6.31E-02	0.00E+00	6.51E-01
1990	-5.85E-01	-5.85E-01	-7.86E-03	5.64E-02	0.00E+00	1.77E-01
1991	-6.14E-01	-6.14E-01	1.88E-02	4.65E-02	0.00E+00	-3.31E-02
1992	-8.15E-01	-8.15E-01	1.07E-02	-4.44E-02	2.26E-17	-1.60E-01
1993	-1.63E+00	-1.63E+00	8.38E-03	-2.61E-02	0.00E+00	3.40E-02
1994	1.01E+00	1.01E+00	1.62E-03	-9.08E-02	0.00E+00	-7.40E-02
1995	4.57E-01	4.57E-01	-1.65E-02	-8.23E-02	0.00E+00	5.12E-01
1996	1.02E+00	1.02E+00	-2.35E-02	-5.30E-02	0.00E+00	5.81E-01
1997	5.15E-01	5.15E-01	-2.68E-02	3.16E-01	-5.55E-17	2.68E-01
1998	2.40E-01	2.40E-01	-1.48E-02	1.99E-01	0.00E+00	3.32E-01

1999	-7.04E-01	-7.04E-01	-1.04E-02	1.05E-01	-6.94E-18	4.33E-01
2000	-3.49E-01	-3.49E-01	1.60E-03	7.73E-02	0.00E+00	1.52E-01
2001	4.12E-01	4.12E-01	-1.21E-02	2.93E-02	0.00E+00	-7.21E-02
2002	-1.50E-01	-1.50E-01	-4.52E-03	2.17E-02	0.00E+00	-1.02E-01
2003	-2.87E-01	-2.87E-01	6.74E-03	-3.84E-03	0.00E+00	-3.55E-01
2004	1.47E-02	1.47E-02	2.11E-02	3.64E-03	-3.47E-18	-7.33E-02
2005	-3.01E-01	-3.01E-01	2.46E-02	1.20E-02	-5.55E-17	-1.30E-01
2006	4.78E-01	4.78E-01	1.38E-02	-2.66E-03	0.00E+00	-1.01E-01
2007	-1.45E-01	-1.45E-01	1.52E-02	-5.05E-02	0.00E+00	-6.80E-03
2008	-1.50E-01	-1.50E-01	2.08E-02	-3.07E-02	0.00E+00	3.62E-02
2009	-1.03E-01	-1.03E-01	2.81E-03	-4.41E-02	5.55E-17	4.80E-02

Table H.30 Process errors from the stressor (temperature) models in MEF02.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	2.68E-05	-9.30E-04	6.76E-05	1.02E-05	0.00E+00	-3.96E-05
1990	-9.17E-05	-1.28E-02	3.54E-05	-1.81E-05	0.00E+00	-2.77E-05
1991	1.15E-05	3.29E-02	1.32E-05	-6.25E-05	0.00E+00	5.31E-05
1992	-1.07E-04	9.05E-02	-1.37E-05	-2.25E-05	0.00E+00	3.85E-05
1993	-2.05E-04	1.11E-01	-4.12E-05	-2.25E-05	0.00E+00	-2.38E-05
1994	-2.70E-04	1.28E-01	-3.20E-05	-2.25E-05	-6.94E-18	-4.78E-05
1995	-2.62E-04	1.59E-01	-3.23E-05	-3.06E-05	-5.55E-17	5.59E-06
1996	-2.83E-04	4.23E-02	-5.65E-05	-4.35E-05	5.55E-17	-1.05E-04
1997	-2.12E-04	2.29E-02	-6.28E-05	-3.97E-05	0.00E+00	-7.11E-05
1998	-1.19E-04	2.56E-02	-5.27E-05	-2.92E-05	0.00E+00	-2.95E-05
1999	-1.47E-04	-7.35E-03	-3.24E-05	-9.00E-06	0.00E+00	-8.00E-07
2000	-3.42E-05	-2.88E-03	-3.08E-05	-3.65E-06	0.00E+00	2.14E-05
2001	1.08E-04	3.72E-02	-1.16E-05	-2.13E-05	0.00E+00	5.91E-05
2002	-5.02E-05	6.74E-02	-1.24E-05	-1.81E-05	2.28E-18	9.36E-05
2003	-2.58E-05	6.82E-02	3.90E-06	-1.48E-05	0.00E+00	9.80E-05
2004	-4.65E-05	1.54E-01	1.69E-05	-8.19E-06	0.00E+00	1.27E-04
2005	-9.87E-05	1.70E-01	4.50E-05	-1.26E-05	0.00E+00	1.01E-04
2006	-1.68E-04	1.03E-01	8.43E-05	4.35E-06	-5.55E-17	7.60E-05
2007	-7.69E-05	5.18E-02	6.90E-05	-1.44E-05	5.55E-17	7.88E-05
2008	3.40E-05	-2.72E-02	4.24E-05	1.61E-05	0.00E+00	5.95E-05
2009	6.60E-05	-1.18E-02	3.53E-05	1.70E-06	2.78E-17	1.39E-05

Table H.31 Process errors from the stressor (temperature) models in MEF05.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	1.35E-04	3.28E-02	8.62E-05	2.41E-05	0.00E+00	7.28E-05
1990	2.54E-04	1.46E-01	1.02E-04	3.29E-05	0.00E+00	1.98E-04
1991	2.73E-04	1.14E-01	6.55E-05	-2.10E-05	0.00E+00	1.78E-04
1992	1.13E-04	4.15E-02	4.33E-05	1.35E-05	0.00E+00	1.60E-04

1993	-2.04E-05	4.65E-02	5.30E-05	1.35E-05	0.00E+00	1.12E-04
1994	-1.04E-04	9.51E-02	7.83E-05	1.35E-05	-1.39E-17	1.10E-04
1995	-1.54E-05	1.11E-01	8.22E-05	2.14E-05	5.55E-17	1.34E-04
1996	-3.68E-05	8.16E-02	6.30E-05	1.40E-05	-2.78E-17	1.03E-04
1997	-2.48E-05	3.56E-02	4.92E-05	-2.01E-06	0.00E+00	8.64E-05
1998	5.68E-06	-3.33E-02	2.71E-05	-8.62E-07	0.00E+00	7.52E-05
1999	-1.47E-05	-2.34E-02	4.46E-05	8.01E-06	0.00E+00	7.80E-05
2000	6.30E-05	-1.81E-02	6.82E-05	1.86E-05	0.00E+00	1.04E-04
2001	3.58E-05	3.16E-02	6.84E-05	1.48E-05	0.00E+00	1.33E-04
2002	-4.13E-05	6.93E-02	5.93E-05	1.68E-05	3.25E-19	1.74E-04
2003	-5.25E-06	5.34E-02	4.84E-05	8.83E-06	0.00E+00	1.83E-04
2004	1.57E-04	1.75E-01	4.83E-05	2.92E-06	0.00E+00	1.59E-04
2005	1.51E-04	1.19E-01	7.30E-05	1.42E-05	0.00E+00	1.38E-04
2006	4.01E-05	-6.44E-02	1.00E-04	8.42E-06	2.78E-17	1.22E-04
2007	5.82E-05	-8.04E-02	7.57E-05	-8.17E-06	-2.78E-17	9.44E-05
2008	1.23E-04	-3.70E-02	6.48E-05	-4.10E-06	0.00E+00	6.45E-05
2009	4.09E-05	-1.02E-01	5.10E-05	3.51E-06	0.00E+00	2.46E-05

Table H.32 Process errors from the stressor (temperature) models in MEF04.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	1.29E-04	-1.09E-01	5.61E-05	1.55E-05	0.00E+00	6.38E-05
1990	2.44E-04	3.43E-02	7.19E-05	3.89E-05	1.39E-17	1.18E-04
1991	2.87E-04	2.99E-02	2.91E-05	-5.61E-06	0.00E+00	7.08E-05
1992	3.30E-04	6.01E-02	1.27E-05	-5.61E-06	0.00E+00	8.29E-05
1993	3.67E-04	7.68E-02	1.38E-05	-5.61E-06	-1.39E-17	8.01E-05
1994	4.03E-04	1.35E-01	5.86E-05	-5.61E-06	3.47E-18	1.10E-04
1995	4.53E-04	1.69E-01	9.83E-05	-9.28E-06	0.00E+00	1.80E-04
1996	3.71E-04	1.77E-01	8.86E-05	-2.47E-05	1.39E-17	8.91E-05
1997	3.92E-04	6.70E-02	2.75E-05	-3.06E-05	0.00E+00	5.85E-05
1998	4.27E-04	5.51E-02	2.23E-05	-2.94E-05	0.00E+00	8.51E-05
1999	3.77E-04	6.76E-02	4.35E-05	-2.35E-05	0.00E+00	1.32E-04
2000	4.10E-04	1.18E-01	4.07E-05	-2.61E-05	0.00E+00	1.54E-04
2001	4.74E-04	-2.28E-02	6.62E-05	-9.27E-06	0.00E+00	1.43E-04
2002	3.47E-04	5.88E-02	7.21E-05	-1.84E-06	-2.49E-18	1.84E-04
2003	3.36E-04	9.00E-02	4.79E-05	5.98E-06	0.00E+00	1.53E-04
2004	2.54E-04	1.26E-01	5.56E-05	8.18E-06	0.00E+00	1.66E-04
2005	-1.09E-05	1.14E-01	1.23E-04	2.36E-05	0.00E+00	1.53E-04
2006	4.86E-05	1.01E-02	1.26E-04	3.32E-05	0.00E+00	1.36E-04
2007	9.52E-06	-3.63E-02	1.21E-04	1.36E-05	1.39E-17	1.10E-04
2008	4.83E-05	-6.00E-02	9.75E-05	1.79E-05	0.00E+00	9.55E-05
2009	4.80E-05	-7.65E-02	7.13E-05	9.85E-06	-1.39E-17	-3.73E-05

Table H.33 Process errors from the stressor (temperature) models in MEF06.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	1.66E-05	-1.24E-02	4.43E-05	1.07E-05	0.00E+00	3.14E-05
1990	1.17E-04	1.25E-01	7.52E-05	1.84E-06	5.55E-17	6.71E-05
1991	2.16E-04	1.51E-01	5.10E-05	-2.33E-05	0.00E+00	1.52E-04
1992	2.74E-04	1.32E-01	6.57E-06	2.03E-05	0.00E+00	1.24E-04
1993	3.18E-04	1.01E-01	1.17E-05	2.03E-05	0.00E+00	1.05E-04
1994	3.54E-04	-2.48E-02	2.69E-05	2.03E-05	-1.39E-17	1.14E-04
1995	4.02E-04	1.90E-02	3.32E-05	2.04E-05	1.11E-16	8.09E-05
1996	3.50E-04	6.22E-02	3.30E-05	1.09E-05	5.55E-17	1.05E-04
1997	3.57E-04	2.93E-02	2.72E-05	-6.35E-06	0.00E+00	7.03E-05
1998	4.09E-04	7.66E-03	2.13E-05	4.82E-06	0.00E+00	1.14E-04
1999	3.70E-04	1.98E-03	1.47E-05	1.25E-05	0.00E+00	1.42E-04
2000	4.65E-04	5.75E-02	1.88E-05	1.69E-05	0.00E+00	1.44E-04
2001	4.83E-04	3.88E-02	-3.55E-05	3.82E-05	0.00E+00	1.54E-04
2002	3.47E-04	3.76E-02	-4.82E-05	4.98E-05	-1.67E-17	1.30E-04
2003	2.21E-04	4.17E-02	-3.40E-05	3.80E-05	0.00E+00	6.68E-05
2004	1.02E-04	4.49E-02	-7.09E-06	3.29E-05	0.00E+00	5.97E-05
2005	1.27E-05	8.68E-02	1.63E-05	1.94E-05	0.00E+00	1.14E-05
2006	-6.76E-05	7.37E-02	4.02E-06	1.66E-05	-1.11E-16	1.23E-07
2007	2.78E-17	-2.78E-17	2.78E-17	-1.11E-16	-1.11E-16	0.00E+00
2008	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2009	-2.78E-17	5.55E-17	1.39E-17	5.55E-17	-5.55E-17	1.39E-17

Table H.34 Process errors from the stressor (water year) models in SEF77.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	-0.31951	0.00E+00	0.00E+00	-0.1278	0.00E+00	0.00E+00
1990	-0.55451	0.00E+00	0.00E+00	-0.07995	0.00E+00	0.00E+00
1991	0.450434	0.00E+00	0.00E+00	-0.11278	0.00E+00	0.00E+00
1992	0.35433	0.00E+00	0.00E+00	0.472778	5.55E-17	5.55E-17
1993	-0.36445	-2.78E-17	-3.47E-18	0.20815	0.00E+00	0.00E+00
1994	-0.83736	-2.78E-17	3.47E-18	-0.16162	0.00E+00	2.78E-17
1995	0.718427	5.55E-17	3.47E-18	0.769967	-8.33E-17	2.78E-17
1996	0.466811	2.78E-17	-1.73E-18	0.549746	-6.94E-17	2.78E-17
1997	0.30372	0.00E+00	0.00E+00	0.375268	-2.78E-17	-9.71E-17
1998	0.231986	-2.78E-17	2.60E-18	0.268184	-3.47E-18	3.47E-18
1999	0.205718	2.78E-17	-2.60E-18	0.196891	3.47E-18	-3.47E-18
2000	0.201148	0.00E+00	0.00E+00	0.144092	2.78E-17	9.71E-17
2001	0.201564	-2.78E-17	1.73E-18	0.101656	6.94E-17	-2.78E-17
2002	0.174532	-5.55E-17	-3.47E-18	0.065622	8.33E-17	-2.78E-17
2003	0.015899	2.78E-17	-3.47E-18	0.034213	0.00E+00	-2.78E-17
2004	-0.22589	0.00E+00	0.00E+00	0.008506	0.00E+00	0.00E+00

2005	-0.77193	0.00E+00	0.00E+00	0.001636	0.00E+00	0.00E+00
2006	-0.09325	0.00E+00	6.94E-18	0.0957	0.00E+00	0.00E+00
2007	-0.23101	0.00E+00	0.00E+00	0.780284	0.00E+00	-5.55E-17
2008	0.569205	0.00E+00	0.00E+00	-0.38236	-5.55E-17	0.00E+00
2009	-0.15831	-1.11E-16	1.39E-17	0.075209	0.00E+00	0.00E+00

Table H.35 Process errors from the stressor (water year) models in SEF80.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	-3.46E-01	1.73E-18	-1.39E-17	1.39E-17	0.00E+00	0.00E+00
1990	-1.84E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1991	-1.98E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1992	1.33E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	-5.55E-17
1993	5.45E-02	0.00E+00	0.00E+00	-6.94E-18	-6.94E-18	-2.78E-17
1994	-2.82E-01	1.73E-18	0.00E+00	-6.94E-18	1.04E-17	2.78E-17
1995	2.49E-01	1.73E-18	1.39E-17	0.00E+00	-1.04E-17	1.11E-16
1996	2.76E-01	-8.67E-19	1.39E-17	-3.47E-18	6.94E-18	0.00E+00
1997	2.39E-01	8.67E-19	-5.20E-18	5.20E-18	-1.39E-17	9.02E-17
1998	2.09E-01	-4.34E-19	6.94E-18	1.21E-17	-8.24E-18	-5.20E-17
1999	1.92E-01	4.34E-19	-6.94E-18	-1.21E-17	8.24E-18	5.20E-17
2000	1.85E-01	-8.67E-19	5.20E-18	-5.20E-18	1.39E-17	-9.02E-17
2001	1.80E-01	8.67E-19	-1.39E-17	3.47E-18	-6.94E-18	0.00E+00
2002	1.56E-01	-1.73E-18	0.00E+00	0.00E+00	1.04E-17	-1.11E-16
2003	7.00E-02	0.00E+00	0.00E+00	6.94E-18	-1.04E-17	-2.78E-17
2004	-1.77E-01	0.00E+00	0.00E+00	0.00E+00	-6.94E-18	2.78E-17
2005	-3.22E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2006	-3.12E-01	-1.73E-18	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2007	-2.56E-01	0.00E+00	-1.39E-17	1.39E-17	0.00E+00	0.00E+00
2008	2.97E-01	-1.73E-18	1.39E-17	-1.39E-17	0.00E+00	5.55E-17
2009	1.26E-02	0.00E+00	0.00E+00	2.78E-17	1.39E-17	5.55E-17

Table H.36 Process errors from the no-stressor models in TLW32.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	0.00E+00	-2.50E-02	1.64E-03	0.00E+00	9.58E-03	1.05E-03
1990	0.00E+00	-2.50E-01	-1.89E-03	0.00E+00	-9.88E-02	-1.07E-04
1991	0.00E+00	-6.05E-02	-6.15E-03	0.00E+00	-2.59E-02	-3.02E-05
1992	0.00E+00	3.59E-03	-7.01E-03	0.00E+00	-9.19E-04	1.11E-03
1993	0.00E+00	-1.57E-01	-3.66E-03	0.00E+00	-7.78E-02	-1.78E-04
1994	0.00E+00	-1.92E-01	-4.04E-04	0.00E+00	-1.65E-02	-9.65E-04
1995	0.00E+00	-1.51E-01	-6.43E-04	0.00E+00	-7.98E-02	-5.42E-04
1996	0.00E+00	-3.88E-01	4.21E-03	0.00E+00	-1.71E-02	-3.60E-03
1997	0.00E+00	-4.73E-01	9.44E-03	0.00E+00	-2.28E-02	2.68E-04
1998	0.00E+00	-2.46E-01	7.63E-03	0.00E+00	5.12E-02	9.78E-04

1999	0.00E+00	-1.55E-01	3.83E-03	0.00E+00	3.32E-03	1.79E-03
2000	0.00E+00	1.01E-01	4.75E-04	0.00E+00	1.76E-02	-3.85E-04
2001	0.00E+00	-1.34E-02	-4.49E-03	0.00E+00	3.24E-02	-6.28E-04
2002	0.00E+00	1.12E-01	-9.91E-04	0.00E+00	4.41E-02	1.05E-03
2003	0.00E+00	1.39E-02	1.25E-03	0.00E+00	6.54E-02	3.14E-04
2004	0.00E+00	-3.34E-02	4.30E-03	0.00E+00	-3.36E-02	-1.38E-03
2005	0.00E+00	2.96E-02	3.30E-03	0.00E+00	1.42E-02	-2.48E-03
2006	0.00E+00	-4.36E-02	2.16E-03	0.00E+00	2.39E-02	-4.72E-03
2007	0.00E+00	-1.54E-01	2.88E-03	0.00E+00	-4.19E-02	-7.63E-03
2008	0.00E+00	-2.71E-01	8.20E-03	0.00E+00	-1.21E-01	-9.56E-03
2009	0.00E+00	-1.56E-01	5.47E-03	0.00E+00	-6.03E-02	-5.15E-03

Table H.37 Process errors from the no-stressor models in TLW35.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	0.00E+00	3.35E-02	6.42E-04	-1.18E-01	3.33E-02	-2.04E-03
1990	0.00E+00	-2.04E-01	-4.20E-03	1.22E-01	-1.40E-01	-6.05E-03
1991	0.00E+00	-1.59E-01	-1.20E-02	-1.07E-01	-9.78E-02	-6.05E-03
1992	0.00E+00	-1.60E-01	-1.68E-02	-8.53E-03	-5.92E-02	-7.82E-03
1993	0.00E+00	-6.14E-02	-1.46E-02	-2.65E-01	-2.64E-02	-8.45E-03
1994	0.00E+00	-7.29E-04	-1.09E-02	-1.14E-01	3.83E-02	-6.47E-03
1995	0.00E+00	-8.57E-02	-2.05E-02	6.10E-02	-2.85E-02	-4.97E-03
1996	0.00E+00	-1.59E-01	-2.27E-02	-1.81E-01	1.38E-02	-3.22E-03
1997	0.00E+00	-2.08E-01	-1.35E-02	2.34E-01	5.88E-02	5.69E-04
1998	0.00E+00	-2.18E-01	-2.00E-02	2.85E-02	-1.19E-02	2.38E-03
1999	0.00E+00	-1.56E-01	-1.60E-02	-9.13E-02	-4.40E-02	2.17E-03
2000	0.00E+00	5.25E-02	-8.70E-03	8.05E-02	-8.34E-04	3.21E-03
2001	0.00E+00	1.28E-01	-1.03E-02	-1.31E-01	6.52E-02	2.75E-03
2002	0.00E+00	1.54E-01	-7.09E-03	-1.69E-01	-2.13E-02	6.47E-03
2003	0.00E+00	7.50E-02	-1.74E-03	2.94E-02	-1.08E-03	4.11E-03
2004	0.00E+00	-9.20E-02	5.78E-04	2.04E-02	-2.12E-02	4.05E-03
2005	0.00E+00	-1.24E-02	4.04E-03	-5.46E-02	4.87E-02	5.66E-04
2006	0.00E+00	6.84E-02	7.62E-03	-5.00E-02	2.72E-02	-8.00E-04
2007	0.00E+00	-1.15E-01	9.18E-03	-1.40E-01	-3.59E-02	-5.15E-03
2008	0.00E+00	-3.35E-01	1.06E-02	1.03E-01	-9.05E-02	-8.31E-03
2009	0.00E+00	-2.48E-01	4.76E-03	2.47E-02	-4.81E-02	-5.27E-03

Table H.38 Process errors from the no-stressor models in TLW38.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	3.22E-01	-3.56E-02	1.13E-03	1.95E-03	1.23E-01	-1.93E-03
1990	-2.15E-02	-2.43E-01	2.97E-04	-2.42E-02	9.46E-02	5.70E-03
1991	9.17E-02	-1.29E-01	4.64E-04	-3.30E-02	3.43E-02	9.16E-03
1992	-2.43E-01	-5.71E-02	9.27E-04	-3.69E-02	-4.38E-03	9.39E-03

1993	2.05E-01	4.35E-02	2.66E-03	-6.86E-03	-2.51E-02	1.66E-02
1994	-6.92E-02	9.10E-02	3.08E-03	2.58E-02	-6.50E-03	1.14E-02
1995	2.84E-01	3.00E-02	3.09E-03	5.54E-02	1.59E-02	1.16E-02
1996	-2.22E-01	-1.17E-01	3.00E-03	3.56E-02	7.97E-02	2.12E-02
1997	3.42E-01	-3.49E-01	4.95E-03	7.30E-02	1.17E-01	1.97E-02
1998	-4.50E-02	-1.37E-01	1.06E-03	2.10E-02	1.42E-01	2.11E-02
1999	-3.63E-01	-5.37E-02	7.99E-04	2.44E-03	7.09E-02	2.43E-02
2000	1.36E-01	7.63E-03	2.10E-03	1.27E-02	-2.18E-02	1.44E-02
2001	2.77E-01	-1.41E-01	3.25E-03	4.21E-02	-4.12E-02	8.05E-03
2002	-9.43E-02	3.81E-02	2.23E-03	1.67E-02	6.47E-02	4.71E-03
2003	-2.49E-01	8.10E-02	3.13E-03	2.11E-02	2.24E-02	2.54E-03
2004	-1.35E-01	-1.39E-02	4.54E-03	3.91E-02	1.84E-02	4.66E-03
2005	3.23E-01	2.36E-02	5.45E-03	5.15E-02	7.34E-02	1.00E-02
2006	6.89E-01	6.81E-02	3.33E-03	2.34E-02	7.20E-02	1.32E-02
2007	-2.00E-01	-2.26E-01	2.55E-03	9.94E-03	6.53E-02	3.27E-03
2008	6.38E-02	-2.56E-01	1.31E-03	-1.17E-02	6.61E-02	3.14E-03
2009	-5.61E-01	-1.23E-01	-7.44E-04	-3.20E-02	-2.59E-03	2.72E-03

Table H.39 Process errors from the no-stressor models in TLW31.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	4.97E-02	-9.44E-02	4.33E-04	-3.37E-02	-1.21E-02	2.12E-04
1990	-2.47E-02	-4.17E-01	6.86E-05	-7.87E-02	-3.83E-02	-3.07E-04
1991	-3.64E-01	-2.78E-01	-1.99E-04	-1.26E-01	-2.58E-02	-6.12E-05
1992	-3.02E-01	-1.22E-01	1.47E-04	-1.50E-01	-2.44E-02	6.34E-04
1993	5.60E-01	-4.58E-02	1.22E-03	-1.60E-01	-1.62E-02	3.64E-04
1994	3.71E-01	-1.05E-03	2.30E-03	-1.42E-01	-7.42E-03	1.58E-03
1995	9.74E-02	-4.80E-02	1.60E-03	-1.28E-01	-4.45E-03	3.79E-04
1996	-3.75E-01	-9.78E-02	2.30E-03	-1.61E-01	-5.39E-03	-6.09E-04
1997	1.73E+00	-1.84E-01	3.97E-03	-1.24E-01	1.68E-03	1.59E-04
1998	1.26E+00	-2.43E-02	2.89E-03	-2.10E-01	1.57E-02	1.48E-04
1999	-3.87E-01	-1.85E-01	-1.38E-03	-1.25E-01	3.71E-02	5.69E-04
2000	-1.00E+00	-3.90E-02	-4.91E-03	-4.24E-02	5.65E-02	1.49E-03
2001	-1.45E+00	-2.18E-02	-6.50E-03	-1.23E-02	7.18E-02	9.84E-04
2002	-7.84E-01	6.77E-02	-6.58E-03	-7.17E-03	6.98E-02	9.03E-04
2003	-1.13E+00	-7.01E-02	-5.89E-03	9.96E-03	6.49E-02	5.38E-04
2004	-2.12E-01	-2.45E-01	-4.22E-03	4.34E-02	4.74E-02	-4.65E-05
2005	-8.91E-02	-1.79E-01	-3.79E-03	5.90E-02	4.67E-02	-6.13E-04
2006	3.58E-01	-1.54E-01	-2.90E-03	-4.82E-03	3.42E-02	-1.14E-03
2007	1.99E-01	-8.22E-02	-2.01E-03	-9.39E-03	1.22E-02	-3.47E-03
2008	-3.98E-01	-2.21E-01	-5.65E-04	-5.32E-02	4.06E-03	-3.96E-03
2009	-4.19E-01	-1.40E-01	-2.46E-04	-4.89E-02	-2.21E-03	-2.13E-03

Table H.40 Process errors from the no-stressor models in TLW33.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	2.08E-01	-4.55E-02	9.86E-04	-3.54E-02	3.23E-02	2.61E-04
1990	9.76E-02	-2.56E-01	3.83E-04	-9.22E-02	-3.27E-02	-9.33E-04
1991	-2.74E-01	-2.74E-01	-3.20E-04	-2.61E-01	-4.73E-02	-1.29E-03
1992	-2.11E-01	-7.86E-02	1.31E-04	-2.20E-01	-5.06E-02	-8.34E-04
1993	4.10E-01	3.06E-03	1.66E-03	-4.08E-01	-3.10E-02	-1.04E-03
1994	2.33E-01	1.32E-02	3.39E-03	-2.33E-01	3.42E-03	-2.46E-03
1995	1.31E-01	-1.43E-01	3.07E-03	-1.86E-01	-2.20E-03	-2.63E-03
1996	-4.83E-01	-1.05E-01	4.29E-03	-1.84E-01	3.60E-03	-3.20E-03
1997	1.43E+00	-1.78E-01	7.38E-03	3.17E-02	-5.39E-03	-1.37E-03
1998	4.20E-01	-1.63E-01	3.59E-03	8.73E-03	4.68E-02	-1.62E-03
1999	-7.06E-01	-1.43E-02	-2.06E-03	2.43E-02	7.89E-02	-1.26E-03
2000	-6.25E-01	-3.80E-02	-4.13E-03	3.76E-03	8.75E-02	-1.96E-03
2001	-2.88E-01	2.45E-02	-5.35E-03	-1.25E-01	9.74E-02	-1.97E-03
2002	1.02E-01	6.78E-02	-5.58E-03	-1.89E-01	7.84E-02	-1.16E-03
2003	-4.16E-01	1.12E-01	-5.73E-03	-1.64E-01	8.31E-02	-1.29E-03
2004	-3.05E-01	5.71E-02	-5.36E-03	-1.12E-01	4.70E-02	-2.16E-03
2005	-1.94E-01	1.42E-01	-4.54E-03	-1.15E-01	5.72E-02	-2.76E-03
2006	1.43E-01	1.18E-01	-3.35E-03	-2.16E-01	2.95E-02	-2.89E-03
2007	9.94E-01	-7.32E-02	-2.27E-03	-2.59E-01	6.12E-03	-4.51E-03
2008	-5.90E-01	-3.41E-01	-8.66E-04	4.89E-02	-2.73E-02	-4.83E-03
2009	-7.51E-01	-2.36E-01	-7.50E-05	-4.94E-03	-2.06E-02	-1.95E-03

Table H.41 Process errors from the no-stressor models in TLW34.

Year	NO_3-N	NH_4-N	Ca	SO_4-S	DOC	TDP
1989	1.13E-01	-1.42E-02	1.20E-03	-1.20E-01	-1.15E-02	2.08E-04
1990	1.10E-01	-2.38E-01	-2.28E-03	-9.63E-02	-7.21E-02	-5.77E-04
1991	-2.28E-01	-1.60E-01	-4.52E-03	-2.07E-01	-4.39E-02	2.09E-04
1992	-1.80E-01	-8.55E-02	-5.82E-03	-1.91E-01	-3.98E-02	-3.06E-04
1993	2.95E-01	4.23E-02	-2.83E-03	-4.04E-01	-1.79E-02	-1.84E-04
1994	1.04E-01	3.46E-02	2.17E-03	-2.34E-01	1.35E-02	4.40E-04
1995	1.70E-01	-3.86E-02	4.42E-03	-1.26E-01	3.54E-03	8.64E-04
1996	-2.67E-01	-1.64E-01	8.81E-03	-1.75E-01	1.08E-02	1.39E-04
1997	5.35E-01	-2.47E-01	1.84E-02	1.18E-01	1.90E-02	1.58E-03
1998	5.77E-01	-2.25E-01	1.41E-02	-2.16E-01	3.63E-02	2.31E-03
1999	-2.22E-01	-1.31E-01	9.70E-03	-1.72E-01	3.32E-02	2.22E-03
2000	-3.46E-01	2.87E-02	9.78E-03	-1.56E-02	3.91E-02	2.44E-03
2001	-1.76E-01	2.74E-02	8.64E-03	-3.34E-02	5.75E-02	2.16E-03
2002	-8.03E-02	1.45E-01	7.25E-03	-8.58E-02	4.23E-02	2.50E-03
2003	-3.16E-01	1.24E-02	6.64E-03	-8.35E-02	3.57E-02	2.23E-03
2004	-2.12E-01	-1.35E-01	8.83E-03	1.68E-02	-1.05E-02	1.25E-03

2005	6.29E-03	-4.81E-02	9.82E-03	1.45E-02	-1.95E-03	8.66E-04
2006	1.96E-02	7.08E-02	7.17E-03	-1.36E-01	-1.09E-02	2.35E-04
2007	6.88E-01	-1.74E-01	5.11E-03	-1.74E-01	-3.93E-02	-2.86E-03
2008	-3.94E-01	-2.73E-01	2.42E-03	-2.89E-02	-2.17E-02	-3.19E-03
2009	-5.49E-01	-1.86E-01	9.45E-05	-4.83E-02	-1.75E-02	-1.48E-03

Appendix I Early warning signal detection results

Early warning signals of decreased stability were detected in most catchments (>70%; Table I.1). Most (>90%) p values of Theil-Sen slopes of standard deviations were less than 0.05. Decreasing Theil-Sen slopes of standard deviations were not test for the significance because that decreasing slopes indicate the stabilizing signals of biogeochemical stability.

Table I.1 Significant ($p < 0.1$) Theil-Sen slopes of standard deviations of process errors in 7-year moving windows (1989-2010); blank cells indicate no significant trend; shaded cells indicate managed catchments.

Catchment	Mean daily SO_4-S ($mg\ L^{-1}\ yr^{-1}$)	Mean daily NO_3-N ($mg\ L^{-1}\ yr^{-1}$)	Mean daily NH_4-N ($mg\ L^{-1}\ yr^{-1}$)	Mean daily TDP ($mg\ L^{-1}\ yr^{-1}$)	Mean daily DOC ($mg\ L^{-1}\ yr^{-1}$)	Mean daily Ca ($mg\ L^{-1}\ yr^{-1}$)
HJA06	1.60×10^{-02}			1.30×10^{-02}		1.59×10^{-03}
HJA07			1.42×10^{-19}			
HJA08		5.93×10^{-12}	3.26×10^{-07}	4.63×10^{-03}		4.60×10^{-04}
HJA09				4.15×10^{-03}		
HJA10		7.98×10^{-19}		1.65×10^{-19}		
ELA01	4.28×10^{-03}		6.90×10^{-04}	7.65×10^{-07}		
ELA02						
ELA03		2.84×10^{-03}		7.40×10^{-07}	7.05×10-20	
MEF02						
MEF04						
MEF05			2.79×10^{-03}			
MEF06						
TLW31		2.50×10^{-02}		4.22×10^{-05}	7.30×10^{-04}	1.10×10^{-04}
TLW32				1.20×10^{-04}		
TLW33		1.65×10^{-02}				
TLW34		8.19×10^{-03}	1.23×10^{-03}	6.18×10^{-05}		
TLW35			3.38×10^{-03}			
TLW38		8.03×10^{-03}				1.54×10^{-05}
DOR00						
DOR03						
DOR05		4.54×10^{-03}	4.46×10^{-03}			
DOR06		8.41×10^{-03}	6.80×10^{-03}			2.30×10^{-04}
BBWM01	1.28×10^{-18}	3.39×10^{-03}	1.16×10^{-18}		5.57×10^{-19}	1.58×10^{-19}
BBWM02	1.21×10^{-02}	3.72×10^{-03}		4.45×10^{-19}	1.31×10^{-18}	1.58×10^{-19}
HBEF01	1.50×10^{-02}				1.00×10^{-06}	
HBEF06					1.14×10^{-07}	
HBEF07	1.07×10^{-02}	3.86×10^{-02}	7.20×10^{-04}	5.16×10^{-02}		
HBEF08	1.62×10^{-02}	1.97×10^{-02}	9.10×10^{-04}	3.03×10^{-02}		4.20×10^{-07}
HBEF09		4.22×10^{-02}		4.53×10^{-02}	6.74×10-20	
CTW02[1]				2.17×10^{-06}		
CTW07[1]				2.70×10^{-06}	7.47×10^{-07}	
CTW17[1]				2.47×10^{-06}		
CTW18[1]	6.86×10^{-07}	8.00×10^{-03}	4.40×10^{-03}	2.39×10^{-06}		
SEF77						7.64×10-20
SEF80					1.37×10^{-19}	
LEF01	1.67×10^{-03}					5.71×10^{-05}
LEF02	2.18×10^{-03}					7.10×10^{-05}
LEF03	2.06×10^{-03}					5.29×10^{-05}
LEF04						5.38×10^{-04}
LEF05				2.67×10^{-02}		
LEF06	1.97×10^{-03}					6.03×10^{-05}

[1]2002 to 2017 at CWT

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