

Utah State University

DigitalCommons@USU

All Graduate Theses and Dissertations

Graduate Studies

8-2020

Boron in the Pariette Wetlands, Uinta Basin, UT

Palak Vasudeva
Utah State University

Follow this and additional works at: <https://digitalcommons.usu.edu/etd>



Part of the [Soil Science Commons](#)

Recommended Citation

Vasudeva, Palak, "Boron in the Pariette Wetlands, Uinta Basin, UT" (2020). *All Graduate Theses and Dissertations*. 7799.

<https://digitalcommons.usu.edu/etd/7799>

This Thesis is brought to you for free and open access by the Graduate Studies at DigitalCommons@USU. It has been accepted for inclusion in All Graduate Theses and Dissertations by an authorized administrator of DigitalCommons@USU. For more information, please contact digitalcommons@usu.edu.



BORON IN THE PARIETTE WETLANDS,

UINTA BASIN, UT

by

Palak Vasudeva

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

of

MASTER OF SCIENCE

in

Soil Science

Approved:

Astrid R. Jacobson, Ph.D.
Major Professor

Jeanette M. Norton, Ph.D.
Committee Member

Grant E. Cardon, Ph.D.
Committee Member

Richard S. Inouye, Ph.D.
Vice Provost of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2020

Copyright © Palak Vasudeva 2020

All Rights Reserved

ABSTRACT

Boron in the Pariette Wetlands, Uinta Basin, Utah

by

Palak Vasudeva, Master of Science

Utah State University, 2020

Major Professor: Dr. Astrid R. Jacobson
Department: Plants, Soils and Climate

Boron, a natural mineral found in marine shales, is present in the Uinta formation underlying the Uinta Basin, Utah. Mining in fossil fuel fields and application of excess irrigation water on agricultural lands in the Pariette watershed (Uinta Basin) leads to mobilization of B from soil, derived in part from the Uinta formation, via surface run off and drainage. Water quality monitoring records from 2006- 2009 reported violations of Utah's B standard for irrigation water 43-100% of the time in the Pariette Wetlands. This study determines B distribution in abiotic (water, sediments) and biotic (benthic macroinvertebrates, aquatic vegetation, fish, bird eggs) samples and establishes correlations between B concentrations in the samples.

Abiotic samples had average B concentrations of $2.87 \pm 0.8 \text{ mg L}^{-1}$ in water and 51.65 mg kg^{-1} in sediments. These levels exceed the lowest-observable-adverse-effect levels (LOAELs) for aquatic plants and organisms like crustaceans, a B sensitive benthic macroinvertebrate (BMI). The average B concentration in macroinvertebrates ($28.45 \pm 12.04 \text{ mg kg}^{-1}$) exceeded the B concentrations of their habitat (water, sediments).

Macroinvertebrate biodiversity was low. Standardized-counts of taxa abundance indicated the increased presence of pollution-tolerant taxa like *Chironomidae*. Depleted freshwater BMI communities of *Ephemeroptera*, *Plecoptera* and *Trichoptera* indicated a stressed, impaired environment. B concentrations in the submerged plants (*Potamogeton*, *Chara*) were higher than in emergent species (*Typha domingensis* and *Typha latifolia*, *Scirpus acutus*, *Phragmites australis*), and in the water, suggesting possible bioaccumulation. B concentrations in waterfowl and fish food sources (e.g., macroinvertebrates) were not high enough to impact adult birds or freshwater fish tolerant of poor water quality (high pH, EC_e).

Simple linear correlations between B in bird eggs and fish and their habitats and food sources were poor to non-existent; however, positive correlations along with high p-values obtained using Mantel tests suggest possible pathways for exposure to B via ingestion of toxic food sources. We concluded that B bioconcentrates in aquatic vegetation, but does not biomagnify in the aquatic food-chain in the Parquette Wetlands. In addition to continued water monitoring, we recommend using submerged vegetation and macroinvertebrates to alert site managers to possible adverse effects of B on wetland fish and bird eggs.

PUBLIC ABSTRACT

Boron in the Pariette Wetlands, Uinta Basin, Utah

Palak Vasudeva

Boron is a naturally occurring mineral in shale and coal beds formed in marine environments, as found in the Uinta Basin. Mining activity and the application of excess irrigation water on agricultural lands in the Pariette watershed lead to mobilization of B via surface run off. Water quality monitoring records from 2006- 2009 reported violations of Utah B standard for irrigation water 43-100% of the time, for water flowing through the Pariette Wetlands. This study aims to determine B distribution in abiotic (water, sediments) and biotic samples (macroinvertebrates, aquatic vegetation, fish, bird eggs), and to establish correlations between B concentrations in the samples.

Abiotic samples had average B concentrations of $2.87 \pm 0.8 \text{ mg L}^{-1}$ in water and 51.65 mg kg^{-1} in sediments. The concentrations exceeded established lowest-observable-adverse-effect levels (LOAELs) for aquatic plants and sensitive invertebrates like crustaceans. The total average B concentration in benthic macroinvertebrates ($28.45 \pm 12.04 \text{ mg kg}^{-1}$) was higher than B concentrations in their habitat (sediment and water). Benthic macroinvertebrate (BMI) biodiversity was low in all four wetland units with increased populations of pollution tolerant taxa like *Chironomidae* (midges). Reduced numbers of freshwater BMIs such as *Ephemeroptera* (mayflies), *Plecoptera* (stoneflies) or *Trichoptera* (caddisflies) indicate environmental stress and impaired conditions. Submerged plants (*Potamogeton* (pondweed) and *Chara* (stonewort)) had higher total

average B concentrations than emergent plants (*Typha domingensis* and *Typha latifolia* (cattails), *Scirpus acutus* (bulrush), and *Phragmites australis* (common reed)), and higher B concentrations than the water, suggesting B bioconcentration. The B content in waterfowl and fish food sources were not high enough to impact adult birds or freshwater fish tolerant of poor water quality. Simple linear statistical correlations between B in biotic samples (bird eggs, fish) and their habitats and food sources were poor to non-existent; however, positive correlations and high p-values established using Mantel test coefficients suggest possible pathways for exposure to B via ingestion. We concluded that even though B bioconcentrates in aquatic vegetation it is not biomagnifying in aquatic food-chain components we investigated in the Parquette Wetlands. In addition to continued water monitoring, we recommend using submerged vegetation and macroinvertebrates to alert site managers to adverse effects of B on wetland fish and bird eggs.

ACKNOWLEDGMENTS

I would like to express my gratitude to my amazing parents, Amrit and Shelly, who taught me the value of an education and the role of hard work in accomplishing my dreams. Thank you to my wonderful sister, Aakriti. I am blessed to share my life with her. I am indebted to Anurag Singh, who guided and inspired me to realize a better life. I appreciate the love and support of Wasif Shaikh and Renuka Gupta in fulfillment of a promise to help me complete my degree.

I am grateful for the instruction and mentoring of my advisor, Dr. Jacobson, whose advice and guidance have helped me become a better researcher and diligent worker. For input that has enhanced my research, I wish to thank my committee members Dr. Jeanette Norton and Dr. Grant Cardon. Thank you to Dr. David Powelson of the USU Soil Chemistry Lab Group for help with laboratory training and analytical assistance.

I would also like to express my appreciation to John Manoha and Swadesh Patra who encouraged me to complete my degree. Finally, thanks to my friends and colleagues at the Utah State University Logan campus for believing, supporting and encouraging me to complete this thesis.

Palak Vasudeva

CONTENTS

	Page
ABSTRACT	iii
PUBLIC ABSTRACT	v
ACKNOWLEDGMENTS	vii
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ABBREVIATIONS	xii
CHAPTER	
I. LITERATURE REVIEW	1
Introduction	1
Occurrence and Uses	3
Environmental Release and Fate	4
Boron Importance and Toxicity	11
Boron and the Pariette Wetlands	18
Pariette Wetlands	19
References	24
II. BORON IN PARIETTE WETLANDS.....	36
Introduction	36
Materials and Methods	39
Results and Discussion.....	50
Conclusions	65
References	67
APPENDICES.....	94

LIST OF TABLES

Table	Page
1-1	Water Quality Standards for Water in the Pariette Draw Watershed35
2-1	Water quality characteristics of ponds in Pariette Wetlands from the taxonomic classification of BMI split samples by NAMC.....90
2-2	Mantel correlations between abiotic and biotic samples collected in the Pariette Wetlands.91
2-3	Common and scientific names along with feeding behavior of the 15 waterfowl species for which egg samples were collected at sites in the Pariette Wetlands, UT in July, 2014 (https://www.ducks.org/).....92
2-4a	Site-wise concentrations of ions present in pond water samples (n = 18) collected at the Pariette Wetlands analyzed using ICP–AES93
2-4b	Visual MINTEQ (Gustafsson, 2014) results detailing dominant species and their distribution in pond water samples collected at the Pariette Wetlands.94
A1	Input data (B concentrations) used to compute statistical correlations96
A2	Visual MINTEQ input parameters and data for calculating the dominant species distribution in the pond water samples collected at Pariette Wetlands119

LIST OF FIGURES

Figure	Page
1-1 Chemical structures of common forms of B. I. Borate Ion ($\text{B}(\text{OH})_4^-$) II. Boric Acid (H_3BO_3) III. Boron Oxide (B_2O_3) IV. Anhydrous Borax ($\text{Na}_2\text{B}_4\text{O}_7$) (modified from Kim et al., 2016).....	34
2-1a Map of Utah showing Pariette Watershed location (blue) within the Uintah Basin (green) in the North – East part of the state (modified from Wingert and Adams, 2010).....	74
2-1b Detailed Map of the Pariette Watershed showing the three main land-use components – Agricultural area, Pariette Draw and the Pariette Wetlands (modified from Morrison et al., 2015).....	75
2-2 Map of individual ponds in each unit at Pariette Wetlands. The sampling sites for bird eggs (orange circles), fish (pink squares) and other samples – water, sediments, BMIs and aquatic vegetation (green triangles) are also shown (Jones, 2014).....	76
2-3 Monthly average B mass flux (2009) calculated using water flow data measured at the UDEQ monitoring stations in the Pariette Wetlands (2008–2009 dataset, Wingert and Adams, 2010).....	77
2-4a Pondwater pH measured at three sites in each pond sampled within the four units at the Pariette Wetlands.....	78
2-4b Speciation diagram for B as a function of pH as predicted by the Visual MINTEQ.....	79
2-5 B concentrations in pond water in four units of the Pariette Wetlands.	80
2-6 Total plant-available B concentrations in the pond sediment layers at depths 0-2 and 2-5 cm collected from all four units in the Pariette Wetlands.	81
2-7 Box and whisker plot of the total B content in BMI samples collected at four pond-units in the Pariette Wetlands.	82
2-8 Box and whisker plot comparison of total B content in roots, shoots and inflorescence of emergent aquatic vegetation species (<i>Typha domingensis</i> and <i>Typha latifolia</i> (cattails) and <i>Scirpus acutus</i> (bulrush) collected at four units of the Pariette Wetlands.	83

2-9	Total B concentration in submerged aquatic vegetation species <i>Potamogeton filiformis</i> (pondweed) and <i>Chara spp.</i> (stonewort) collected at the Pariette Wetlands.	84
2-10	Total B concentrations in all freshwater fish species collected within the four units in the Pariette Wetlands.	85
2-11	B distribution in <i>Lepomis cyanellus</i> (green sunfish), which were sampled extensively in all four units of the Pariette Wetland complex.	86
2-12	Box and whisker plot demonstrating B distribution in waterfowl eggs collected at sampling sites in all four pond-units at the Pariette Wetlands.	87
2-13	Box and whisker plot displaying B distribution in the dabbling eggs of American Coot, <i>Fulica Americana</i> , sampled at sites in all four pond units of the Pariette Wetland complex	88
2-14	Infographic describing B bioconcentration and bioaccumulation pathways in the Pariette Wetland food web.	89

LIST OF ABBREVIATIONS

pKa	Acid Dissociation Constant
ECe	Electrical Conductivity of a Saturated Paste Extract
B	Boron
Se	Selenium
TDS	Total Dissolved Solids
EDTA	Ethylenediaminetetraacetic Acid
SOM	Soil Organic Matter
BMI	Benthic Macro Invertebrates
SAR	Sodium Adsorption Ratio
SRM	Standard Reference Materials
DW	Dry Weight
WW	Wet Weight
ppm	Parts Per Million
TT	Toxicity Threshold
NOAEL	No Observed Adverse Effect Level
LOAEL	Lowest Observed Adverse Effect Level
LD ₅₀	Lethal Dose for 50% mortality
LD ₁₀₀	Lethal Dose for 100% mortality
MATC	Maximum Acceptable Toxicant Concentration
TMDL	Total Maximum Daily Load
SD	Standard Deviation
MDL	Method Detection Limit
QA/QC	Quality Assurance/Quality Control
COV	Coefficient Of Variance
NIST	National Institute of Standards and Technology
UDWQ	Utah Division of Water Quality
BLM	Bureau of Land Management
UDEQ	Utah Department of Environmental Quality
NRCS	Natural Resources Conservation Service
UWQB	Utah Water Quality Board
EPA	Environmental Protection Agency
USUAL	Utah State University Analytical Laboratory
TERL	Trace Element Research Laboratory
ICP-AES	Inductively Coupled Plasma–Atomic Emission Spectroscopy

CHAPTER 1

LITERATURE REVIEW

1. Introduction

Boron is an inorganic, non-volatile, dark-brown metalloid with a specific gravity of 2.34 g cm^{-3} . Pure boron exists as black, monoclinic crystals that are insoluble in water. They melt at $2300 \text{ }^\circ\text{C}$ and sublime at $2550 \text{ }^\circ\text{C}$ (Eisler, 1990; USEPA 1994a). This Group IIIA element (Atomic no. = 5) has three valence electrons in its outer shell. Boron is chemically as diverse as carbon with a +3 oxidation state (electron deficient), and thus rarely exists in its elemental form (Eisler, 1990). Impure B occurs in nature as a brown or yellow amorphous powder. It has a strong affinity for oxygen (O) but also binds with ions like hydrogen (H), sulfur (S), nitrogen (N) sodium (Na), calcium (Ca), or magnesium (Mg) to form inorganic borates (Parks and Edwards, 2005; Cotton et al., 1999; Budavari et al., 1996; Holleman et al., 1985). Boron oxide is naturally present in 200 minerals in the earth's crust as borax, kernite, colemite and ulexite (USGS 2008). The most common and ecologically significant forms of B are borates (Fig. 1-1) like boron oxide (B_2O_3), boric acid (H_3BO_3) and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$) with most B compounds eventually transforming to these forms (Eisler, 1990; EPA, 2008).

Borates are oxyanions with B bound to three oxygen atoms as shown in Fig. 1-1 (Parks and Edwards, 2005). They occur in the clay rich sediments of sedimentary rocks such as colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$), boronatrocalcite ($\text{CaB}_4\text{O}_7\text{NaBO}_2 \cdot 8\text{H}_2\text{O}$), boracite ($\text{Mg}_7\text{Cl}_2\text{B}_{16}\text{O}_{30}$) and are released into the environment (air, water) by weathering processes

(Butterwick et al., 1989). Borates are also mobilized during soil organic matter (SOM) decomposition, desorption from soil minerals surfaces, land application of municipal sewage waste water, irrigation with water from fields near coal beds, through coal burning or geothermal steam power plants, by industries like copper smelters and fiberglass production, and through surface run off from fields amended with herbicides and fertilizers (Butterwick et al., 1989; Howe, 1998; Koç, 2007).

Boric Acid (H_3BO_3), also known as hydrogen borate, occurs in its free state in many volcanic regions. Sea water contains the highest quantities of boric acid and its salts (Eisler, 1990). It behaves as a weak Lewis acid upon dissociating in freshwater at a pKa of 9.24 at standard temperature conditions (25 °C) with solubility directly dependent on temperature (Kochkodan et al., 2015). The melting and boiling point of boric acid are 169 °C and 300 °C, respectively (Eisler, 1990). It was first artificially synthesized in 1707 (Greenwood and Thomas, 1973).

Borax (sodium tetraborate decahydrate; $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$) is the most common borate with a melting point of 75°C and a boiling point of 320°C (Eisler, 1990). Historically, it was traded by the Babylonians (> 4,000 years ago) for use in cleaning and welding of gold. The Romans and Egyptians used boron compounds to manufacture borosilicate glass. Borax was also used as a cleaning agent in ancient Greek and Roman empires (Greenwood and Thomas 1973). By 1556, borax was widely used throughout Europe as flux and a food preservative in Europe and America but was eventually discontinued (Greenwood and Thomas, 1973).

2. Occurrences and uses

Boron is the 51st most abundant element on the earth's crust with an average worldwide concentration of 8 mg kg⁻¹ (approximately 0.0008%) (Cotton et al., 1999). Elemental B is unavailable in nature but oxygenated forms like inorganic borates are mined and extracted from sedimentary rocks, like shale, and coal beds on the ocean floor (ATSDR, 1992; HSDB, 2004). Historically, the earliest source of borax were geysers in Tuscany, Italy which were responsible for the supply of boric acid to Europe from 1820–1950s (Matterson, 1980). Sodium borates were discovered at Kırka and Anatolia, Turkey in 1960 and have been developed to meet the increasing worldwide demand for B compounds (Kiliç, 2004). Borate deposits discovered in California and Nevada (United States) produce ulexite ($\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 5\text{B}_2\text{O}_3\cdot 16\text{H}_2\text{O}$) and colemanite ($2\text{CaO}\cdot 3\text{B}_2\text{O}_3\cdot 5\text{H}_2\text{O}$) (Matterson, 1980). The 2nd largest borate ore deposit in Boron, California (Kramer deposit) was discovered in 1913, subsequently producing minerals including colemanite (1913), tincal ($\text{Na}_2\text{B}_4\text{O}_4\cdot 10\text{H}_2\text{O}$; 1925) and rasorite (kernite, $\text{Na}_2\text{O}\cdot 2\text{B}_2\text{O}_3\cdot 4\text{H}_2\text{O}$; 1926) (Travis and Cocks, 1984). Presently, the largest producers and consumers of B compounds are Turkey, United States and Russia followed by Argentina, Chile and China (USGS, 2004).

2.1. Major Uses of Boron

Boron, after separation from its mineral ore, is used in multiple commercial industries such as addition to glass components to produce fiberglass with increased mechanical strength and chemical durability (Smith, 1986). The glass industry consumes a majority (56%) of the B mined in the United States with 42% used in the manufacture of insulation fiberglass and 24% for textile grade fiberglass (Argust, 1998). Textile grade fiberglass includes low-thermal expanding glasses (Heat resistant Pyrex, Borosilicate

glass), ceramic glazes, frits and enamels produced only by using a low-sodium mineral ore of boron like colemanite to amplify glass transition temperature of the components (Smith, 1986).

Other industries utilizing high quantities of B are personal care items – detergents, soaps, bleaches, cosmetics (10%), agricultural micronutrients (7%), and miscellaneous uses – flame retardants, catalysts, purification agents and leather tanning (27%) (Rio Tinto Borax, 2004; USGS, 2004; USGS, 2009). Organic herbicides and insecticides made from borates are widely used to protect crops and pressure treat wood to protect it from rot (Williams and Amburgey, 1987).

3. ENVIRONMENTAL RELEASE AND FATE

Sedimentary rocks contain B mineral deposits with highest B content in lacustrine, marine or fluvial sediments. Boron is released into the environment by the slow, natural weathering of bedrock containing these sediments and via volcanic or geothermal processes (Butterwick et al., 1989). Boron concentrations range from 15 to 300 mg kg⁻¹ for rocks, < 10–20 mg kg⁻¹ for soils, 0.1 – 0.5 mg L⁻¹ for surface waters and 5 mg L⁻¹ for seawater (ECETOC, 1997). Moore (1991) estimated the annual, natural release of B at 360,000 tons of which the anthropogenic sources include atmospheric release from power plants, chemical plants and manufacturing facilities; wastewater discharge (containing boron from domestic washing agents) and agricultural run-off (containing dissolved boron from fertilizers, herbicides, insecticides) (Emiroğlu, 2010). Highly mobile, non-bonded B from coal ash in landfills can leach into the hydrological system via the soil system. Boron released from aforementioned anthropogenic sources along with natural sources increase

the diffusion of B into the environment (Arslan, 2013). The mobile B cycles from soils and water bodies to organic matter and the abiotic environment as decaying matter.

3.1. Atmosphere/Air

Boron enters the atmosphere from ash in areas with high volcanic activity or due to boric acid volatilization from seawater. With an estimated B removal from marine sources ranging between 800,000 – 4 million tons y^{-1} of the total global release, seawater evaporation is deemed the largest contributor of B in the atmosphere (Anderson et al., 1994a). Stable isotope studies of rainwater provide proof for sea salt sublimation as a source of atmospheric B (ATSDR, 1992; HSDB, 2004). For example, in French coastal areas sea salt has been observed to contribute 22.3% of B in the atmosphere. Sea salt contributions to atmospheric B decrease inland where geologic (crustal dust), biogenic, and anthropogenic sources (e.g., fossil fuel burning, fertilizer applications) become dominant (Millot et al., 2010). Boron percentages in dust samples from borax packaging facilities ranged between 11.8 to 15.2% by weight (Culver et al., 1994a). Anthropogenic sources of B like fly ash produced in burning of coal or biomass, contribute approximately 9-27% of total anthropogenic B (180,000 – 650,000 tons y^{-1}) released to the atmosphere (Bertine and Goldberg, 1971; Anderson et al., 1994a). Other sources like aerosols of boron compounds (borides, boron oxides, borates, organoboranes or halides such as boron trichloride or trifluoride), borate particulate matter in areas where borates are processed for commercial products also majorly contribute to atmospheric boron (ATSDR, 1992; Culver et al., 1994; HSDB, 2004; Parks and Edwards, 2005). Due to low B volatility, the ambient atmospheric B levels in the United States are not significant, between $< 5 \times 10^{-7} \text{ mg m}^{-3}$ and $8 \times 10^{-5} \text{ mg m}^{-3}$ with an average of $2 \times 10^{-5} \text{ mg m}^{-3}$ (Howe, 1998). However, due to the huge volume of

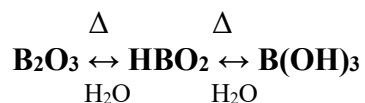
the atmosphere these low concentrations can potentially become significant (WHO, 1998). Particulate B emissions cannot be degraded in the atmosphere and eventually accumulate on the surfaces of large water bodies such as oceans, seas and water reservoirs by the processes of dry deposition and precipitation (Culver et al., 1994b; Parks and Edwards, 2005).

3.2. *Water*

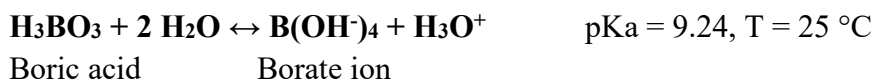
Boron is highly water soluble and hence widely distributed in hydrological systems. In nature borates are released to groundwater from bedrock with high B contents, streams flowing through areas with B-rich sedimentary or clayey soils, and coastal drainage basins. Anthropogenic sources primarily include irrigation water run-off from fields amended with B-containing fertilizers or pesticides and municipal sewage (Waggot, 1969; Deverel and Millard, 1988; Butterwick et al., 1989; Howe et al., 1998). A survey of 1,577 surface-water samples from sites across the United States detected B in 98% of the samples with concentrations between 0.001 and 5 mg L⁻¹. Boron content in water varies with local geology and hydrological features, proximity to seawater and anthropogenic sources (Argust, 1998). In the United States, average B concentrations in surface and ground water fluctuate between 0.017 and 1.904 mg L⁻¹, averaging at 0.1 mg L⁻¹. However, there is a lack of consensus between reported B concentrations in water reserves such as groundwater, surface water and ice (Kemp, P. H., 1956; Helmann, H. and Schumacher, M., 1977; USEPA 1986b; Butterwick et al., 1989).

In order to understand B mobility, it is important to consider geological, hydrological and organic factors influencing its partitioning. Parameters like background B concentrations, temperature, salinity and pH can greatly affect the chemical species of B

present. Boron is mined from its ore as boric oxide (B_2O_3), which yields boric acid (H_3BO_3 , $B(OH)_3$) after undergoing an exothermic reaction with water (Perry and Suffet, 1994; Howe, 1998; Kochkodan et al., 2015). The chemical multi-reaction is described as:



Boric acid dissociates into borate ions ($B(OH^-)_4$) in the presence of freshwater with an acid dissociation constant (pKa) of 9.24 ($T=25\text{ }^\circ\text{C}$). As temperature, pH and water salinity vary, boric acid solubility in water changes affecting the dominant species concentration (Kochkodan et al., 2015). Boric acid solubility increases with increase in temperature and pH. Undissociated boric acid is the dominant B species at low pH while dissociated borate ions dominate high pH ranges in the aqueous solution (Perry and Suffet, 1994; Howe, 1998). The equilibrium reaction for the dissociation of boric acid is expressed as follows:



Multiple research studies report salinity as a negative influence on boric acid dissociation in water with 76% of the seawater B existing as undissociated boric acid (H_3BO_3) and 24% as borate ion ($B(OH^-)_4$) either in its free state or complexed with metal ions (Mellor, 1980; Eisler, 1990; Davis, 2000; Parks and Edwards, 2005). On the other hand, fresh water tends to contain equal percentages of undissociated boric acid (H_3BO_3) and complexed or free state borate anion ($B[OH]^{-4}$) (Choi and Chen, 1979; Eisler, 1990; Parks and Edwards, 2005). Chemical reactions like acid-base reactions, co-precipitation or polymerization with aluminum (Al), silicon (Si) or iron (Fe) in water and adsorption-desorption reactions

(highest in pH range 7.5-9) affect the mobilization of waterborne B to soils and sediments (Biggar and Fireman, 1960; Rai et al., 1986; Cotton et al., 1999).

3.3. Soils

Boron is present in rocks and soils in low concentrations (approximately 10-20 ppm), but sources can also include atmospheric deposition, decomposing organic matter, rising water tables, rock weathering, application of fertilizers or landfill leaching (Arora and Chahal, 2010). Majority of B in soil solutions comes from agricultural fertilizers or application of irrigation water to soil (ECETOC, 1997; Nable, Banuelos and Paul, 1997). The U.S. soil boron concentration varies from 20 to 300 mg kg⁻¹ with an average of 31 mg kg⁻¹ (Powell et al., 1997).

Boron mobility in soils is altered by type and content of clay minerals, amount of amorphous Al/Fe oxides, soil organic matter (SOM), soil texture and soil pH and salinity (Bingham et al., 1971; Bingham et al., 1985; Sakata 1987; Yermiyahu et al., 1995; Goldberg et al., 2005; Communar and Keren, 2006). For example, Coarse soils with CaCO₃ deposits and low SOM show increased B sorption at high soil pH; whereas, coarse soils rich in Al/Fe oxides show increased B sorption at low soil pH (Griffin and Burau, 1974; Rai et al., 1986; Butterwick et al., 1989; Howe, 1998; Arora and Chahal, 2010). Research with amorphous Al oxide first shows B adsorption increasing as pH increase from 6 to 8 (maxima at pH = 8) and then decreasing even though pH keeps going higher (Sims and Bingham, 1968 a,b). Goldberg and Glaubig (1988) showed that B adsorption maxima (as observed by Sims and Bingham) starts to shift to lower pH (by one pH unit) with increasing residence times. This behavior is attributed to the formation of an insoluble Al hydroxide. In their experiment, they also noticed a significant decrease in boron adsorption after the

addition of Si ions into the solution. They deduced that when B was added to the ion solution alone or before the addition of Si ions, its adsorption was the highest. This suggested that B was unable to displace Si from the adsorption sites even though it is capable of effectively competing for the same sites (Goldberg and Glaubig, 1988). Su and Suarez (1995) found that B forms inner-sphere complexes not only with Al/Fe hydroxides, but also with clay minerals like allophane and kaolinite. However, almost no B sorbed to quartz or calcite. The presence of aragonite favors co-precipitation of B more than calcite. This happens because both aragonite formation and B co-precipitation are favored in the presence of Mg (Parks and Edwards, 2005). Interestingly, B co-precipitation with calcite increases with increasing sodium chloride (NaCl) concentrations; whereas, B co-precipitation with aragonite decreases with NaCl. It has also been noted that volcanic soils, which develop in areas of high geothermal activity, are rich in B (Eisler, 1990; Howe, 1998; Parks and Edwards, 2005).

3.4. Sediments

The geometric mean of B concentrations in 16 Great Lake riparian-environment sediments ranged from 0.5–7.9 mg kg⁻¹ dry weight in 1993–94 (Lowe and Day, 2002). Similarly, a survey of sediments in uncontaminated lakes in British Columbia reported boron concentrations ranging from 2.8–20.5 mg kg⁻¹ dry weight (Moss and Nagpal, 2003). A survey of B in California evaporation pond sediments used the baseline mean B concentrations of 23 mg kg⁻¹ for soils of the western states as a background value for comparison with B concentrations in the collected pond sediment samples (Perry et al., 1994). In that study, sediments (0–7 cm) in 95 evaporation ponds receiving irrigation runoff from California's Tulare Basin had B concentrations ranging from 18.9–472 mg kg⁻¹ with

a geometric mean of 112 mg kg^{-1} in samples collected in 1988-1989 (Perry et al., 1994). There was a close relationship between the B concentrations in the sediments, the soils on which the ponds were located and the geological setting. The highest geometric means were found on alluvial fans derived from marine sediments known to be enriched in B (Perry et al., 1994). In wetland systems, B may be bound to organic matter or clays in the sediments or suspended matter (USDI, 1998). Majority of B in aquatic systems is expected to sorb onto clayey sediments which decrease the amount of B released into soil solution so that only 5% of the B is phytoavailable (Maier and Knight, 1991; Moss and Nagpal, 2003; Arora and Chahal, 2010). Boric acid and borate ions remain in a state of stable equilibrium in aquatic and plant ecosystems making it easier for B not adsorbed onto sediments or taken up by the plants to be bioavailable for aquatic organisms over long periods of time (Perry et al., 1994). Microbial activity releases high quantities of boron to the ecosystem from organic matter during oxidation processes in aerobic environments (Parks and Edwards, 2005).

3.5. Biota

Boron is an essential micronutrient for plants, which is mostly present in its non-ionized form in soils at a pH optimum for plant growth (Goldberg, 1993). It plays a vital role in carbohydrate metabolism, sugar translocation, pollen germination, hormone action, growth, nucleic acid synthesis and membrane structure function in plants (Parks and Edwards, 2005). It has shown to help in the maturation of long bones in chicks (Hunt, 1994). It positively influences rat brain activity along with decreased calcium, magnesium and phosphorus absorption in its absence (Parks and Edwards, 2005). Some arbitrary evidence shows the importance of B in the utilization and metabolism of calcium in

humans. There are indications that B helps to improve motor function, response to estrogen ingestion and prevention of arthritis (Nielsen, 1994; Newnham, 1994). Contrarily, multiple confirmed studies show excessive B causing toxicity issues.

4. Boron importance and toxicity

Several research studies reported elevated ambient B concentrations in areas associated with seawater, marine sediments and thermal springs/ground water nearby large deposits of B minerals. The high background concentrations may further be elevated by human activities such as agricultural and mine drainage water, municipal waste, coal fired power plants and coal ash in landfills (Eisler, 1990; Howe, 1998; Parks and Edwards, 2005). As such, research investigating eco-toxicological concerns and risks associated with the movement of B through the environment and its interaction with plant and animal ecosystems has become a primary concern (Argust, 1998). Research reported B bioconcentration (increase in contaminant concentration due to absorption from medium) in aquatic vegetation and bioaccumulation (increase in contaminant concentration by ingestion) in macroinvertebrates and fish in aquatic environments (USDI, 1998). For example, a 7-day exposure of green algae (*Chlorella pyrenoidosa*) to boric acid concentrations of 50–100 mg L⁻¹ resulted in bioconcentration of B by the algae (Fernandez et al., 1984). Similarly, filamentous algae and aquatic insect samples collected from the San Joaquin Valley in California also reported high B concentrations ranging from 390 to 787 mg kg⁻¹ (algae) and 22 to 340 mg kg⁻¹ (insects), even though they were exposed to tile drainage with lower concentrations of B (12–41 mg L⁻¹) (Ohlendorf et al., 1986; Schuler, 1987; Hothem and Ohlendorf, 1989). Aquatic plants like duckweeds (*Lemna gibba*) were

found to bioaccumulate B along with other nutrients up to concentrations of 248 mg kg^{-1} and were termed as 'hyper bioaccumulators' effective for phytoremediation in wetlands or wastewater treatment facilities (Glandon and McNabb, 1978; Inoue et al., 1980; Del-Campo Marin and Oron, 2007). In spite of many studies evidencing B bioconcentration, it is estimated that B does not biomagnify (increase in contaminant concentration in a food chain) in an aquatic food chain (WHO, 1998).

In order to quantify and determine aquatic contaminant toxicity levels for living organisms concentration terms such as toxicity-threshold (TT), no-observed-adverse-effect level (NOAEL), lowest-observed-adverse-effect level (LOAEL), and lethal dose (LD_{50} , LD_{100}) are used to design water quality standards and design specific limits to prevent phytotoxicity. These limits called total-maximum-daily-loads (TMDLs) are defined as the maximum concentration of a water pollutant that can be assimilated in a water body without affecting its water quality standard. TT represents the lowest concentration of a substance that can consistently produce symptoms of toxicity in a population. NOAEL and LOAEL, respectively define the highest and lowest concentration of a contaminant producing no adverse effects in the population exposed. LD_{50} and LD_{100} are used to represent the contaminant dosage resulting in 50% and 100% mortality in organism populations. These concentration limits change depending on the species and kinds of living organisms being protected. Other countries may establish water quality criteria at other B concentrations and for other reasons. For example, in South Africa the B water quality criterion is established at 1 mg L^{-1} to protect the aquatic plant ecosystem (Roux et al., 1996). Similarly, the European Union drinking water quality criterion is 1 mg L^{-1} ;

whereas in Canada and New Zealand, the B limits in drinking water are 5 mg L⁻¹ and 1.4 mg L⁻¹, respectively (Parks and Edwards, 2005).

4.1. Aquatic organisms

4.1.1. Macroinvertebrates

Boric acid, often used as an effective control tool for terrestrial invertebrates like termites, cockroaches, ants etc., works by attacking a multitude of bodily functions that eventually kill these insects thus demonstrating the toxic effects of boron. However, there is little literature on B effects on aquatic invertebrates. Existing data suggest that although extremely high B concentrations (approx., 115–2,797 mg L⁻¹) may be necessary to kill aquatic invertebrates, adverse effects are observed at much lower concentrations (USDI, 1998). A research study by Gersich (1984) on the aquatic invertebrate *Daphnia magna* (water flea) reported reduced fecundity (fertility). There was a decrease in the brood number, total young produced, mean brood size and mean body length of the *Daphnia*. The LOAEL was reported as 13 mg L⁻¹. Lewis and Valentine (1981) also conducted an exposure study on *Daphnia* neonates using boric acid, observing no effect at B concentrations of 6.4 mg L⁻¹, but as exposure time increased to 48 hours, LD₅₀ and LD₁₀₀ were measured at 115–246 mg L⁻¹ and 420 mg L⁻¹, respectively. Another macroinvertebrate species, *Chironomus decorus* (midges) were found to be more tolerant than *Daphnia* with LD₅₀ for boric acid at 1,376 mg L⁻¹ when exposed for 48 hours even though a significant reduction in their growth rate was noted at LOAEL 20 mg L⁻¹ (Maier and Knight, 1991). Amongst marine aquatic invertebrates, mysid shrimp (*Mysidopsis bahia*) showed toxicity to elevated B at 170 mg L⁻¹, salinity = 2×10^{-8} mg L⁻¹ (Pillard et al., 2002). Studies also showed that sea urchin (*Anthocardaris crassispina*) embryos succumbed to boric acid

concentrations of 75 mg L^{-1} while mosquito larvae for three different species showed LD_{100} at boric acid concentrations $> 524 \text{ mg L}^{-1}$ for an exposure time of 48 hours (Koyabashi, 1971; EPA, 1976).

4.1.2. Fish

A number of studies conducted in aquatic systems with elevated B concentrations have established possible bioaccumulation in fish depending on their habitat. Marine species have been observed to remain unaffected by high B concentrations than the fresh water counterparts. This is due to higher B distribution in seawater. Fresh water species from the Cold River drainage area in Western Canada were analyzed by Tsui and McCart (1981) to check for possible correlations between B bioaccumulation and feeding behavior of the fish: **Predators** – northern pike (*Esox Lucius*), lake trout (*Salvelinus namaycush*); **Plankton-feeders** – lake herring (*Coregonus artedii*) and **Bottom feeders** – lake whitefish (*Coregonus clupeaformis*), white sucker (*Catostomus commersoni*). The authors found high B concentrations in the muscle tissues of all species. The average B concentration in the fish ranged from 3.23 to $12.4 \mu\text{g g}^{-1}$ (wet weight) at $0.063 \text{ mg B L}^{-1}$ in water. However, a similar study conducted in the Precambrian Shield lake in Ontario, Canada; protected from human impact; showed lower B content (1.8 – $2.9 \mu\text{g g}^{-1}$ and $2.6 \mu\text{g g}^{-1}$, wet weights) in the undeveloped muscle tissue in freshwater fish (blue gill and common carp) and soft tissue of the clam (*Elliptio dilitata*) (Wren et al., 1983). The fresh water organism most sensitive to boron toxicity is the rainbow trout, having a LOAEL of 0.1 mg L^{-1} (Parks and Edwards, 2005). Samples of mosquitofish (*Gambusia affinis*) collected from the San Joaquin River and its tributaries receiving agricultural subsurface drainage showed elevated B concentrations between 3.5 and $5 \mu\text{g g}^{-1}$ B (wet weights) due to natural boron

deposits and their mining in the adjacent areas (Saiki and May, 1988). Studies by Soucek et al. (2011) reported acute boron toxicity for aquatic organisms like fish, stonefly and mollusks at LD₅₀ ranging from 79.7 to 544 mg L⁻¹.

4.2. Aquatic Plants

Boron is important for carbohydrate metabolism, sugar translocation, pollen germination, hormone action, growth, nucleic acid synthesis and membrane structure function in higher plants. On one side of the spectrum, plants with a B deficiency display symptoms like stunted root and leaf growth, bark splitting, reduced pollen germination; while on the opposite side of the spectrum, high B concentrations in the soil solution leads to phytotoxicity (Parks and Edwards, 2005). Toxicity symptoms includes chlorosis of the leaf ultimately causing leaf loss along with loss of photosynthetic and reproductive capability, resulting in plant death (Parks and Edwards, 2005). In most plant species, the gap between B deficiency and toxicity varies between 2–5 mg L⁻¹; however, there are some agricultural crops and aquatic plants that are more resilient to high B levels and can tolerate up to 10 mg L⁻¹ in water without displaying symptoms of toxicity (Sprague et al., 1972; Gupta et al., 1985; Butterwick et al., 1989; Eisler, 1990). Sensitive plant species, like *Elodea canadensis* (waterweed) display B sensitivity at ambient levels of 1 mg L⁻¹ (Perry et al., 1994). Another commonly found plant, *Hydrocotyle umbellata* became chlorotic at B concentrations < 1 mg L⁻¹ (Powell et al., 1997). Furthermore, some plants, like dicotyledons, bioconcentrate and store more B than monocotyledons (Cowgill, 1974). Widgeon grass, growing abundantly in the Kesterson reservoir in San Joaquin Valley of California, accumulated up to 120 – 780 mg kg⁻¹, DW, B with the highest value (1630 mg kg⁻¹) recorded in an evaporation pond. Such a high quantity of dietary B is enough to cause

irreparable damage to avian reproduction if consumed as the sole food source (Hothem and Ohlendorf, 1989). Other studies conducted in the same region supported bioconcentration claims showing elevated B concentrations in widgeon grass seed (430-3500 mg kg⁻¹) and algae (390-790 mg kg⁻¹) at low water (2-5 mg L⁻¹) and sediment concentrations (20 mg kg⁻¹) (Schuler, 1987; Hoffman et al., 1991). Emergent aquatic plants take up B from the soil/sediment solution, and most floating plants absorb it from the water and sediments. Submerged plants, however, take up B only from water (Hutchison, 1975). Of all these types, floating plants accumulate the highest amount of boron in their leaves (Boyd and Walley, 1972; Gupta et al., 1985). In a study by Perry et al. (1994), the NOAEL and TT for crops and aquatic plants was found to be at 0.5 mg L⁻¹ and 10 mg L⁻¹, respectively.

4.3. *Birds*

Even though there is evidence that small quantities of B is essential in birds, it is classified as a potential teratogen. This classification is based on the results of a study by Landauer (1952) involving injection of boric acid and borax in domestic chicken embryos producing mortality and developmental abnormalities. Numerous studies were conducted to ascertain toxic effects of elevated B on birds revealing that bird eggs and embryos at early growth and developmental stages are susceptible to increased B concentrations (Parks and Edwards, 2005). The developmental abnormalities caused by high concentrations of B include rumplessness, facial defects, melanin formation, adversely affected brain biochemistry and reduction in duckling weight gain (Landauer, 1952). The TT for boron in bird eggs is measured at 20 mg kg⁻¹ and NOAEL at 13 mg kg⁻¹ showing that elevated dietary B concentrations in the range 30-100 mg kg⁻¹ affect waterfowl duckling growth rates (Smith and Anders, 1989; Eisler, 1990; Stanley et al., 1996). Another study with

mallard ducklings found B concentration up to 100-300 mg kg⁻¹ resulted in tissue residues while concentrations of 1000 mg kg⁻¹ reduced survival rate drastically (Eisler, 1990). A study in 1995 by Pendleton et al., showed that when male adult mallard ducks were exposed to dietary B at 1600 mg kg⁻¹ for 48 days, high concentrations were detected in blood, brains and livers of the birds 15 days after the start of the experiment. Even though with a clean diet, B was eliminated within a day, this study showed possible accumulation of B by birds. Another study found that the livers of aquatic birds from northern and southern areas of the Grassland District of California, in 1985–1988 during the wintering and breeding periods, had elevated B concentrations fluctuating between 1.4 and 40 mg kg⁻¹ B (DW) (Paveglio et al., 1992).

4.4. Human Beings

Boron is not an important nutrient in the human body except for counteracting fluoride intoxication symptoms and prevention of bone demineralization and calcium loss (Nielsen et al., 1987; Zhou et al., 1987). It gets assimilated in the human body in small quantities due to slow excretion rates (EPA, 1975). Boron and its compounds are neither mutagenic nor carcinogenic based on the results of an assay which showed that B does not affect the behavior of a known mutagen, benzo(a)pyrene (Eisler, 1990). However, some animal embryo studies have shown elevated B to behave as a teratogen (Parks and Edwards, 2005). A study by EPA in 1976 showed that when B was injected into amphibian embryos, it produced abnormal development of the neural tube, notochord, tail and limbs. Most studies examining the effects of elevated B in mammals have reported the greatest risk to human newborns. In human beings, an oral dose of 1-3 g boric acid (0.3-0.8 g kg⁻¹, BW) was lethal to newborns, 5-6 g boric acid (0.7 g kg⁻¹, BW) was fatal to infants while

15-20 g boric acid ($0.25\text{--}0.3\text{ g kg}^{-1}$, BW) produced fatality in adults. Boric acid concentrations $< 4\text{ g boric acid}$ administered to adults produced no toxicosis (Sprague, 1972; EPA, 1975; Dixon et al., 1976; Seigel and Wasson, 1986; Eisler 1990). The authors also discovered that 15-20 g boric acid (equivalent to $0.25\text{--}0.3\text{ g kg}^{-1}$, BW) in adults was fatal preceded by severe symptoms of seizures, vomiting and elevated boron levels in body organs. Some accidental cases of B poisoning in infants by pacifiers, addition of boric acid to infant formulas and use of boric acid as a diapering powder have been documented (EPA, 1975; O'Sullivan and Taylor, 1983; Siegel and Wasson, 1986). There is a considerable margin between toxic dose and dietary B concentrations for mammals. Possible death caused by paralysis of the central nervous system and gastrointestinal irritation, however, is rare (NAS, 1980). However, elevated B via ingestion may be responsible for weight loss and reduced growth rate in mammals, which could be exacerbated by ingestion of B-contaminated drinking water (Dixon et al., 1976; Green and Weeth, 1977; Seal and Weeth, 1980). For male workers associated with work place exposure to high B concentrations, weakened sexual activity with a decrease in sperm count, volume and motility has been observed (EPA, 1975).

5. Boron and the Pariette Wetlands

According to the US Environmental Protection Agency (EPA), all states are required to develop water quality standards and designate each water body a specific use based on these standards. In Utah, these standards consist of three components:

- i. Beneficial uses that show human usage of water. For example, aquatic life support, agriculture, drinking water supply and recreation.

- ii. Criteria showing water condition to support the beneficial uses. For example: Numeric criteria like TMDL representing maximum contaminant concentration allowed and general criteria like water must be free from floating debris, oil/scum, color and odor producing materials, nutrients causing algal blooms, sludge, substances harmful to aquatic life etc.
- iii. Situations when new or increased discharge of contaminants is allowed by the state under Anti-degradation Policy.

Based on Utah's Division of Water Quality (UDWQ) assessment for the Pariette Draw in 2002 and 2004 303(d), the B concentrations in the water flowing into the Pariette Wetlands have been observed to exceed the total maximum daily loads, especially during spring and fall run off. Table 1-1 summarizes the water body characteristics for the Pariette Draw Watershed. According to the considerable literature and research dedicated to the topic, B may be sorbed to sediments and bioaccumulated or bioconcentrated by wetland plant and aquatic macro invertebrates. Since wetland plants and aquatic organisms serve as food sources for the migratory and resident bird populations in the wetlands, and B is an avian teratogen, an estimate of B ingestion exposure to wetland birds is warranted.

6. Pariette Wetlands

The Uintah Basin covers approximately 10,890 square miles in the northeastern corner of the state of Utah in the United States of America. It includes Duchesne, Uintah and Daggett counties along with parts of Summit, Wasatch, Carbon, Emery and Grand. The Pariette Draw watershed lays part in the Uintah and Duchesne counties and part in the Uintah and Ouray Indian reservations. It occupies 81,843 hectares in the Uinta basin. The

Pariette Wetlands cover 3,665 hectares and form a complex that comprises of 23 manmade gravity fed ponds, which are divided into 4 units (Fig 1). This is the largest wetland development in Utah and was created in the early 1970s by the Bureau of Land Management (BLM). Approximately one third of the system (1023 ha) is classified as wetland or riparian (UDEQ, 2010). Sources of water for this wetland include non-point source run-off, input from ephemeral streams and irrigation run-off through the Pleasant Valley canal. As a result, the wetlands receive water throughout the year in sharp contrast to the arid surroundings. Over the last 40 years, this desert oasis has become a habitat for over 105 species of mammals, waterfowl and raptors, and provides seasonal habitat for migrating birds (UDEQ, 2010).

Monitoring of the pond waters in the mid-2000s revealed levels of selenium (Se), B, and total dissolved salts exceeding the total maximum daily loads (UDEQ, 2010). Driven in large part by the threat of Se toxicity to waterfowl, numerous studies have been conducted in the area to investigate the sources of Se, how it is being mobilized, its content in the wetland soils, sediments, vegetation, and pond water, along with its risk to wetland fish and birds. Few, studies have investigated B.

6.1. Geography/Geology

The Uinta Basin includes the Rocky Mountain Basin, Wyoming Basin and Colorado Plateau (UDEQ, 2005). Of the rock strata forming the basin, the Uinta formation in particular occurs at the surface in the Pariette Wetlands (Stephens et al., 1992). The Uinta formation is a part of the highly erodible Uinta Basin containing shale coal beds formed in coastal marine environments. Hence, this area is a significant natural source of total dissolved solids (TDS), selenium (Se) and boron (B) (UDEQ 2005). Stratigraphic

cross sections of the formation reveal complex depositional inter-fingering associated with fluvial, marginal-lacustrine, and lacustrine environments (Dubiel, 2003). This formation consists of fine and coarse sandstones and gravel with cherty and calcareous interlayering, gray-green calcareous claystone, and mud-supported carbonate units (Cope, 1882; Ryder et al., 1976). The watershed lies in the most northerly section of the Colorado Plateau. It cuts through tertiary-aged deposits including the lower Oligocene Duchesne River Formation and Eocene Uinta formation. It is located in the eastern portion of the Lower Green-Desolation Canyon hydrologic unit (HUC 14060005-002), draining into the Green River; a tributary to the Colorado River. The watershed is bound by the Duchesne river drainage (Elevation: 1524 m) to the north, the Tavaputs Plateau (Elevation: 2438 m) to the south and west, and the Green River Valley to the east (UDEQ, 2010).

Soils in the watershed were formed in alluvial deposits from mixed sedimentary rocks. Soil textures range from rocky, gravelly soils at high elevations with hilly terrain to fine-textured, sandy-loam or loam soil in the river basins, valley floors and floodplains (Dubiel, 2003). The Pariette Watershed soils are categorized as 54% loams and 43% sandy loams or sands. The surface soil texture influences run-off and infiltration rates; whereas, subsurface characteristics influence waterholding capacity, leaching potential, permeability and plant available water supply. Together these factors help to determine the fate of pollutants in the soil. Due to the easily weathered saline and sodium rich bedrock, salinity and sodicity are widespread in the surface soil and water resources. Furthermore, high rates of evapotranspiration in the hot and arid summer climate result in the build-up of salts in the soils, which occur as salt blooms on soil surfaces. Higher salinity and sodicity affects soil structure, which can alter water infiltration and aeration rates, and raise soil pH

affecting nutrient availability to plants. Based on infiltration rates and run-off characteristics, the NRCS has described four soil hydrologic groups (Wingert and Adams, 2010). The Pariette Draw Watershed soils are mostly classified in group B (29%) and D (54%) characterized by slow infiltration rates and high surface run-offs. They also have high salinity and sodicity that make them a potential source area for B, Se and TDS. However, the soils in the agricultural Pleasant Valley and the northern portion along the Pariette wetlands and upstream perennial streams, have sodium adsorption ratios (SARs) in the moderately to strongly sodic range (UDEQ, 2010) and have been classified as group C by NRCS.

The climate is semi-arid with sparse vegetation, hot summers and severe winter cold. Winter precipitation occurs mainly as snow, while summer precipitation is mostly rainfall. The average annual precipitation for the Pariette Draw Watershed averages 224 mm per year, but reaches as high as 457 mm at higher elevations. At the northern end of the watershed, where the Pariette Wetlands are located, precipitation averages 127–152 mm per year (UDEQ, 2010). Temperatures can differ by ≥ 40 °F in the watershed.

6.2. Land Use and Watershed Hydrology

In the semi-arid Pariette Draw, 63% of the land cover is dominated by salt desert scrub (26%), sagebrush (18%), and pinyon-juniper (18%). A detailed water related database developed by the Utah Department of Natural Resources, Division of Water Resources (1995) shows that 5% of the total watershed area is devoted to water related land use. However, much of the water-related landuse borders the Pariette Wetlands and perennial streams feeding the wetlands including riparian woodland and shrub land, wet meadows, pastures, and agriculture. For example, agricultural land occupies only 4.2% of

the watershed but those 3,103 ha are concentrated in Pleasant Valley along the headwaters of streams feeding the Pariette Wetlands (UDEQ, 2010; Wingert and Adams, 2010).

The natural Pariette Draw Watershed hydrology is dominated by spring runoff and to a lesser degree brief, intense summer storms. Eighty-six percent of the rivers or streams in the watershed are classified as intermittent streams initiated by runoff or precipitation. However, irrigation and engineered projects including the construction of canals, diversions points, and wetlands have altered the natural hydrology (BLM, 2005). High evapotranspiration rates and fine-textured soils in the low-lying areas of the main water bodies (permanent streams and canals) feeding the wetlands, also affect water movement.

Irrigation accounts for 72% of water-related land use in the watershed (UDEQ, 2010). The source of the agricultural irrigation water is predominantly high quality water from the Duchesne River, applied by sprinklers. Open water in perennial streams found predominantly in the headwaters of the wetlands makes up the next highest water-related land-use at 15%. Riparian areas, largely located downstream along the wetlands, make up 9 % (UDEQ, 2010).

6.3. Water Quality Monitoring

The primary sources of the impairments in the Pariette Watershed were identified as natural geologic formations, subsurface flows from irrigation and stream bank erosion (UDWQ, 2009). Analysis of water samples from the Utah Department of Environmental Quality (UDEQ) monitoring stations in 2002 identified B concentrations:

- i. Station 4933476 – Below Pariette Draw Flood Control Structure
0.443 – 2.36 mg L⁻¹, (avg. 1.16 mg L⁻¹, n=18, 2006-2009)

- ii. Station 4993370 – Midway along the chain of wetland ponds
0.63 – 2.05 mg L⁻¹ (avg. 1.31 mg L⁻¹, n=9, 2008-2009)
- iii. Station 4933440 – 1 mile above Pariette Draw and Green River confluence
0.092 – 3.0 mg L⁻¹ (avg. 1.68 mg L⁻¹, n=54, 1993-2009)

Between 1995 and 2001 the B water criteria standard was exceeded in 83% of the samples while from 2006-2009 the standard was exceeded 69% of the time. Boron loading throughout the year showed no distinct trend; however, there was a weak pattern of increasing concentration under low flow conditions that decreased during storm or run-off events (UDEQ, 2010; Wingert and Adams, 2010). On average, B concentrations were slightly higher (1.45×) at the outlet than at the inlet. Boron is highly soluble and is thought to be transported through the system without adsorbing onto sediments or bioconcentration in aquatic vegetation, benthic macroinvertebrates, and fish or bird eggs such as waterfowl (UDEQ, 2010). However, water flow into the wetlands is on average 14 times higher at the inlet than at the outlet (Jones, 2014), suggesting that some boron may indeed be retained within the wetland system or lost through seepage to groundwater.

References

- Agency for Toxic Substances and Disease Registry (ATSDR). 1992. Toxicological Profile for Boron. Agency for Toxic Substances and Disease Registry, Public Health Service, U.S. Department of Health and Human Services. <http://www.atsdr.cdc.gov/toxprofiles/tp26.html>.
- Anderson, D.L., W.C. Cunningham, T.R. Lindstrom, 1994. Concentrations and intakes of H, B, S, K, Na, Cl, and NaCl in Foods. *J. Food Compos. Anal.* 7, 59-82.
- Argust, P., 1998. Distribution of boron in the environment. *Biol. Trace Elem Res.* 66(1-3), 131-143.

- Arora, S., D.S. Chahal, 2007. Suitability of adsorption isotherms for behavior of boron in soils varying in clay and organic matter content. *Agrochimica* 51(4&5), 182–193.
- Arora, S., D.S. Chahal, 2010. Effect of soil properties on boron adsorption and release in arid and semi-arid benchmark soils. *Commun. Soil Sci. Plant Anal.* 41, 2532-2544.
- Arslan, N., 2013. Invisible face of boron pollution in fluvial ecosystem: The level in the tissues of sentinel and nectonic organisms. *Ambio* 42, 715-723.
- Bertine, K.K., E.D. Goldberg, 1971. Fossil fuel combustion and the major sedimentary cycle. *Science* 173, 233-235.
- Biggar, J.W., M. Fireman, 1960. Boron adsorption and release by soils. *Soil Sci. Soc. Am. Proc.* 24, 115–120.
- Bingham, F.T., A.L. Page, N.T. Coleman, K. Flach, 1971. Boron adsorption characteristics of selected amorphous soils from Mexico and Hawaii. *Soil Sci. Soc. Am. J.* 35, 546-550.
- Bingham, F.T., J.E. Strong, J.D. Rhoades, R. Keren, 1985. An Application of the Maas-Hoffman Salinity Response Model for Boron Toxicity. *Soil Sci. Soc. Am. J.* 49, 672-674.
- Boyd, C.E., W.W. Walley, 1972. Studies of the biogeochemistry of boron. I. Concentrations in surface waters, rainfall and aquatic plants. *Am. Midl. Nat.* 88, 1-14.
- Budavari, S., M.J. O’Neal, A. Smith, P.E. Heckelman, J.F. Kinneary, 1996. *The Merck Index: An encyclopedia of chemicals, drugs, and biologicals*. Whitehouse Station: Merck and Co.
- Bureau of Land Management (BLM). 2005. Vernal resource management plan draft environmental impact statement.
http://www.blm.gov/ut/st/en/fo/vernal/planning/rmp/draft_rmp_eis/draft_rmp_eis.print.html
- Butterwick, L., N. de Oude, K. Raymond, 1989. Safety Assessment of boron in aquatic and terrestrial environments. *Ecotoxicol. Environ. Safe.* 17, 339-371.
- California Regional Water Quality Control Board, Central Valley Region (CRWQC B, CVR), 1988. Amendments to the Water Quality Control Board for the San Joaquin Basin (5C) for The Control of Agricultural subsurface Drainage Discharges.
- Choi, W.W., K.Y. Chen, 1979. Evaluation of boron removal by adsorption on solids. *Environ. Sci. Technol.* 13(2), 189-196.

- Communar, G., R. Keren, 2006. Rate limited boron transport in soils: The effect of soil texture and solution pH. *Soil Sci. Soc. Am. J.* 70, 882–892.
- Cope, E.D., 1882. The tertiary formations of the central region of the United States. *Am. Nat.* 16(3), 177-195.
- Cotton, F.A., G. Wilkinson, C.A. Murillo, 1999. Boron. In: *Advanced inorganic chemistry*. 6th Ed. New-York, NY: John Wiley & Sons, Inc., 131-174.
- Cowgill, U.M., 1974. The hydrochemistry of Linsley Pond. II. The chemical composition of aquatic macrophytes. *Arch. Hydrobiol. Suppl.* 45, 1-119.
- Culver B.D., P.T. Shen, T.H. Taylor, A. Lee-Feldstein, H. Anton-Culver, P.L. Strong, 1994a. The relationship of blood-boron and urine-boron to boron exposure in borax-workers and the usefulness of urine-boron as an exposure marker. *Environ. Health Perspect.* 102(7), 133-137.
- Culver B.D., R.G. Smith, R.J. Brotherton, P.L. Strong, T.M. Gray, 1994b. Chapter 44: Boron. *In*, Clayton, G.D., F.E. Clayton, Eds. *Patty's industrial hygiene and toxicology*. John Wiley and Sons, New York, New York.
- Culver, B.D., P.T. Shen, T.H. Taylor, 1994. The relationship of blood- and urine-boron exposure in borax - workers and usefulness of urine-boron as an exposure marker. *Environ. Health Perspect.* 102, 133-137.
- Davis, H. H., 2000. Boron: A literature summary for developing water quality objectives. California Environmental Protection Agency, Regional Water Quality Control Board, Central Valley Region; San Joaquin River Basin Plan Amendment.
- Del-Campo Marin, C.M., G. Oron, 2007. Boron removal by the duckweed *Lemna gibba*: A potential method for the remediation of boron polluted waters. *Water Res.* 41, 4579-4584.
- Deverel, S.J., S.P. Millard, 1988. Distribution and mobility of selenium and other trace elements in shallow groundwater of the western San Joaquin Valley, California. *Environ. Sci. Technol.* 22, 697-702.
- Dixon, R., I. Lee, R. Sherins, 1976. Methods to assess reproductive effects of environmental chemicals: Studies of cadmium and boron administered orally. *Environ. Health Perspect.* 13, 59-67.
- Dubiel, R. F., 2003. Geology, depositional models, and oil and gas assessment of the Green River total petroleum system, Uinta-Piceance Province, Eastern Utah and Western Colorado. USGS Uinta-Piceance Assessment Team. Chapter 5 of *Petroleum Systems and Geologic Assessment of Oil and Gas in the Uinta-Piceance Province, Utah and Colorado*. U. S. Geological Survey, Information Services. Denver, CO.

- ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals). 1997. Ecotoxicology of some inorganic borates—Interim report, Brussels, special report No. 11.
- Eisler, R., 1990. Boron hazards to fish, wildlife and invertebrates: A Synoptic review. Biological Report 85:1-20.
- Emiroğlu, Ö., A. Çiçek, N. Arslan, A. Aksan, M. Rüzgar, 2010. Boron concentration in water, sediment and different organisms around large borate deposits of Turkey. Bull. Environ. Contam. Toxicol. 84(4), 427-431.
- Environmental Protection Agency (EPA), 1986. Quality criteria for water, U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Washington. Report EPA/440/5-86-001.
- Environmental Protection Agency (EPA), 2008. Regulatory determinations support document for selected contaminants from the second drinking water contaminant candidate list (CCL 2). Chapter 3, Report 815-R-08-012.
- Environmental Protection Agency (EPA). 1975. Preliminary investigation of effects on the environment of boron, indium, nickel, selenium, tin, vanadium and their compounds. Boron Report 56/2-75-005A, Vol. 1:111 pp.
- Fernandez, E., E. Sanchez, I. Bonilla, P. Mateo, P. Ortega, 1984. Effect of boron on the growth and cell composition of *Chlorella pyrenoidosa*. Phyton-Int. J Exp. Bot. 44, 125-131.
- Gersich, F.M., 1984. Evaluation of static renewal chronic toxicity test method for *Daphnia magna* Straus using boric acid, Environ. Toxicol. Chem. 3, 89-94.
- Glandon, R.P., C.D. McNabb, 1978. The uptake of boron by *Lemna minor*. Aquat. Bot. 4, 53-64.
- Goldberg, S., 1993. Chemistry and mineralogy of boron in soils. In, Gupta, U.C. Ed. Boron and its Role in Crop Production. CRC Press, Boca Raton, FL, USA. pp 3-44.
- Goldberg, S., R.A. Glaubig, 1988. Boron and silicon adsorption on an aluminum oxide. Soil Sci. Soc. Am., 52, 87-91.
- Goldberg, S., P.J. Corwin, D.I. Suarez, 2005. Prediction of boron adsorption by field samples of diverse textures. Soil Sci. Soc. Am. J. 69, 1379–1388.
- Green, G.H., H.J. Weeth, 1977. Responses of heifers ingesting boron in water, J. Animal Sci. 46, 812-818.

- Greenwood, N.N., B.S. Thomas, 1973. The chemistry of boron. Pergamon Press, Elmsford, New York. 326 pp.
- Griffin, R.A., R.G. Burau, 1974. Kinetic and equilibrium studies of boron desorption from soil. *Soil Sci. Soc. Am. Proc.* 38, 892-897.
- Gupta, U.C., Y.W. Jame, C.A. Campbell, W. Nicholaichuk, 1985. Boron toxicity and deficiency: A review. *Can. J. Soil Sci.* 65, 381-409.
- Hazardous Substances Data Bank (HSDB), 2004. <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>.
- Helmann, H., M. Schumacher, 1977. Phosphate, borate und nitrate~dynamik in Auftreten und Umsatz in Rheinstrom. *Tenside Surfact. Det.* 14(6), 321-325.
- Hoffman, D.J., C.J. Sanderson, L.J. LeCaptain, E. Cromartie, G.W. Pendleton, 1991. Interactive effects of boron, selenium and dietary protein on survival, growth and physiology in mallard ducklings. *Arch. Environ. Contam. Toxicol.* 20, 288-294.
- Holleman, A.F., E. Wilberg, N. Wilberg, 1985. *Lehrbuch der Anorganischen Chemie.* Walter de Gruyter Verlag & Co., Berlin. pp. 814-864.
- Hothem, R.L., H.M. Ohlendorf, 1989. Contaminants in foods of aquatic birds at Kesterson Reservoir, California, 1985. *Arch. Environ. Contam. Toxicol.* 18, 773-786.
- Howe, P.D., 1998. A review of boron effects in the environment. *Biol. Trace Elem. Res.* 66, 153-166.
- Hunt, C.D. 1994. The biochemical effects of physiologic amounts of dietary boron in animal nutrition models. *Environ. Health Perspect.* 102(7), 35-43.
- Hutchison, G.E. 1975. *A treatise on limnology, vol. 3: Limnology botany.* John Wiley & Sons, Inc., New York, NY.
- Inoue, T., M. Iwaida, Y. Ito, S. Ogawa, K. Tajima, T. Mine, 1980. A general survey on the borate contents in foods, *J. Food Hyg. Soc. Jpn.* 21(6), 465-471.
- Jones, C.P., 2014. *Biochemistry of Selenium in Pariette Wetlands, Utah.* Graduate Theses and Dissertations, Utah State University.
- Kemp, P.H., 1956. *The Chemistry of Borates, Part 1, Borax Consolidated Ltd., London.*
- Kılıç, A.M. 2004. Importance of boron mine for Turkey and place in the future. In *Proceedings of the 2nd International Boron Symposium, Eskişehir, September 23-25, 2004, p. 34.*

- Kim, S., P.A. Thiessen, E.E. Bolton, J. Chen, G. Fu, A. Gindulyte, L. Han, J. He, S. He, B.A. Shoemaker, J. Wang, B. Yu, J. Zhang, S.H. Bryant, 2016. PubChem substance and compound databases. *Nucleic Acids Res.* 44(D1), 202-213. DOI:10.1093/nar/gkv951.
- Kobayashi, N., 1971. Fertilized sea urchin eggs as an indicatory material for marine pollution bioassay, preliminary experiment. *Publ. Seto Mar. Biol. Lab.* 18(6), 379-406.
- Koç, C., 2007. Effects on environment and agriculture of geothermal wastewater and boron pollution in great Menderes basin. *Environ. Monit. Assess.* 125(1-3), 377-388.
- Landauer, W. 1952. Malformations of chicken embryos produced by boric acid and the probable role of riboflavin in their origin. *J. Exp. Zool.* 120, 469-508.
- Lewis, M.A., L.C. Valentine, 1981. Acute and chronic toxicities of boric-acid to *Daphnia magna* Straus. *Bull. Environ. Contam. Toxicol.* 27(3), 309-315.
- Lowe, T.P., D.D. Day, 2002. Metal concentrations in zebra mussels and sediments from embayments and riverine environments of eastern Lake Erie, southern Lake Ontario and the Niagara River. *Arch. Environ. Contam. Toxicol.* 43(3), 301-308.
- Maier, K.J., A.W. Knight, 1991. The toxicity of waterborne boron to *Daphnia magna* and *Chironomus decorus* and the effects of water hardness and sulfate on boron toxicity. *Arch. Environ. Contam. Toxicol.* 20, 282-287.
- Matterson, K.J., 1980. Borate ore discovery, mining and beneficiation. In, Thompson R., Welch A.J.E. Eds, Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry Vol. 5 Part A., Boron-oxygen compounds. Pearson Longman, New York, NY.
- Mellor, J.W., 1922. Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 5 Part A, Boron-oxygen compounds. Longmans, Green and Co. LTD, London.
- Millot, R., E. Petelet-Giraud, C. Guerrot, P. Négrel, 2010. Multi-isotopic composition ($\delta^7\text{Li}$ - $\delta^{11}\text{B}$ - δD - $\delta^{18}\text{O}$) of rainwaters in France: origin and spatio-temporal characterization. *Appl. Geochem.*, 25(10), 1510-1524.
- Moore, J.W. 1991. Inorganic Contaminants of Surface Water: Research and Monitoring Priorities. Springer-Verlag, New York, NY
- Moss, S.A., N.K. Nagpal, 2003. Ambient water quality guidelines for boron. Water Protection Section, Ministry of Water, Land and Air Protection, Environmental Protection Division, British Columbia, Canada.
- Nable, R.O., G.S. Banuelos, J.G. Paul, 1997. Boron toxicity. *Plant Soil* 198, 181-198.

- National Academy of Sciences (NAS), 1980. Mineral tolerance of domestic animals. The National Academies Press. Washington, D.C. pp. 71-83.
- Newnham, R.E., 1994. Essentiality of boron for healthy bones and joints. *Environ. Health Perspect.* 102(7), 83-85.
- Nielsen, F.H. 1994. Biochemical and physiologic consequences of boron deprivation in humans. *Environ. Health Perspect.* 102(7), 59-63.
- Nielsen, F.H., C.D. Hunt, L.M. Muller, 1987. Effect of dietary boron on mineral, estrogen and testosterone metabolism in postmenopausal women. *FASEB Monographs*, 1, 394-397.
- O'Sullivan, K., M. Taylor, 1983. Chronic boric acid poisoning in infants. *Arch. Dis. Child.* 58, 737-739.
- Parks, J.L., M. Edwards, 2005. Boron in the environment. *Crit. Rev. Env. Sci. Tec.* 35(2), 81-114.
- Paveglio, F.L., C.M. Bunck, G. H. Heinz, 1992. Selenium and boron in aquatic birds from central California. *J. Wildl. Manage.* 56(1), 31-42.
- Pendleton, G.W., M.W. Whitworth, G.H. Olsen, 1995. Accumulations and loss of arsenic and boron, alone and in combination in mallard ducks. *Environ. Toxicol. Chem.* 14(8), 1357-1364.
- Perry, D.M., I.S. Suffet, M. Wilhelm, J.A. Noblet, A. Maliglig, 1994. Boron environmental chemistry, distribution, bioaccumulation, and toxicity in aquatic system and recommendations for establishment of a boron water quality criterion for natural water in the San Joaquin Valley, California. Final report for Contract No. 1-192-150-0. Submitted to the California Regional Water Quality Control Board, Central Valley Region and the California Environmental Protection Agency. 270 pp.
- Pillard, D.A., D.L. DuFresne, M.C. Mickley, 2002. Development and validation of models predicting the toxicity of major seawater ions to the mysid shrimp, *Americamysis bahia*. *Environ. Toxicol. Chem.* 21(10), 2131-2137.
- Powell, R.L., R.A. Kimerle, G.T. Coyle, G.R. Best, 1997. Ecological risk assessment of a wetland exposed to boron. *Environ. Toxicol. Chem.* 16(11), 2409-2414.
- Rai, D., J.M. Zachara, A.P. Schwab, 1986. Chemical attenuation rates, coefficients, and constants in leachate migration - A critical review. Palo Alto, CA: Electric Power Research Institute, Research Project, 1, 2198-2201.
- Rio Tinto Borax, 2003. Report on Sustainability: Company Overview, Borax Profile. <http://www.borax.com/sereport03>.

- Rio Tinto Borax. 2004. Report on Sustainability: Company Overview, Borax Profile. <http://www.borax.com/sereport03>.
- Roux, D.J., S.H.J. Jooste, H.M. MacKay, 1996. Substance-specific water quality criteria for the protection of South African freshwater ecosystems: Methods for derivation and initial results for some inorganic toxic substances. *S. Afr. J. Sci.* 92, 198-206.
- Ryder, R.T., T.D. Fouch, J.H. Elison, 1976. Early Tertiary sedimentation in the western Uinta Basin, Utah. *Geol. Soc. Am. Bull.* 87(4), 496-512.
- Saiki, M.K., T.W. May, 1988. Trace element residues in bluegills and common carp from the lower San Joaquin River, California, and its tributaries. *Sci. Total Environ.* 74, 199-217.
- Sakata, M. 1987. Relationship between adsorption of arsenic (III) and boron by soil and soil properties. *Environ. Sci. Technol.* 21, 1126-1130.
- Schuler, C.A. 1987. Impacts of agricultural drainwater and contaminants on wetlands at Kesterson Reservoir, California. M. S. thesis, Oregon State University, Corvallis. 136 pp.
- Seal, B. S., H.J. Weeth, 1980. Effect of boron in drinking water on the male laboratory rat, *Bull. Environ. Contam. Toxicol.* 25, 782-789.
- Siegel, E., S. Wason, 1986. Boric acid toxicity, *Pediatr Clin North Am.* 33, 363-367.
- Sims, J. R., F.T. Bingham, 1968a. Retention of boron by layer silicates, sesquioxides and soil materials. II, Sesquioxides. *Soil Sci. Soc. Am.* 32, 364-369.
- Sims, J. R., F.T. Bingham, 1968b. Retention of boron by layer silicates, sesquioxides, and soil materials. III, Iron and aluminum-coated layer silicates and soil materials. *Soil Sci. Soc. Am.* 32, 369-373.
- Smith, G.J., V.P. Anders, 1989. Toxic effects of boron on mallard reproduction. *Environ. Toxicol. Chem.* 8(10), 943-950.
- Smith, R.A., 1986. Boron in glass and glassmaking. *J. Non-Cryst. Solids* 84, 421-432.
- Soucek, D.J., A. Dickinson, B.T. Koch, 2011. Acute and chronic toxicity of boron to a variety of freshwater organisms. *Environ. Toxicol. Chem.* 30(8), 1906-1914.
- Sprague, R.W. 1972. The Ecological Significance of Boron. U.S. Borax Research Corp., Anaheim, CA. 58p.
- Stanley, T.R., G.J. Smith, Jr., D.J. Hoffman, G.H. Heinz, R. Rosscoe, 1996. Effects of boron and selenium on mallard reproduction and duckling growth and survival. *Environ. Toxicol. Chem.* 15:1124-1132.

- Stephens, D. W., B. Waddell, L. Peltz, J.B. Miller, 1992. Detailed study of selenium and selected elements in water, bottom sediment, and biota associated with irrigation drainage in the Middle Green River Basin, Utah, 1988-90. U.S. Geological Survey Water-Resources Investigations Report 92-4084. U.S. Geological Survey, Denver, CO.
- Su, C., D.L. Suarez, 1995. Coordination of adsorbed boron: A FTIR spectroscopic study. *Environmental Science and Technology*, 29, 302-311.
- Travis, N.J., E.J. Cocks, 1984. *The Tincal Trail: A History of Borax*, Harraps Ltd., London.
- Tsui, P.T., P.J. McCart, 1981. Chlorinated hydrocarbon residues and heavy metals in several fish species from the Cold Lake area in Alberta, Canada. *Int. J. Environ. Anal. Chem.*, 10, 277-285.
- United States Department of the Interior (USDI). 1998. Guidelines for interpretation of the biological effects of selected constituents in biota, water, and sediment. National Irrigation Water Quality Program Information Report No. 3, pp. 25-40.
- United States Environmental Protection Agency (US EPA), 1976. Quality Criteria for Water, EPA 440/9-76-023. Washington D.C., 501 pp.
- United States Environmental Protection Agency (USEPA), 1994a. Re-registration Eligibility Decision (RED) – Boric Acid and its Sodium Salts. Office of Prevention, Pesticides, and Toxic Substances.
http://www.epa.gov/oppsrrd1/REDS/old_reids/boric_acid_salts.pdf.
- United States Geological Survey (USGS). 2004. Mineral Commodity Summaries, 2004-Boron. <http://minerals.usgs.gov/minerals/pubs/commodity/boron/boronmcs04.pdf>.
- United States Geological Survey (USGS). 2004. Mineral Commodity Summaries, 2008-Boron. <http://minerals.usgs.gov/minerals/pubs/commodity/boron/boronmcs04.pdf>.
- United States Geological Survey (USGS). 2004. Mineral Commodity Summaries, 2009-Boron. <http://minerals.usgs.gov/minerals/pubs/commodity/boron/boronmcs04.pdf>.
- Utah Department of Environmental Quality (UDEQ), 2005. Uintah Basin Watershed Description. Utah Department of Environmental Quality, Division of Water Resources. www.utah.gov
- Utah Department of Environmental Quality (UDEQ). 2010. TMDLs for total dissolved solids, selenium, and boron in the Pariette Draw watershed. Report prepared for the U. S. EPA Region 9. Utah Department of Environmental Quality, Division of Water Quality, Salt Lake City, UT.
- Utah Division of Water Quality (UDWQ), 2009. Standards of Quality for Waters of the State, Utah Administrative Code R317-2. Salt Lake City, UT.

- Waggot, A., 1969. An investigation of the potential problem of increasing boron concentrations in rivers and water courses. *Water Res.* 3, 749-765.
- Williams, L.H., T.L. Arnburgey, 1987. Integrated protection against lyctid beetle infestations. IV. Resistance of boron-treated wood (*Virola spp.*) to insect and fungal attack. *J. Natural Prod.*, 37, 10-17.
- Wingert, S., C. Adams, 2010. TMDLs for Total Dissolved Solids, Selenium, and Boron in the Pariette Draw Watershed, US Environmental Protection Agency, Region 8.
- World Health Organization (WHO), 1998. Boron, Environmental Health Criteria (EHC) – 204. <http://www.inchem.org/documents/ehc/ehc/ehc204.html>
- Wren, C.D., H.R. MacCrimon, B.R. Loescher, 1983. Examination of bio-accumulation and bio-magnification of metals in a Precambrian shield lake. *Water Air Soil Pollut.* 19, 277-291.
- Yermiyahu, U., R. Keren, Y. Chen. 1995. Boron sorption by soil in the presence of composted organic matter. *Soil Sci. Soc. Am. J.* 59, 405–409.
- Zhou, L.Y., Z.D. Wei, S.Z. Ldu, 1987. Effect of borax in treatment of skeletal fluorosis. *Fluoride* 20, 24-27.

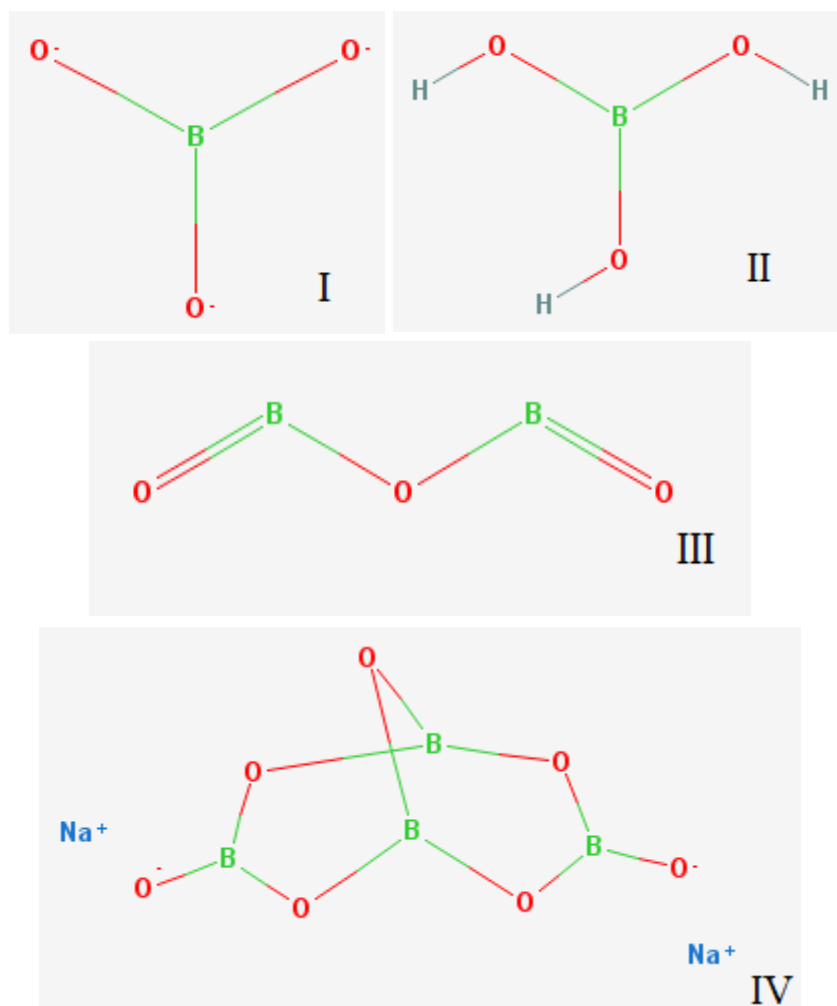


Fig. 1-1: Chemical structures of ecologically common forms of B, **I.** Borate Ion (BO_3^{3-}) **II.** Boric Acid (H_3BO_3) **III.** Boron Oxide (B_2O_3) **IV.** Anhydrous Borax ($\text{Na}_2\text{B}_4\text{O}_7$) (Modified from Kim et al., 2016).

Tale 1-1. Water Quality Standards for Impaired Waters in Pariette Draw Watershed, UT

DESIGNATED USE	DESCRIPTION	BORON ($\mu\text{g L}^{-1}$)
3B	Warm water aquatic life	N/A
3D	Waterfowl	N/A
4	Agriculture	750

CHAPTER 2

BORON IN PARIETTE WETLANDS, UINTA BASIN, UTAH

1. Introduction

Boron (B) is a naturally occurring transition metal found as mineral deposits in igneous, sedimentary and metamorphic rocks. The average surface B concentrations range between 8 – 10 mg kg⁻¹ with the highest concentrations, 500 mg kg⁻¹, found in areas associated with volcanic activity and evaporated marshes/lakes under arid conditions, or with sedimentary rock formed from clay-rich marine sediments (Eisler, 1990; Howe, 1998; Cotton et al., 1999; USGS 2008; Hilal et al., 2011; Trüker et al., 2014). Natural processes like weathering, decomposition of soil organic matter, desorption from clay surfaces and anthropogenic processes such as mining, wastewater discharge (sewage sludge, domestic washing/cleaning agents, fiberglass manufacturing facilities), surface runoff from coal/geothermal steam power plants, and agricultural run-off (agrochemicals such as fertilizers, herbicides, insecticides) mobilize B and often increase its bioavailability to plants and animals (Butterwick et al., 1989; ATSDR, 1992; Howe, 1998; HSDB, 2004; Koç, 2007; EPA, 2008; Emiroğlu, 2010).

The Pariette Watershed is located in Duchesne and Uintah counties on Uintah and Ouray Indian Reservation in the northeastern part of Utah (Wingert and Adams, 2010). A major portion of the 202,239 acres lies in the Uintah Basin (Fig. 2-1a) and is bordered by Duchesne River drainage in the north, Tavaputs Plateau towards south and west, and the Green River valley in the east (Wingert and Adams, 2010). The Uinta formation, one of the lithographic layers underlying the highly erodible Uintah Basin, is persistent in the

watershed and contains shale coal beds formed in coastal marine environments. This area is a significant natural source of total dissolved solids (TDS), selenium (Se) and boron (B) (UDEQ 2005). The dominant land uses in the Pariette Watershed are agriculture (8,494 acres) and oil and natural gas mining (809 acres), which encompass 4.6% of the total land area (Wingert and Adams, 2010). Of the 9,416 acres of water related land use in the watershed, 72% is irrigated agricultural land (Pleasant Valley), 15% riparian zones (Pariette Wetlands) and 9% open water areas including ponds and streams (Pariette Draw) (Fig. 2-1b). The watershed soils are classified into hydrologic soil groups with slow infiltration and high surface run off rates. The Pariette watershed receives between 7 and 40 inches of precipitation coming as snowfall in the winter and isolated thunderstorms in the summer. The Pariette Draw is arid, receiving 6 inches of average annual precipitation, which necessitates irrigation of agricultural lands in Pleasant Valley (Wingert and Adams, 2010). TDS, Se and B are mobilized from the soil when excess irrigation water is applied resulting in elevated downstream concentrations and retention in wetland sediments (Wingert and Adams, 2010; NRCS, 2001). A perennial tributary, Pariette Draw, transports runoff water from these agricultural lands to the Pariette Wetlands, which were constructed in the early 1970s and have been managed by the Bureau of Land Management (BLM) ever since. The wetlands consist of 23 ponds that drain the water into the Green River and ultimately to the Colorado River (Morrison et al., 2015). The Utah Water Quality Board (UWQB) has specified total maximum daily loads (TMDLs) for all water contaminants based on EPA's Clean Water Act, Section 303 (d) and each waterbody in Utah has been assigned a beneficial use based on these standards. Assessments of Pariette Draw and its tributaries from 1995–2001 revealed the watershed in violation of its Class 4, agricultural

use standard due to B concentrations exceeding the Utah water quality standard ($750 \mu\text{g L}^{-1}$) 69% of the time at the flood control inlet (Station 4933746) and 98% of the time at the outlet (Station 4933440). As such, it was listed on Utah's Section 303(d) list of impaired waters in 2002 for TDS and B violations and in 2004 for Se violation (UDEQ, 2004; Wingert and Adams, 2010). These wetlands, often referred to as an oasis of the Uintah Basin, contain diverse vegetation and were developed as a sanctuary for numerous species of waterfowl like the ring-necked pheasant, mourning dove, sand hill and whooping cranes, and raptors including harrier, prairie and peregrine falcons and bald eagles (Stephens et al., 1992; Jones, 2014).

Many research studies point to the significance of B in metabolic, nutritional, hormonal and physiological processes in animals (Nielsen, 1997; Basoglu et al., 2000; Pawa and Ali, 2006; Hunt 2012). As an essential micronutrient in plants, B helps in cell wall synthesis, structure and lignification, sugar transportation, respiration and metabolism of carbohydrates and ribonucleic acid (RNA) (Belvins and Lukaszewski, 1994; Camacho-Cristóbal et al., 2008). While boron is an important micronutrient for proper functioning and growth of all living beings including crop plants, algae, fungi and bacteria, it is toxic in excess. A study examining waterfowl populations in the Pariette Wetlands from 1980 – 2010 reported a reduction in the overall waterfowl population with total populations of common goldeneye and American wigeon increasing significantly, while green winged teal populations decreased (Baird and Etchberger, 2010). Studies in other wetland ecosystems have documented reduced root growth and leaf chlorosis in vascular plants, along with developmental abnormalities and reproductive defects in vertebrates and invertebrates as possible effects of elevated B (Nable et al., 1997; Nielsen, 1997; Belvins

and Lukaszewski, 1998; Hunt 1998; EPA 2008; Kabu and Akosman, 2012). B injection studies with waterfowl eggs indicated that embryos are highly sensitive to boron toxicity with signs of teratogenicity (Paveglio et al., 1992; Pendleton et al., 1995). The elevated Se and B levels measured at UDEQ monitoring stations in the Pariette wetlands along with literature suggesting teratogenic effects to waterfowl embryos prompted our investigative study (Landauer 1952; Smith and Anders, 1989). Since, Se has been studied extensively in the Pariette wetlands, we focused on B. Our research determined the distributions of B in abiotic (water, sediments) and biotic samples (benthic macroinvertebrates, aquatic vegetation, fish and bird eggs), checked for correlations between B levels in abiotic and biotic environmental samples, and looked for evidence of bioconcentration in wetland fish and waterfowl eggs. In addition, we sought an easily sampled abiotic or biotic marker that could be used to predict B concentrations in the wetland fish and bird eggs.

2. Materials and methods

2.1. Site description

The Pariette Wetlands (Fig. 2-1b) are located approximately 1 km upstream from the confluence of Pariette Draw watershed and Green River, a tributary of the Colorado River (Jones, 2014). Water is diverted from the watershed into the wetlands, which are composed of 23 ponds divided into four units. Unit 1 is comprised of Flood control, Desilt, Big Wash and Felters ponds. Unit 2 contains Mallard, Cattail, Big Island, Small Island, Millet and Cliff ponds; whereas, Units 3 and 4 include Pintail and Shoveler, Gadwall and Redhead ponds, respectively (Fig. 2-2).

2.1.1. Water Quality Monitoring

Many water quality monitoring stations were set up by UDEQ Division of Water Quality to collect water inflow (cfs), outflow (cfs), temperature (°C), dissolved oxygen (mg L⁻¹) and contaminant concentration (µg L⁻¹) data in the Pariette Watershed. For the purpose of our research, we used data generated by the water quality monitoring stations located at Flood Control inlet (Station 4933480/4933746) and Pariette Wetlands outlet located downstream of Redhead pond before confluence point (Station 493440) (Wingert and Adams, 2010). The data was collected from 1995–2001 at Station 4933480 and consequently, 2006–2009 at Stations 4933746 and 4933440 in the Pariette Wetlands (Wingert and Adams, 2010). The reported data showed violations of the Utah water quality standard with levels exceeding 750 µg L⁻¹ more than 65% of the time at all stations (Wingert and Adams, 2010). In order to check if B is accumulated and stored in wetland media, we used a data set for the year 2009 with values for average water flow rates (cfs), inlet and outlet B concentration values (µg L⁻¹) at the inlet and outlet station. The amount of B stored in the wetland is calculated using the following mass balance equation:

$$F = Q \times C \times 86400$$

where: F = mass flux of B (g day⁻¹), Q = inflow/outflow discharge (m³ s⁻¹), C = B concentration (g m⁻³), 86400 seconds in 1 day (Stillings et al., 2007; Jones, 2014).

2.2. Field methods for sample collection and preparation

In summer 2014 (June–July), biotic (benthic macroinvertebrates, aquatic vegetation – roots, shoots, inflorescence and submerged vegetation, fish and bird eggs) and abiotic (pond water and sediments) samples were collected from six ponds: Desilt and Felters in Unit 1, Big Island in Unit 2, Pintail in Unit 3 along with Gadwall and Redhead in Unit 4.

The samples were collected near the inlet, outlet and at an interior site close to a bird nesting area within each pond (Fig. 2-2). Field duplicates or triplicates (whenever possible) were collected for each sample type at every sampling point (Jones, 2014). Prior to sampling, all equipment was rinsed with pond water to prevent contamination. All field samples were stored in plastic bags or bottles to prevent leaching of B from borosilicate glass (Jones, 2014). The samples were stored in a cooler under ice and transported to the soils laboratory in Logan, UT.

2.2.1. Water samples

Field measurements of temperature and pH were gathered using a Thermo Scientific Orion Star A221, and redox potential was measured using an Accumet™ platinum Ag/AgCl combination electrode (Jones, 2014). Since colloidal solutions cause severe interference with spectroscopic analysis, the subsamples were filtered through a plain white 0.45 µm (25 mm diameter) Teflon® cellulosic membrane filter. They were acidified with trace metal grade concentrated nitric acid (HNO₃) to prevent microbial growth before being transferred to 25-mL acid-washed, polyethylene, scintillation vials and stored at 4 °C in a cooler before being transported to laboratory for total B analysis (Jones, 2014).

2.2.2. Sediment samples

The sediments were collected using a Kajak – Brinkhurst (KB) corer at three different depths 0-2, 2-5 and 5+ cm from the surface. They were subdivided by sampling site and cooled at 4 °C while transportation to the laboratory where they were frozen at -20 °C (Jones, 2104).

2.2.3. Benthic macroinvertebrate (BMI) samples

The macroinvertebrate samples were collected near bird egg sampling locations in open water areas between emergent vegetation (bulrushes and cattails). D-shaped dip nets were used to collect 40 g composite-samples (wet weight, ww). The samples were rinsed with deionized water to remove detritus/debris and sediments before placing in Whirlpacks[®] using pre-cleaned forceps (Jones, 2014). The BMI samples were split with one half transported to Logan for B analysis and the other half preserved in 90% ethyl alcohol for taxonomic speciation at BLM/USU National Aquatic Monitoring Center (NAMC) (Vinson and Hawkins, 1996; Jones, 2014).

2.2.4. Aquatic vegetation samples

Foraging habits of different bird species were observed to identify parts of aquatic vascular plants to be collected. Sampling sites were chosen based on close vicinity of a bird nest. The plant parts sampled consisted of roots, shoots, flowers and seeds of emergent vegetation and whole submerged plants like duckweed or algae skimmed from the pond surface (Jones, 2014). The vegetation samples were soaked in a 0.3 % surfactant solution of sodium lauryl sulfate followed by a 1 mmol L⁻¹ dilute HCl acid solution and finally rinsed with copious amounts of deionized water (Pilon-Smiths et al., 1999). The washed samples were separated, patted dry, weighed to record fresh weights (fw) and then refrigerated in high density polyethylene plastic bottles (submergent vegetation) or polyethylene Ziploc bags (emergent plant parts) for further analysis. At the Greenville Research Farm, USU, Logan, UT drying/grinding facility, the samples were placed in paper bags and dried in an oven at 80 °C for 24 hours. The dried samples were weighed to record dry weights (DW) and ground to particle size < 0.5 mm in a Wiley Mill. The ground

particles were sieved using a 2.5 mm screen to remove large husk debris and stored in labeled Ziploc bags under ambient laboratory conditions. Any plants not readily identifiable in the field were labeled following botanical techniques, placed in folded newspaper sheets and carried to the lab for proper identification (Jones, 2014).

2.2.5. Fish Samples

Fyke and Seine nets were used to collect whole fish samples. Five fish species per site were allowed for contaminant analysis. Samples were collected at the outlet sites of the Flood Control Dam, North Unit Canal, Big Island Pond, Pintail Pond, Gadwall Pond and Redhead Pond. The species collected included fathead minnow (*Pimephales promelas*), channel catfish (*Ictalurus punctatus*), black bullhead (*Ameiurus melas*), common carp (*Cyprinus carpio*) and green sunfish (*Lepomis cyanellus*). Whole fish samples were stored on ice in a cooler in the field but were frozen at -20°C upon return to the laboratory.

2.2.6. Bird Survey and Egg Samples

Bird species in the Pariette wetlands were identified using a previously established method used by BLM that utilizes bird survey point counts. In this method, sight and sound were used to identify species by trained specialists at fixed points along the route (Jones, 2014). Identified avian species included the black-crowned night heron (*Nycticorax nycticorax*), snowy egret (*Egretta thula*), marsh wren (*Cistothorus palustris*), northern shoveler (*Anas clypeata*), cinnamon teal (*Anas cyanoptera*), mallard (*Anas platyrhynchos*), gadwall (*Anas strepera*), redhead (*Aythya americana*), American coot (*Fulica americana*), American avocet (*Recurvirostra americana*), yellow-headed blackbird (*Xanthocephalus*

xanthocephalus), killdeer (*Charadrius vociferous*), Canada goose (*Branta canadensis*), pied-billed grebe (*Podilymbus podiceps*) and black-necked stilt (*Himantopus mexicanus*).

While sampling bird eggs, samples were not collected from all species identified. With the help of an experienced avian biologist, only one egg per nest per site was collected except for the sites with abandoned nests. Following established field procedures, each collected egg was placed in a paper carton with the air-cell facing upwards and the cartons were then placed on ice packs and transferred to a refrigerator in the laboratory (Jones, 2014).

2.3. Laboratory Procedures for Sample Analyses

2.3.1. Quality Assurance and Control (QA/QC)

While field replicates were collected to ensure sample homogeneity, 10% of the collected field samples were run as duplicates during laboratory analysis to guarantee quality assurance and control (QA/QC). These duplicates were analyzed to check for procedural precision ($COV \pm 25\%$). Additionally 10% samples were spiked with known B concentration to test matrix reliability by checking for interference by verifying the spike recovery ($COV \pm 15\%$). Standard reference materials (SRMs) such as NIST 2709a San Joaquin Soil (sediments), NIST 1573a, Tomato Leaves (aquatic vegetation and BMI samples) and NIST 2976, Mussel tissue (bird and fish tissue samples) were used to check the validity of the analytical procedures by comparing the analyzed values with the certified values; $COV \pm 25\%$ were accepted. To avoid contamination by B leaching from glassware, only high-density polyethylene labware was used. When using borosilicate glassware was unavoidable (using glass digestion tubes for high temperature digestions using concentrated acids), two blanks with 18 M Ω -cm deionized water were included to check

for potential B contamination. All used labware was acid washed and rinsed three times with 18 M Ω -cm deionized water prior to each use.

2.3.2. Colorimetric Analyses

Once clear sample extracts were obtained following the respective procedures for sample analysis, colorimetric reagents were prepared. These reagents included EDTA solution (0.025 mol L⁻¹, analytical grade EDTA salt), acetate buffer solution (final buffer pH = 4.8, analytical grade glacial acetic acid), and azomethine solution (analytical grade L-ascorbic acid, standard azomethine-H). The azomethine solution could be refrigerated up to seven days after which a fresh batch would be prepared. All other reagents were prepared in large batches and stored in polyethylene bottles under refrigeration at 4 °C (Gupta, 1979; Spencer and Erdmann, 1979). The initial steps of the colorimetric analysis required adding 10 mL filtered sample supernatant to a 20 mL acid washed plastic scintillation vial. Then, 10 mL of reagents (1 mL EDTA solution, 2 mL acetate buffer solution, 2 mL deionized water, 5 mL Azomethine-H solution) were added to the same vials. These were capped and shaken to mix contents. The vials were then left undisturbed for 2 – 4 (<4) hours to allow development of a yellow-colored, Azomethine complex (Gupta, 1979; Spencer and Erdmann, 1979). Upon color development, plastic transfer pipettes were used to transfer the colored extracts to plastic cuvettes for spectroscopic analysis at 420 nm with a spectrometer (Spectrosonic 401, Milton Roy Co. Michigan City, IN, USA). The absorbance values generated for each sample were recorded. The Azomethine-H method detection limit (MDL) for B was calculated using EPA method 200.2 and determined to be 0.12 mg L⁻¹ (EPA, 1994). A B stock solution (1000 mg L⁻¹, ACS reagent grade) was prepared and used to make standard solutions with B

concentrations 0.0, 0.4, 0.8, 1.2, 1.6 and 2 mg L⁻¹. These standard concentrations were used to plot the standard curve. The standard curve equation was determined with Excel. The standard equation was used to calculate extract B content (mg L⁻¹) by substituting previously noted sample absorbances (Gupta, 1979; Spencer and Erdmann, 1979).

2.3.3. Water Analyses

2.3.3.1 Boron Analyses

Water samples were transported to the Utah State University Analytical Laboratory (USUAL) in cooled labeled plastic vials for B analysis using Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES). The ICP–AES MDL for the trace metals analyzed, including B, was 0.001 mg L⁻¹. The ICP–AES was set up to analyze and report concentrations of selected elements in the water samples collected at the Pariette wetlands. The replicated samples showed COV ≤ 0.5 % within the limits set for QA/QC. As part of water sample characterization during laboratory analysis, pH and electrical conductivity were measured. The pH meter (Thermo Scientific Orion Model 0290A) was calibrated at 25 °C and magnetic stirrers were used to ensure sample solution uniformity. Electrical conductivity, EC_e was calculated and reported using a conductivity meter (Thermo Scientific Fisher Accumet Excel XL30) at 25 °C in mS cm⁻¹. The COV ≤ 7% was within the error limits set to ensure QA/QC for the replicated samples.

2.3.4. Sediment Analyses

Frozen sediment samples were thawed prior to determining the gravimetric water content and B concentrations. Moist subsamples, approximately 2.0 ± 1.0 g were weighed onto aluminum dishes. These subsamples were dried in a forced air oven (VWR Scientific Products 1350F) at 105 °C for 24 hours before calculating the sediment moisture content

(%). The sorbitol extraction method, developed by Goldberg and Suarez (2014), works on the principle of cis-diol groups in sugar alcohols binding plant available B present in sediments. This method was selected to determine plant available B in the Pariette Wetland sediment samples by weighing 3.00 ± 0.05 g of moist samples into 50-mL polypropylene Oakridge centrifuge tubes. Each sample tube received 30 mL of freshly prepared sorbitol extraction solution (0.2 M sorbitol, 0.01 M sodium chloride) before being capped tightly. All the tubes were placed on an Eberbach reciprocating shaker for 20–24 hours to facilitate continuous mixing. Subsequently the tubes were removed and centrifuged (Thermo Scientific Fisher Sorvall Lynx 4000) at 4 °C, 51500 g-force for 45 minutes till clear supernatants were obtained. The supernatants were decanted into 25-mL plastic, syringe barrels fitted with 0.45 μm (25 mm diameter) plain white cellulosic membrane filters to obtain clear sample extracts (Goldberg and Suarez, 2014). A 10-mL subsample extract was pipetted into 20-mL plastic scintillation vials followed by the addition of colorimetric reagents to determine absorbances at 420 nm. The absorbance values were substituted in the standard equation obtained from the plotted standard curve to determine the extract B concentration (mg B L^{-1}). The extract B concentrations were used to estimate the plant available B in the dry sediment samples (mg B kg^{-1} , DW).

For each sediment sample depth (0–2, 2–5 and 5+ cm) two separate sample runs were analyzed with $\text{COV} < 20\%$ for the samples in each unit per run. The established QA/QC restrictions with respect to lab sample replication per sample run ($\text{COV} < 10\%$), matrix spiking (recovery $< 15\%$), and blanks (B conc. $< \text{MDL}$) were adhered to. Each sample run included analysis and B concentration determination for SRM (NIST 2709a

San Joaquin soil) with recovery COV < 25% to confirm validity of B analysis procedure for sediments.

2.3.5. *Benthic Macroinvertebrate Analyses*

Frozen benthic macroinvertebrate (BMI) samples were thawed and homogenized prior to calculation of their gravimetric water content and total B concentrations. The whole BMI samples were ground to a pulp using a coffee grinder to ensure uniformity before they were digested in acid. All analysis that required working with acids was performed in an acid hood. Moist BMI subsamples with WW corresponding to 0.6-1 g, DW were digested in six milliliters of a 5:1 concentrated nitric acid–perchloric acid solution until approximately 0.5 mL of the clear, digested sample liquid was left in the glass digestion tubes (Zasoski and Burau, 1977). Once the tubes cooled down to room temperature, the digested sample liquids were brought to 12.5 mL volume with 18 MΩ–cm deionized water. Then 10-mL subsamples of these extracts were pipetted into 20-mL acid-washed scintillation vials followed by addition of reagents for the Azomethine–H method (Gupta 1979; Spencer and Erdmann, 1979). Upon color development samples were analyzed spectroscopically at 420 nm to determine total B concentrations in BMI samples.

To ensure procedure precision and accuracy two analytical runs were performed with 10% sample replication, 10% matrix spiking and one procedural blank. Also, a sample of SRM NIST 1573a, Tomato Leaves was included with each run to confirm accuracy of the analytical method. The QA/QC conditions for lab replicates (COV <15%) and SRM analysis (COV <10%) were met with spike recoveries at $\pm 10\%$ well within the acceptable limit. The procedural blanks included to account for contamination by B leaching from

glassware recorded B concentrations < MDL calculated using EPA method 200.2 (EPA, 1994).

2.3.6. Aquatic Vegetation Analyses

Subsamples weighing 0.6–1 g of each dried and ground plant sample (emergent plant parts, whole submergent plants) were digested in a nitric-perchloric acid solution in a similar fashion as BMI samples (Zasoski and Burau, 1977). The digested samples were analyzed for total B content using Azomethine–H colorimetric method (Gupta, 1979; Spencer and Erdmann, 1979).

In order to maintain procedural accuracy and precision, rigorous QC standards were set according to the type of aquatic vegetation. Emergent vegetation parts (roots, shoots and inflorescence) QA/QC standards were set at COV \pm 15% for sample replication and \pm 15% matrix spike recoveries. Submerged vegetation sample QC accepted COV \pm 15% for sample replication and \pm 15% for spike recoveries. Procedural blanks were introduced for all sample runs and the reported B concentration were < MDL. The SRM NIST 1573a (tomato leaves) was included in each analytical run for QA of the nitric–perchloric acid digestion with acceptable error set at \pm 10%.

2.3.7. Bird Egg and Fish Sample Analyses

Within 24 hours of bird egg collection, breakout analyses and dissections were performed in which the egg was cracked open to check for embryonic stage development and developmental abnormalities (Romanoff and Romanoff, 1972; Jones 2014). Using methods described by Hamilton (1952) and Caldwell and Snart (1974), the embryonic age was determined. Embryo developmental stage and presence of blastodisc for unfertilized

eggs were recorded using protocols established by Hoyt in 1979. Proper egg and whole fish measurements were noted before the samples were frozen in chemically cleaned containers and transported to Trace Element Research Lab (TERL), Texas A&M University for contaminant analysis. Heavy metals such as mercury (Hg), lithium (Li), Se and B were analyzed in all tissue samples. Moisture content was analyzed for whole fish samples and B concentrations were reported in ppm, DW. Since bird eggs continue to lose weight after being laid due to respiration and moisture loss, B concentrations were analyzed on a DW basis and reported in mg kg⁻¹, DW. In order to maintain QC, checks such as procedural blanks and sample replicates were included. The relative difference (mean ± SD) for duplicate samples ranged from 1.3 – 14.3%. Matrix spiking and SRM (NIST 2976 Mussel tissue, BC-563) analysis were performed with SRM and spike recoveries for B at 95% ± 1.9 and 93.8% ± 2.5, respectively.

3. Results and Discussion

3.1. Water Characterization Analysis

3.1.1. Mass Balance for Boron

Water quality monitoring stations measured the water flow rate through the Pariette Wetlands at the inlet up to a mile from the point of confluence with the Green river. The average flow rate of water into the wetlands at the inlet of Flood Control pond (UDEQ Station 4933476) for 2008–2009 was 0.544 m³ s⁻¹ (19.2 cfs) with average B concentration of 1.18 mg L⁻¹ (Wingert and Adams, 2010). The average monthly water inflow rate was elevated during the irrigation season (April – October), lowest in August (0.266 m³ s⁻¹, 9.4 cfs), and highest in June (2.004 m³ s⁻¹, 70.8 cfs). When the water flow rate was highest, the observed concentrations of TDS, B and Se were lowest due to higher dilution rates

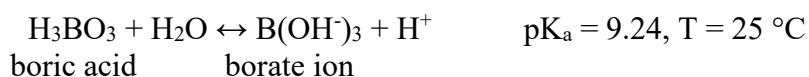
(Wingert and Adams, 2010). At the outlet station (UDEQ Station 4933440) the average B concentration was 1.74 mg L^{-1} at a water flow rate of $0.317 \text{ m}^3 \text{ s}^{-1}$ (11.2 cfs) (Wingert and Adams, 2010). The highest outflow rate was measured in October ($0.708 \text{ m}^3 \text{ s}^{-1}$, 25 cfs) and lowest in August ($0.167 \text{ m}^3 \text{ s}^{-1}$, 5.9 cfs). Fig. 2-3 shows the variation of B mass flux in the Pariette Wetlands for 2008 with peaks observed in March, June and October. The B mass influx and outflux averaged at $40.52 \pm 34.4 \text{ kg day}^{-1}$ and $42.15 \pm 30.8 \text{ kg day}^{-1}$, respectively with a high COV (85% inlet, 73% outlet). The peaks observed in B mass flux can be explained by the occurrence of seasonal storms. We observed no statistical significance difference (one tailed t-test, p value = 0.397) in the average amount of B entering and exiting the wetland system.

The B mass flux measurements for water flowing through the Pariette Wetlands were intermittent and averaged monthly. Also, no additional flux measurements were taken that could throw light on B partitioning in other ecosystem components like deep sediments, aquatic vegetation, BMI, wetland fish or bird eggs. As such it is difficult to conduct a detailed mass balance on B in wetland complex. However, based on the limited data analyzed it appears that unlike Se, B is not accumulating in the Pariette Wetlands even though it might concentrate in specific ecosystem components such as submerged vegetation.

3.1.2. Aqueous speciation of B

The most dominant forms of B in natural aqueous solutions are boric acid (H_3BO_3) and borate ions ($\text{B}(\text{OH})_4^-$) (Kochkodan et al., 2015). The species distribution depends on the first dissociation constant (pK_a) of boric acid. The boric acid pK_a depends greatly on ionic strength and temperature of the solution. The solubility of boric acid decreases from

5.44% at 25 °C to 4.65% at 20 °C (Owen, 1934; Kemp, 1956). Results from another study also show a decrease in boric acid pKa from 9.24 to 8.6 when water salinity increases to 35% (Ezward and Haarhoff, 2011; Kochkodan et al., 2015). The most critical parameter determining ratio of boric acid and borate ions, however, is pH (Kochkodan et al., 2015). The following equilibrium equation can be used to predict B species distribution:



When the solution pH = pK_a = 9.24, the concentrations of dissociated boric acid and borate ions is equal. However, as pH < pK_a the dominant B species will be boric acid (Fig. 2-4b) (Kochkodan et al., 2015). The on-site measurement of pH at the Pariette Wetlands stated pH varying between 7.0 and 9.9 averaging at 8.8 ± 0.8. The lab pH measurements of water samples fluctuated between 7.6 and 9.7 with an average of 8.7 ± 0.6 (Fig. 2-4a). A two tailed t-test showed the field and lab measurements were statistically not significantly different (p-value = 0.523).

The ICP analysis of pond water samples collected throughout the wetlands also determined total element concentrations (Table 2-4a) of which the highest were recorded for Na, S, Mg and Ca. These concentrations were utilized in the calculation of aqueous species concentrations with the help of a speciation model, Visual MINTEQ (version 3.1) (Gustafsson, 2014). The element concentrations were entered as concentrations of the dominant, oxidized species (e.g., Na⁺, SO₄, Mg²⁺ and Ca²⁺). Visual MINTEQ was run at conditions measured at Pariette Wetlands: T_{avg} = 20.5 °C, CO₂ (g) = 0.0042 atm and pond pH measured in the laboratory (Gustafsson, 2014). The speciation results from MINTEQ show large differences in the number of cations and anions measured for each pond within

the wetland complex, most likely due to an incomplete data set of dissolved elements, particularly anions such chloride (Cl^-). The average ionic strength for the water samples was 0.3439 ± 0.4 with highest strength measured at 1.3 (mol L^{-1}) for the interior site at Gadwall. A high ionic strength could introduce error in speciation output results because the Davies equation used to calculate activity coefficients is not valid at ionic strengths above 0.5 mol L^{-1} . Table 2-4b shows composition of the wetland water samples detailing distribution of the dominant species. All water samples contained a high fraction of dissociated SO_4^{2-} and undissociated CaCO_3 and MgCO_3 in their respective aqueous forms in the wetland complex with the highest percentages noted at $\text{pH} > 9$. The percentages of dissociated K^+ and HCO_3^- were consistent throughout the pond units with no observed effect as pH changes. At $\text{pH} > 9$, the percentage of free dissociated Na^+ reduced in the water samples. The speciation of B was also pH dependent with higher proportions of undissociated boric acid (H_3BO_3) present in samples with $\text{pH} < 9$. However, as $\text{pH} > 9$, dihydrogen borate (H_2BO_3^-) becomes the dominant B form. This was observed at eight of the 18 water sampling sites in the Pariette Wetlands, thus confirming dominant B species as undissociated boric acid at these sites. Fig. 2-4b represents a speciation diagram displaying the major B species in the pond water sampled at Pariette Wetlands.

3.2. Boron Toxicity Analysis

3.2.1. Water

The pond water sampled in Pariette Wetlands, July 2014 were analyzed to determine total B concentrations fluctuating between 2.66 and 5.17 mg L^{-1} , averaging at $2.87 \pm 0.8 \text{ mg L}^{-1}$. The B content was 4 – 6 times the B water quality standard of 0.75 mg L^{-1} , set by UDEQ and UDWQ. A study of Se, B and Mo concentrations in the Lower San

Joaquin River, California, reported total B concentration in water between 0.012 and 0.041 mg L⁻¹ (Schuler, 1987; Saiki et al., 1993). This river receives surface run off and brackish tile drainage water from an area with high ambient levels of B due to marine shale present in the bedrock similar to the ponds in Pariette Wetlands. Our measured B concentrations were 100 times the concentrations measured in Lower San Joaquin River and exceeded LOAELs for all aquatic plants (0.5 mg L⁻¹) and sensitive BMI species like crustaceans (2.8 mg L⁻¹) that show decreasing embryo survival rates as B levels increase (Schuler 1987; Howe, 1998; Soucek et al., 2011). However, the water B concentrations were lower than established LOAELs for macroinvertebrates like *Daphnia magna* (6–13 mg L⁻¹) and freshwater fish (6.4 mg L⁻¹) (Gersich 1984; Perry et al., 1994; Howe, 1998). A chronic exposure (21 days) study examining the effects of B on submerged macrophytes reported significant reduction in their net photosynthetic capacity as compared to controls at B concentrations of 2 and 5 mg L⁻¹ for *Elodea canadensis* (waterweed) and *Myriophyllum alterniflorum* (watermilfoil), respectively. The authors also determined the LC₅₀ for both macrophyte species at 5 mg L⁻¹ which lies in the range of the measured B levels in water samples at the Pariette wetland complex (Nobel, 1981). Fig. 2-5 is a box plot representation of the total B concentrations measured in water samples from ponds in all 4 units of the Pariette Wetlands.

3.2.2. Sediments

Measured pH values for the top sediment layer (0–2 cm) were statistically same as the water pH, which is expected given this sediment layer was saturated with pond water. Sediment B concentrations were measured for samples collected from all depths. A two tailed, paired t-test was used to determine if B concentrations in samples from depths 2–5

and > 5 cm were statistically different. The p-value (> 0.05) indicated no statistical difference in B concentrations at depths 2 – 5 cm and below 5 cm. Colorimetric analyses of sediment sample extracts from Pariette Wetlands reported the lowest B concentration at Felters pond inlet site (25.60 mg kg^{-1} , DW) and the highest concentration at Redhead pond interior site (96.61 mg kg^{-1} , DW). The average B concentration in the sediment top layer was $51.65 \pm 21.8 \text{ mg kg}^{-1}$, DW while the average B concentration in 2–5 cm layer was $26.72 \pm 22.93 \text{ mg kg}^{-1}$, DW. A box plot comparison of plant available B in sediments from depths 0 – 2 cm and 2 – 5 cm in the wetlands is presented in Fig. 2-6.

A study by CAWQCB (1990) on sediment quality in the evaporation ponds in San Joaquin Valley, CA reported average B concentrations of 112 mg kg^{-1} , DW. The study also reported average B concentrations (91 , 155 and 140 mg kg^{-1} , DW) in three separate sampling settings (lake bed, alluvial fan and basin trough area). An ICP – MS analysis of the bulk rock and soil samples collected from marine shale bedrock, coal and natural gas beds in the lower Uinta formation in the Pariette Draw reported high background average B levels of 79.31 and 89.19 mg kg^{-1} , DW, respectively (Powell, 1997; Wingert and Adams, 2010; Morrison et al., 2015). The higher B content in our samples may be attributed to B present in the bedrock, particularly Uinta formation. Even though the Pariette Wetlands waters and sediments have higher B concentrations than the national average, we found no specific evidence corroborating bioconcentration of B in the wetland sediments.

3.2.3. *Benthic Macroinvertebrates*

The taxonomic speciation of BMI split samples by NAMC provides detailed insight into water quality in the Pariette Wetlands using ecological indicators like taxa richness, evenness and abundance and types of functional feeding groups to assess freshwater

biological integrity. Taxa richness (number of unique species in the sampling area) was < 13 for all pond units. The taxa evenness (dominance of a single species in a sampling area) measured by Simpson's diversity index approached 1 for Desilt (Unit 1), Big Island (Unit 2) and Gadwall (Unit 4) ponds. These values point to possible monoculture with the presence of a single dominant BMI species in the wetlands. The Shannon's diversity index, an indirect measurement of low BMI diversity, was < 2.5 for all wetland ponds. The standardized compositional matrices report an increased perturbation in the water quality. High population numbers of tolerant taxa like *Physidae*, *Corixidae*, *Chironomidae* and *Coenagrionidae* and non-existent numbers of sensitive taxa like *Ephemeroptera*, *Plecoptera* and *Trichoptera* suggest the Pariette Wetland ponds are contaminated with stressful environments.

Tolerance indices like Hilsenhoff Biotic Index (HBI) and USFS community tolerance quotient are used to evaluate and identify aquatic ecosystems undergoing ecological stress. The HBI scores between 0 (taxa in unpolluted water) and 10 (taxa in severely polluted water) help in detecting nutrient enrichment, fine sediment loading or low dissolved oxygen content and thermal impacts in natural water systems (Hilsenhoff, 1987; Hilsenhoff 1988). The HBI scores for the wetlands varied from 4–7 indicating nutrient enrichment. The USFS quotient values are scored from 2 to 108 based on the abundance of taxa present in high quality, unpolluted water or severely polluted waters (Winget and Magnum, 1979). The measured values for Pariette Wetlands are high and vary between 93 and 108. The pond units 1 and 4 had USFS quotient values above 100 (103 and 104, respectively) and reported a high abundance of tolerant taxa. Observations from three different sampling sites near Kırka, Turkey also showed a decrease in taxa richness and

diversity in areas with elevated B concentrations (Emiroğlu et al., 2010). The tabulated results (Table 2-1) provide detailed insight into deteriorating water quality, stressed living conditions and lack of BMI diversity at the sampling sites in Pariette Wetlands.

The B toxicity analysis of BMI samples revealed concentrations ranging from 10.9 mg kg⁻¹, DW (lowest, Redhead interior site) to 51.07 mg kg⁻¹, DW (highest, Pintail inlet site) averaging at 28.45 ± 12.04 mg kg⁻¹, DW (Fig. 2-7). An amendment to the San Joaquin River Basin plan lists a B concentration of 13 mg L⁻¹ as the LOAEL for *Daphnia magna* (crustacean) (Butterwick et al., 1989; CEPA, 2000). This amendment also specified a European study that reported toxicity in *D. magna* when exposed to B levels > 6 mg L⁻¹ for 21 days (ECETOC, 1997). Results summarized from an acute (48 hour exposure) toxicity test on *D. magna* and *Chironomous decorus* (Diptera) showed lethal and sub lethal toxicity to B at LC₅₀ 141 and 1376 mg L⁻¹, respectively. However, *C. decorus* displayed reduced growth rates when exposed to B levels at 20 mg L⁻¹ for 48 hours (Maier and Knight, 1991). Independent chronic toxicity (21 day exposure) tests conducted by Lewis and Valentine (1981) and Gersich (1984) estimated *D. magna* LC₅₀ values for B levels at 53.2 and 52.2 mg L⁻¹. The average B concentration in Pariette Wetland samples are higher than LOAEL for *D. magna* and are capable of resulting in reduced growth rates for *C. decorus* which are abundantly present at the sampling sites (Table 2-1). It was also observed that B concentrations were elevated in subsamples that were abundant in beetles (*Corixidae*), crustaceans (*Physidae*), and dragonflies (*Odonates*). A possible repercussion of low BMI diversity at sites with high B concentrations could be reduced waterfowl populations in the wetland management area as observed by Baird and Etchberger (2010) although thorough research would be required to support this claim.

3.2.4. Aquatic Vegetation

Emergent Vegetation. Four species of emergent vascular plants – cattails (*Typha spp.*), bulrushes (*Scirpus spp.*), reeds (*Phragmites aus.*) and alkali bulrush (*Scirpus mar.*) were identified from the collected samples. Total B concentrations were determined in all parts (roots, shoots and inflorescence) of the emergent plants. Of all the plant species (cattails, bulrush, reeds and alkali bulrush) only *Typha latifolia* (cattails) and *Scirpus* (bulrush) were collected in all pond units. The highest B concentrations were measured in *Phragmites* (reed) roots at the Redhead interior site in Unit 4 (146.86 mg kg⁻¹, DW), *Scirpus* (bulrush) shoots at Redhead outlet in Unit 4 (140 mg kg⁻¹, DW) and *Scirpus* (bulrush) inflorescence at Felters inlet in Unit 1 (114.21 mg kg⁻¹, DW). The average B content in *T. latifolia* samples collected from all pond units varied between 27–56, 29–53 and 10–22 mg kg⁻¹, DW for roots, shoots and inflorescence, respectively. Similarly, *Scirpus* samples measured average B values in the ranges 36–119, 26–93 and 8–32 mg kg⁻¹, DW for roots, shoots and inflorescence, respectively. A pot study reporting effect of rising water B concentration (up to 8 mg L⁻¹) on *P. australis* (reeds) revealed high tolerance for an exposure time of 2–3 months (Marks et al., 1994; Bergmann et al., 1995; WHO, 1998). Many studies have postulated long term exposure to B levels ≤ 10 mg L⁻¹ resulting in leaf damage, reduced growth and yield of emergent vascular plants with possible bioconcentration (Schuler 1987; Smith and Anders, 1989; Roux et al., 1996; Powell, 1997; USBR 1998; Parks et al., 2005). The B levels in emergent vegetation parts collected in Pariette Wetlands are elevated even though ambient water levels (2.87 mg L⁻¹) are low. Our results seem to be in agreement with researchers suggesting bioconcentration of B in aquatic vascular plants.

Submergent Vegetation. Out of the three species of submerged vegetation that were collected at Pariette wetlands, *Potamogeton* (pondweed) and *Myriophylla* (watermilfoil) are categorized as submergent vegetation; whereas, *Chara* (muskgrass) is an algae. *Potamogeton* and *Chara* are submergent species that were sampled in all pond units with total B concentrations observed between 100 – 1150 mg kg⁻¹, DW (COV ± 25%) and 50 and 150 mg kg⁻¹, DW (COV ± 25%), respectively. Ohlendorf et al., (1986) reported average B concentrations in wetland submerged vegetation exposed to elevated B at 382 mg kg⁻¹, DW in the Kesterson National Wildlife Refuge. A study comparing B concentrations in vegetation samples collected over 2 years, 1984 and 1985 at the Kesterson National Wildlife Refuge reported higher B concentrations in 1985 than 1984 with B content varying between 120 and 780 mg kg⁻¹, DW and a maximum B recorded at 1630 mg kg⁻¹, DW for widgeon grass (Hothem and Ohlendorf, 1989). Schuler (1987) reported B accumulation in filamentous algae growing in brackish drainage water with elevated B content (12–41 mg L⁻¹) and fresh water with low B (1.4–2.2 mg L⁻¹) in San Joaquin Valley. The B concentrations in the algae species varied from 390–787 mg kg⁻¹, DW to 64–140 mg kg⁻¹, DW (Schuler, 1987; Saiki et al., 1993). Results from these studies support our observations of B bioconcentration in submerged aquatic plants in low ambient habitat levels (Schuler 1987; Smith and Anders, 1989; Saiki et al., 1993; Roux et al., 1996; USBR 1998; Parks et al., 2005).

Figs. 2-8 and 2-9 are graphical representations of total B content in aquatic vegetation sampled at the Pariette Wetlands and provide a comparison between the levels observed in the respective identified species. The median (x), maximum and minimum B values are shown along with the sample size (n). For emergent vegetation, even though

difference in the lowest and highest B concentration was large, a species-wise (Cattails and Bulrush) comparison showed no particular correlations. There was great variation in the B levels between the two main species of submerged vegetation identified. *Potamogeton* categorized as a submerged aquatic plant could be absorbing B from sediments as well as surrounding water. This could be a contributing factor to higher constituent concentrations.

3.2.5. Fish

The main wetland fish samples identified included freshwater species like Black bullhead catfish (*Ameiurus melas*), Fathead minnow (*Pimephales promelas*), Flannelmouth sucker (*Catostomus latipinnis*), Green sunfish (*Lepomis cyanellus*) and Red shiner (*Cyprinella lutrensis*). The Flannelmouth sucker, a freshwater fish, is uncommon in Lower Colorado River Basin (LCRB). This omnivorous fish lives in fast moving water feeding on an abundance of *Diptera* (chironomids), *Ephemeroptera*, *Trichoptera*, *Plecoptera*, organic matter and sediment. The collected specimens for this species were not analyzed for B since they were not present beyond the Flood control in Unit 1. Apart from the Flannelmouth sucker, the remaining four species collected in the Wetlands are commonly found all over US in ponds, small lakes and wetlands. These freshwater species are classified by a high tolerance for stressed environments and harsh living conditions categorized by poor water quality. The total B content in all fish samples were measured in ppm, DW (mg kg^{-1} , DW) varying from 0.88 to 14.4 (Fig. 2-10). The species wise distribution of B varied with fish dietary preferences, age and size. For example: the average B content in Black bullhead catfish ($n = 3$, 1 unit), Red shiners ($n = 10$, 2 units), Fathead minnow ($n = 5$, 1 unit) and green sunfish ($n = 18$, 3 units) was 9.5 ± 1.7 ; 2.1 ± 0.6 ; 1.3 ± 0.3 and $5.6 \pm 4.6 \text{ mg kg}^{-1}$, DW respectively. All fish samples collected varied in size

(length, weight) and age with majority being adults measuring 8.5 cm in length with average weight of 8.83 g. The catfish, red shiners and minnows feed on BMIs, plant detritus and algae along with adult insects. Green sunfish was the most abundantly collected freshwater species in wetland ponds. It had the largest observed variation in unit wise total B content with specimens from Units 2 and 4 containing B between 1.4 and 7.8 mg kg⁻¹, DW; whereas, samples from Unit 3 reported an average B content of 12.6 mg kg⁻¹, DW. The green sunfish feeds mostly on macroinvertebrate larvae, snails and other smaller invertebrates. Considering food preferences to be the same for all collected samples, a detailed examination of the specimens revealed that the fish from Unit 3 (Pintail pond) weighed more than the wetland average (up to 15 g), were longer than the wetland average (up to 11 cm) and were adult in maturity (Fig. 2-11). These sample characteristics along with exposure to elevated ambient B concentration in pond water could be a major contributing factor towards high B concentrations in the samples from Unit 3. A research study on the effects elevated B concentrations for varying exposure times reported an increase in fish mortality rates with increasing exposure times even if the B concentrations were consistently decreasing (NAS, 1972). The study documented increased mortality in western mosquito fish (*Gambusia affinis*) when the exposure time was increased from 1 to 6 days, even though B concentrations were reduced by an order of magnitude from 1360 to 215 mg L⁻¹ (NAS, 1972). Another long-term exposure (28 days) study examining the effects of elevated B in surface drainage water to the freshwater fish Chinook salmon and Striped bass in the Lower San Joaquin River reported B accumulation up to 200 mg kg⁻¹, DW (Saiki et al., 1992). An acute toxicity test performed to check freshwater fish sensitivity to elevated B resulted in the rainbow trout (*Oncorhynchus mykiss*) and zebrafish

(*Brachydanio rerio*) showing adverse effects at B concentrations as low as 10 mg L⁻¹ (WHO, 1998). A study for Procter and Gamble (Black et al., 1993) verified reduction in growth of nonsalmonid fish species (e.g., fathead minnow) after 30 and 60 days of exposure to water with B levels at 24 and 88 mg L⁻¹. The B content of the Pariette pond waters is lower than the observed LOAEL (6.4 mg L⁻¹) for freshwater fish (Howe, 1998) and about 4 to 6 times lower than the concentrations measured in the 1979 study. Hence, it is safe to assume that the fish species in Pariette Wetlands are at no immediate risk of toxicity from B. However examining the results from multiple studies on B toxicity effects to freshwater fish upon prolonged exposure to B concentrations higher than 10 mg L⁻¹ necessitate continued monitoring of B levels in the wetland ecosystem to prevent future issues.

3.2.6. Bird eggs

Several waterfowl species were identified in the Pariette Wetlands, however, egg samples were not collected for all. Eggs were collected for 15 different species, which we divided into 3 separate groups based on their feeding behavior (Table 2-3). Dabblers feeding on emergent shoots, submerged plants, seeds and macroinvertebrates included species like the American coot (*Fulica americana*) and cinnamon teal (*Anas cyanoptera*). Divers (e.g., pied-billed grebes) and probers (e.g., spotted sandpipers) feed on BMIs and fish; whereas, ground foragers (e.g., marsh wrens and yellow-headed black birds) eat insects and seeds. The B concentrations in bird eggs segregated by their feeding behavior were graphically represented using boxplots in Fig. 2-12. Bird eggs of divers/probers (n = 7) and ground foragers (n = 14) had B concentrations < 2 mg kg⁻¹, DW; whereas, the dabbler eggs (n = 29) reported B concentrations between 2–4 mg kg⁻¹, DW. American Coots were the most extensively sampled waterfowl species in the Pariette Wetlands and

B distribution in their eggs ($n = 22$) reported the highest concentrations up to 7.68 mg kg^{-1} B, DW (Fig. 2-13). Their egg concentrations were further analyzed using an ecological statistical test to examine possible correlations between B content in eggs and B levels in their food sources (Table 2-2).

3.3. Statistical Tests and Correlations

In order to establish whether correlations occur between B distributions in abiotic (water and sediments) and biotic (BMIs, aquatic vegetation) samples, and suggest a logical pathway for bioconcentration of B, statistical tests were performed. First, the sampling sites were spatially correlated to ensure geographic similarity. Also, we needed a statistical test that would take into account B bioconcentration from multiple sources in the wetland ecosystem. Simple linear statistical correlations were poor to non-existent and were hampered by a limited sample size and lack of co-localization between bird egg samples (collected where they were found) and all the other samples collected. Thus, the linear correlations were unable to provide any insight on B mobilization in the wetlands. Simple and Partial Mantel tests are statistical tests of the correlation between two matrices. The data in the matrices may be estimates of the physical distance between objects, differences in an environmental parameter that is numeric and continuous (e.g., pH or B concentration), or even difference in population genetics. Mantel tests are frequently used for establishing species-environment correlations in ecology. Thus, we chose this as a statistical approach to develop geospatial correlations between the environmental sites and sampled components. We used RStudio version 1.1.463 (<https://www.rstudio.com>) to run the Mantel tests and generate one-tailed p -values ($p\text{-val}_1$) and Mantel- r coefficients. These

statistics helped to corroborate if the B concentration in the same sample type is similar over a large geographical area within the wetland complex.

Our null hypothesis (H_0) assumes the concentrations to be similar and Table 2-2 provides evidence for and against the probability of our null hypothesis being true. The abiotic samples from the Parquette wetlands – water and sediment, exhibited relatively low B concentrations; whereas, elevated B levels were observed in emergent and submerged vegetation. The positive Mantel correlations that exist between, i) sediment B concentrations and B concentrations in emergent shoots, BMIs, and ii) water B concentrations and emergent shoots, roots B concentrations, suggest a causal relationship (Fig. 2-14).

The wetland ecosystem also included freshwater fish, which are an important food source for waterfowl species. In order to determine B exposure from fish to waterfowl, we first devised a partial Mantel test to determine any correlations between the fish species and their dietary preferences including BMIs, submerged plants along with their habitat i.e., water and sediment (intentional and non-intentional ingestion exposure). The results of this partial Mantel test determined the fish B concentrations to be positively correlated to B content in sediments and submerged plants but negative correlations with living habitat (pond water) and BMIs. Hence, a possible route for B accumulation in the wetland fish via sediments and submerged plants was established as shown in Fig. 2-14.

Since wetland waterfowl ingest aquatic flora, BMIs and fish as their major food source, it was hypothesized that elevated B concentrations in bird eggs could be a result of B accumulation from specific food sources like water, sediments, aquatic vegetation, benthic macroinvertebrates or fish based on their food gathering behavior. Waterfowl were

divided into two groups based on their dominant feeding behavior. Dabblers tend to feed at or near the water surface ingesting algae and small water creatures. They are primarily vegetarian, but will eat insects and crustaceans in addition to the leaves, stems and buds of aquatic plants. Probers, on the otherhand, are entirely carnivorous. They are largely shorebirds that probe into mud and sediments for worms, insect larva, crustaceans, benthic invertebrates, and small vertebrates. Divers are primarily fish eaters. Partial Mantel tests were conducted between B levels in food sources specific to waterfowl feeding behavior. For example, B concentrations in dabbler eggs were run against B concentrations in BMIs, and emergent and submerged vegetation; whereas, B concentrations in prober/diver eggs were run against B concentrations in BMIs and fish. The Mantel tests yielded positive correlations between B concentrations in i) miscellaneous dabbler eggs and emergent shoots, ii) American Coot (dabbler) eggs and BMIs, emergent roots and shoots, and iii) Divers/Probers and BMIs and fish, especially Green sunfish. The p – values > 0.5 indicate a high probability of sampling sites with similar B concentrations in food sources having similar B content in bird eggs, suggesting a viable ingestion pathway for B in birds (Fig. 2-14).

4. Conclusions

Although boron is an essential element used in metabolic, nutritional, hormonal and physiological processes in plants and animals, at high concentrations it can pose toxicity threats to sensitive species present in the Pariette Wetlands. Our investigations show the B concentrations in Pariette pond waters exceed established LOAEL for several aquatic plants and organisms like crustaceans (more sensitive to elevated B than other BMIs).

Concentrations of B are elevated in the wetland sediments due to the presence of marine shale in the bedrock, and mobilization of B throughout the wetland complex. The B concentration in benthic macroinvertebrates was higher than ambient B concentration in their habitat. Macroinvertebrate biodiversity was low for all ponds in the complex. The standardized counts of abundant taxa indicate an increased presence of pollution tolerant taxa like *Chironomidae* and non-existent populations of freshwater BMI such as *Ephemeroptera*, *Plecoptera* or *Trichoptera*. This points toward impaired pond conditions and increased environmental stress in the wetlands. Even though stressors such as elevated Se and dissolved salts have been documented in the wetlands, high B concentrations may also be contributing to ecosystem stress (Wingert and Adams, 2010). The low BMI diversity could be indirectly impacting waterfowl biodiversity in the wetlands; however, more direct research is required to support this hypothesis (Baird and Etchberger, 2014). The reported values for B in submerged as well as emergent vegetation were high suggesting possible B bioaccumulation. The submerged vegetation species had higher B concentrations than the emergent vegetation. We theorized if *Potamogeton* and *Chara* form the primary food source for waterfowl in the Pariette Wetlands, B toxicity to waterfowl could become an issue. However, other waterfowl food sources like BMIs, water and sediments did not have B concentrations high enough to impact adult birds or freshwater fish tolerant of poor water quality (high pH and EC_e). Simple linear statistical correlations between B in bird eggs or fish and B in respective habitat and food sources were poor to non-existent. Nonetheless, simple and partial Mantel tests yielded positive test coefficients (mmantel-r) along with high p-values suggesting possible pathways for B exposure via ingestion of toxic food sources. Literature from areas with similar ambient and dietary B

concentrations (Kesterson Wildlife Refuge and Lower San Joaquin River Valley) suggests that dietary intake of B impacts baby birds (CAWQCB, 1990; WHO, 1998). A number of studies have investigated the accumulation of B in aquatic food ecosystem components such as plants, insects and fish (Saiki and May, 1988; Hothem and Ohlendorf, 1989; Smith and Anders, 1989; Paveglio et al., 1992; Saiki et al., 1993) suggesting that although B can concentrate in aquatic vegetation (emergent and submergent), it does not biomagnify in aquatic food-chains. Although our research results support their conclusions, in order to prevent future toxicity issues we recommend continued monitoring of B concentrations in water as well as occasional monitoring of B in submerged vegetation since it bioconcentrates B even when B concentrations in the water are low. Also, BMI samples should be periodically collected and analyzed for B to provide a reliable overview of water quality in the wetlands. Both, submerged aquatic vegetation and BMIs could be used as easily sampled indicators of the threat of B to the wetland fish and bird embryos.

References

- Agency for Toxic Substances and Disease Registry (ATSDR), 1992. Toxicological Profile for Boron. Agency for Toxic Substances and Disease Registry, Public Health Service, U.S. Department of Health and Human Services. <http://www.atsdr.cdc.gov/toxprofiles/tp26.html>.
- Baird, D., Etchberger, R., 2010. Waterfowl population trends, Pariette Wetlands, Utah 1980 – 2010. Utah State University.
- Basoglu, A., Sevinc, M., Guzelbektas, H., Civelek, T., 2000. Effect of borax on lipid profile in dogs. *J. Vet. Res.* 4(6), 153–156.
- Blevins D. G., K. M. Lukaszewski, 1994. Proposed physiologic functions of boron in plants pertinent to animal and human metabolism. *Environ. Health. Perspect.* 102(7), 31-33.

- Blevins, D.G., K.M. Lukaszewski, 1998. Boron in plant structure and function. *Annu. Rev. Plant. Physiol. Plant. Mol. Biol.* 49, 481–500.
- Bergmann, W., P. Bruchlos, G. Marks, 1995. A contribution to the question of the limit value for boron in water for *Ogragnutes australis* seed. *Tensidem Surfact. Det.* 32, 229-237.
- Black, J.A., J.B. Barnum, W.J. Birge, 1993. An integrated assessment of the biological effects of boron to the rainbow trout. *Chemosphere* 26, 1383-1413.
- Boyd, C.E., W.W. Walley, 1972. Studies of the biogeochemistry of boron concentrations in surface waters, rainfall and aquatic plants. *Am. Midl. Nat.* 88, 1-14.
- Butterwick, L., N. de Oude, K. Raymond, 1989. Safety assessment of boron in aquatic and terrestrial environments. *Ecotoxicol. Environ. Saf.* 17(3), 339-371.
- California Environmental Protection Agency (CEPA), 2000. Boron: A Literature Summary for Developing Water Quality Objectives, San Joaquin River Basin Plan Amendment.
- Caldwell, P.J., A.E. Snart, 1974. A photographic index for aging mallard embryos, *J. Wildl. Manage.* 38, 298-301.
- Camacho-Cristóbal, J.J., J. Rexach, A.G. Fontes, 2008. Boron in plants: deficiency and toxicity. *J. Integr. Plant Biol.* 50(10), 1247–1255.
- Cotton, F.A., G. Wilkinson, C.A. Murillo, 1999. Boron. In: *Advanced inorganic chemistry*. 6th Ed. New-York, NY: John Wiley & Sons, Inc., 131-174.
- European Center for Ecotoxicology and Toxicology of Chemicals (ECETOC), 1997. *Ecotoxicology of Some Interim Borates*. Interim Report, 99.
- Eisler, R., 1990. Boron hazards to fish, wildlife and invertebrates: A Synoptic review, *Biological Report* 85, 1-20.
- Emiroğlu, Ö, A. Çiçek, N. Arslan, S. Aksan, M. Rüzgar, 2010. Boron concentration in water, sediment and different organisms around large borate deposits of Turkey. *Bull. Environ. Contam. Toxicol.* 84(4), 427-431.
- Ezward, J.K., J. Haarhoff, 2011. Seawater pretreatment for reverse osmosis: chemistry, contaminants and coagulation. *Water Res.* 45, 5428-5440.
- Gersich, F.M., 1984. Evaluation of a static renewal chronic toxicity test method for *Daphnia-magna* Straus using boric-acid. *Environ. Tox. & Chem.* 3(1), 89-94.
- Goldberg, S., D.L. Suarez, 2014. A new soil test for quantitative measurement of available and adsorbed boron, *Soil Sci. Soc. Am. J.* 78, 480–485.

- Graff, A., E. Barrez, P. Baranek, M. Bachet, P. Benezeth, 2017. Complexation of nickel ions by boric acid or (poly)borates, *J. Soln. Chem.* 46, 25-43.
- Gupta, U.C., 1979. Some Factors affecting the determination of hot water soluble boron from podzol soils using Azomethine-H method, *Can. J. Soil Sci.* 59, 241-247.
- Gustafsson, J.P. (2014) Visual MINTEQ ver. 3.1. KTH, SEED Stockholm, Sweden. <https://vminteq.lwr.kth.se/>
- Hamilton, H.L., 1952. Lillie's development in the chick, 3rd Edition. Rinehart and Winston, New York.
- Hilal, N., G.J. Kim, C. Somerfield, 2011. Boron removal from saline water: A comprehensive review. *Desalination* 273, 23–35.
- Hilsenhoff, W.L., 1987. An improved biotic index of organic stream pollution. *Great Lakes Entomol.* 20(1), 31–40.
- Hilsenhoff, W.L., 1988. Rapid field assessment of organic pollution with a family-level biotic index, *J. N. Am. Benthol. Soc.* 7(1), 65–68.
- Hothem, R. L., H.M. Ohlendorf, 1989. Contaminants in foods of aquatic birds at Kesterson Reservoir, California, 1985, *Arch. Environ. Contam. Toxicol.* 18(6), 773-786.
- Howe, P.D., 1998. A review of boron effects in the environment. *Biol. Trace Elem. Res. J.* 66, 153-166.
- Hoyt, D.F., 1979. Practical methods of estimating volume and fresh weight of bird eggs. *The Auk* 96(1), 73-77.
- Hazardous Substances Data Bank (HSDB), 2004. <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>.
- Hunt, C. D., 1998. One possible role of dietary boron in higher animals and humans. *Biol. Trace Elem. Res. J.* 66, 205–225.
- Hunt, C.D., 2012. Dietary boron: Progress in establishing essential roles in human physiology. *J. Trace Elem. Med. Biol.* 26, 157–160.
- Hutchison, G.E. 1975. A treatise on limnology-limnology botany. John Wiley, New York.
- Jones, C.P., 2014. Biochemistry of selenium in Pariette Wetlands, Utah. Graduate Theses and Dissertations, Utah State University.
- Kabu, M., M.S. Akosman, 2012. Biological effects of boron. *Rev. Environ. Contam. Toxicol.* 225, 57-75.

- Kemp, P.H., 1956. The chemistry of borates, W. S. Cowell LTD, Ipswich.
- Koç, C., 2007. Effects on environment and agriculture of geothermal wastewater and boron pollution in great Menderes basin. *Environ. Monit. Assess.* 125(1-3), 377-388.
- Kochkodan, V., N.B. Darwish, N. Hilal, 2015. The chemistry of boron in water. *In* Kabay, N., Bryjak, M., and Hilal, N. (Eds) *Boron Separation Processes*, Elsevier B. V. Amsterdam, The Netherlands.
- Landauer, W., 1952. Malformations of chicken embryos produced by boric acid and the probable role of riboflavin in their origin, *J. Exp. Zool.* 120, 469-508.
- Lewis, M.A., L.C. Valentine, 1981. Acute and chronic toxicities of boric acid to *Daphnia magna* straps. *Bull. Environ. Contam. Toxicol.* 27, 309 – 315.
- Maier, K.J., A.W. Knight, 1991. The toxicity of waterborne boron to *Daphnia magna* and *Chironimus decorus* and the effects of water hardness and sulfate on boron toxicity. *Arch. Environ. Contam. Toxicol.* 20, 282 – 287.
- Marks, G., P. Bruchlos, W. Bergmann, 1994. Experimental results on the tolerance of *Phragmites australis* seed. Proceedings of VDLUFA Congress, Jena, Germany, 19, 705 – 708 (in German).
- Morrison, J.M., M.L.W. Tuttle, J.W. Fahy, 2015. Results of mineral, chemical, and sulfate isotopic analyses of water, soil, rocks, and soil extracts from the Pariette Draw Watershed, Uinta Basin, Utah. United States Geological Survey OFR- 2015-1132.
- Nable, R.O., G.S. Bãnuelos, J.G. Paul, 1997. Boron toxicity. *Plant Soil* 193, 181–198.
- National Academy of Sciences (NAS), 1980. Boron: mineral tolerance of domestic animals. National Research Council, Animal Nutrition, 71-83.
- Nielsen, F.H., 1997. Boron in human and animal nutrition. *Plant Soil* 193, 199–208.
- Nobel, W., 1981. The effect of boron on submerged soft-water macrophytes. *Angew Bot* 55, 501-514 (in German with English summary).
- Natural Resource Conservation Service (NRCS), 1993. Soil Survey Manual. <http://soils.usda.gov/technical/manual/>.
- Ohlendorf, H.M., D.J. Hoffman, M.K. Saiki, T.W. Aldrech, 1986. Embryonic mortality and abnormalities of aquatic birds: Apparent impacts of selenium from irrigation drainwater. *Sci. Total Environ.* 52, 49–63.
- Owen, B.B., 1934. The dissociation constant of boric acid from 10 to 50 °C. *J. Am. Chem. Soc.* 56, 1695-1697.

- Parks, J. L., M. Edwards, 2005. Boron in the environment, *Crit. Rev. Environ. Sci. Technol.* 35(2), 81–114.
- Paveglio, F.L., C.M. Bunck, G.H. Heinz, 1992. Selenium and boron in aquatic birds from central California. *J. Wildl. Manage.* 56(1), 31-42.
- Pawa, S., S. Ali, 2006. Boron ameliorates fulminant hepatic failure by counteracting the changes associated with the oxidative stress. *Chem. Bio. Interact.* 160(2), 89–98.
- Pendleton, G.W., M.W. Whitworth, G.H. Olsen, 1995. Accumulations and loss of arsenic and boron, alone and in combination in mallard ducks. *Environ. Toxicol. Chem.* 14(8), 1357-1364.
- Perry, D.M., I.S. Suffet, M. Wilhelm, J.A. Noblet, A. Maliglig, 1994. Boron environmental chemistry, distribution, bioaccumulation, and toxicity in aquatic system and recommendations for establishment of a boron water quality criterion for natural water in the San Joaquin Valley, California. Final report for contract number 1-192-150-0, submitted to the California Regional Water Quality Control Board, Central Valley Region, and the California Environmental Protection Agency. 270 pp.
- Pilon-Smits, E.A.H., M.P. De Souza, G. Hong, A. Amini, R.C. Bravo, S.T. Payabyab, N. Terry, 1999. Selenium volatilization and accumulation by twenty aquatic plant species. *J. Environ. Qual.* 28(3), 1011-1018.
- Powell, R.L., R.A. Kimerle, G.T. Coyle, G.R. Best, 1997. Ecological risk assessment of a wetland exposed to boron. *Environ. Toxicol. Chem.* 16(11), 2409-2414.
- Romanoff, A.L., A.J. Romanoff, 1972. *Pathogenesis of the Avian Embryo*. Wiley-Interscience, New York, NY.
- Roux, D.J., S.H.J. Jooste, H.M. MacKay, 1996. Substance-specific water quality criteria for the protection of South African freshwater ecosystems: methods for derivation and initial results for some inorganic toxic substances. *S. Afr. J. Sci.* 92, 198-206.
- RStudio Team, 2015. RStudio: Integrated Development for R. RStudio, Inc., Boston, MA. <http://www.rstudio.com/>.
- Saiki, M.K., T.W. May, 1988. Trace element residues in bluegills and common carp from the lower San Joaquin River, California, and its tributaries. *Sci. Total Environ.* 74, 199-217.
- Saiki, M.K., M.R. Jennings, R.H. Wiedmeyer, R.H., 1992. Toxicity of agricultural subsurface drainwater from the San Joaquin Valley, California, to juvenile Chinook salmon and Striped bass. *Trans. Am. Fish. Soc.* 121, 78-93.

- Saiki, M.K., M.R. Jennings, W.G. Brumbaugh, 1993. Boron, Molybdenum, and Selenium in Aquatic Food Chains from the Lower San Joaquin River and Its Tributaries, California. *Arch. Environ. Contam. Toxicol.* 24, 307–319.
- Schuler, C.A. 1987. Impacts of agricultural drainwater and contaminants on wetlands at Kesterson Reservoir, California. M. S. thesis, Oregon State University, Corvallis. 136 pp.
- Schoderboeck, L., S. Mühlegger, A. Losert, C. Gausterer, R. Hornek, 2011. Effects Assessment: Boron compounds in the aquatic environment. *Chemosphere* 82, 483-487.
- Smith, G.J., V.P. Anders, 1989. Toxic effects of boron on mallard reproduction. *Environ. Toxicol. Chem.* 8(10), 943-950.
- Spencer, R.R., D.E. Erdmann, 1979. Azomethine-H colorimetric method for determining dissolved boron in water. *Environ. Sci. Technol.* 13(8), 954-956.
- Soucek, D.J., A. Dickinson, B.T. Koch, 2011. Acute and chronic toxicity of boron to a variety of freshwater organisms. *Environ. Toxicol. Chem.* 30(8), 1906-1914.
- Stephens, D.W., B. Waddell, L. Peltz, J.B. Miller, 1992. Detailed study of selenium and selected elements in water, bottom sediment, and biota associated with irrigation drainage in the Middle Green River Basin, Utah, 1988-90. U.S. Geological Survey Water-Resources Investigations Report 92-4084. U.S. Geological Survey, Denver, CO.
- Stillings, L.L., P.J. Willard, M.C. Amacher. 2007. Kinetics of selenium release in mine waste from the Meade Peak Phosphatic Shale, Phosphoria Formation, Wooley Valley, Idaho, USA. *Chem. Geol.* 269, 113-123.
- Türker, O.C., J. Vymazal, C. Türe, 2014. Constructed wetlands for boron removal: A review. *Ecol. Eng.* 64, 35-359.
- United States Environmental Protection Agency (US EPA), 1994. Method 200.2-1, Revision 2.8: Sample preparation procedure for spectrochemical determination of total recoverable elements. Report 40 CFR Part 136.
- United States Environmental Protection Agency (EPA), 2008. Regulatory determinations support document for selected contaminants from the second drinking water contaminant candidate list (CCL 2). EPA Report 815-R-08-012.
- United States Department of the Interior. 1998. Guidelines for interpretation of the biological effects of selected constituents in biota, water, and sediments. National Irrigation Water Quality Program Information Report No. 3. https://clu-in.org/download/contaminantfocus/arsenic/Dept_Interior_Guidelines.pdf

- United States Geological Survey (USGS). 2008. Mineral Commodity Summaries, 2008-Boron. <http://minerals.usgs.gov/minerals/pubs/commodity/boron/boronmcs04.pdf>.
- UDEQ 2004. TMDL Water Quality Study of the Virgin River Watershed, Utah. Utah Department of Environmental Quality. Division of Water Quality. September 20, 2004.
http://www.waterquality.utah.gov/TMDL/Virgin_River_Watershed_TMDL.pdf
- Utah Department of Environmental Quality (UDEQ), 2005. Uintah Basin Watershed Description. Utah Department of Environmental Quality, Division of Water Resources. www.utah.gov.
- Vinson, M.R., C.P. Hawkins, 1996. Effects of sampling area and subsampling procedure on comparisons of taxa richness among streams. *J. N. Am. Benthol. Soc.* 15(3), 392-399.
- World Health Organization (WHO), 1998. Boron, environmental health criteria (EHC) – 204. <http://www.inchem.org/documents/ehc/ehc/ehc204.html>
- Wingert, S., C. Adams, 2010, TMDLs for total dissolved solids, selenium, and boron in the Pariette Draw Watershed, US Environmental Protection Agency, Region 8.
- Winget, R.N., F.A. Mangum, 1979. Biotic Condition Index: Integrated biological, physical and chemical stream parameters for management, US Department of Agriculture, Forest Service, Intermountain Region, Ogden, UT.
- Zasoski, R.J., R.G. Burau, 1977. Rapid nitric-perchloric acid digestion method for multi-element tissue analysis, *Commun. Soil Sci. Plant Anal.* 8(5), 425-436.



Fig. 2-1a. Map of Utah showing Pariette Watershed location (blue) within the Uintah Basin (green) in the North – East part of the state (modified from Wingert and Adams, 2010).

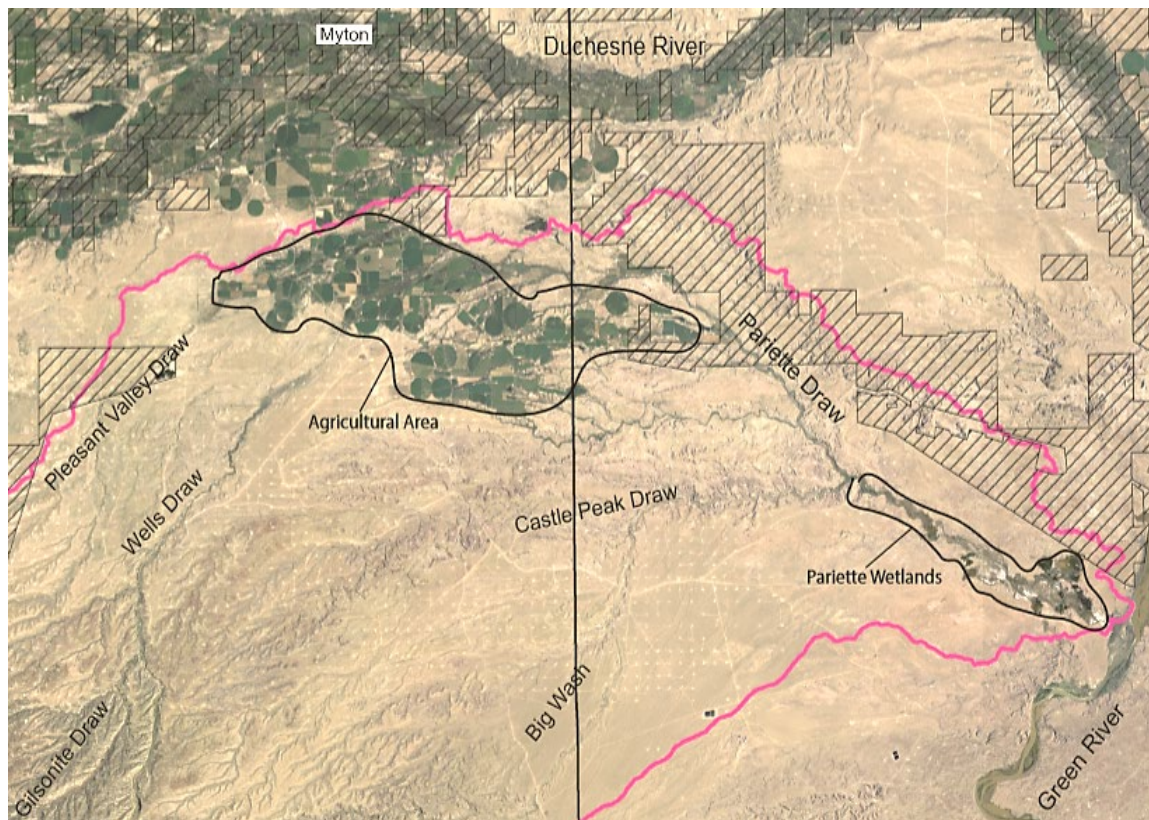


Fig. 2-1b. Detailed Map of the Pariette Watershed showing the three main land use components – Agricultural area, Pariette Draw and the Pariette Wetlands (modified from Morrison et al., 2015).

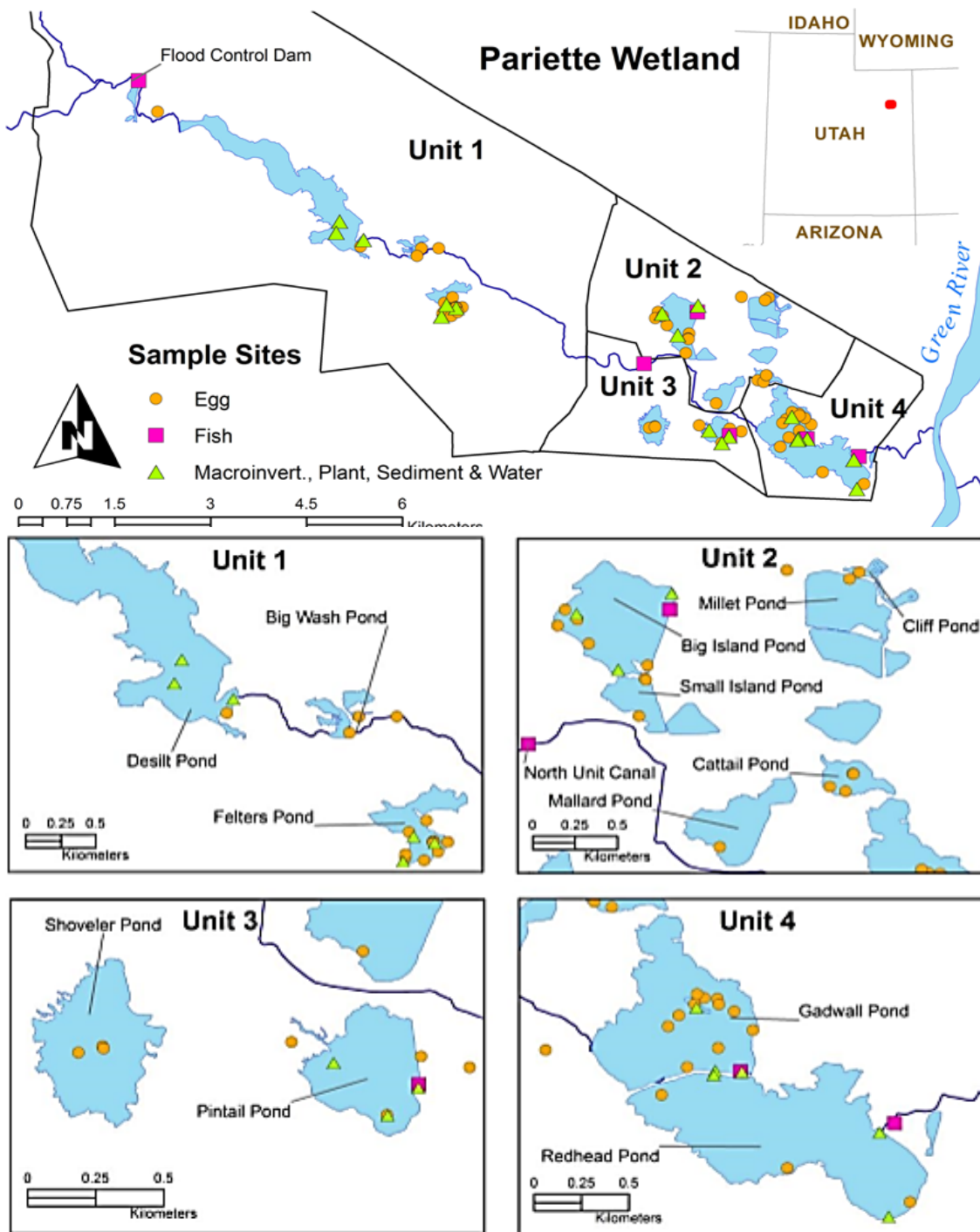


Fig. 2-2. Map of all pond units along with individual ponds in each unit at the Pariette Wetlands. The sampling sites for Bird eggs (orange circles), Fish (pink squares) and other samples – Water, Sediments, BMIs and Aquatic vegetation (green triangles) are also shown (Jones, 2014).

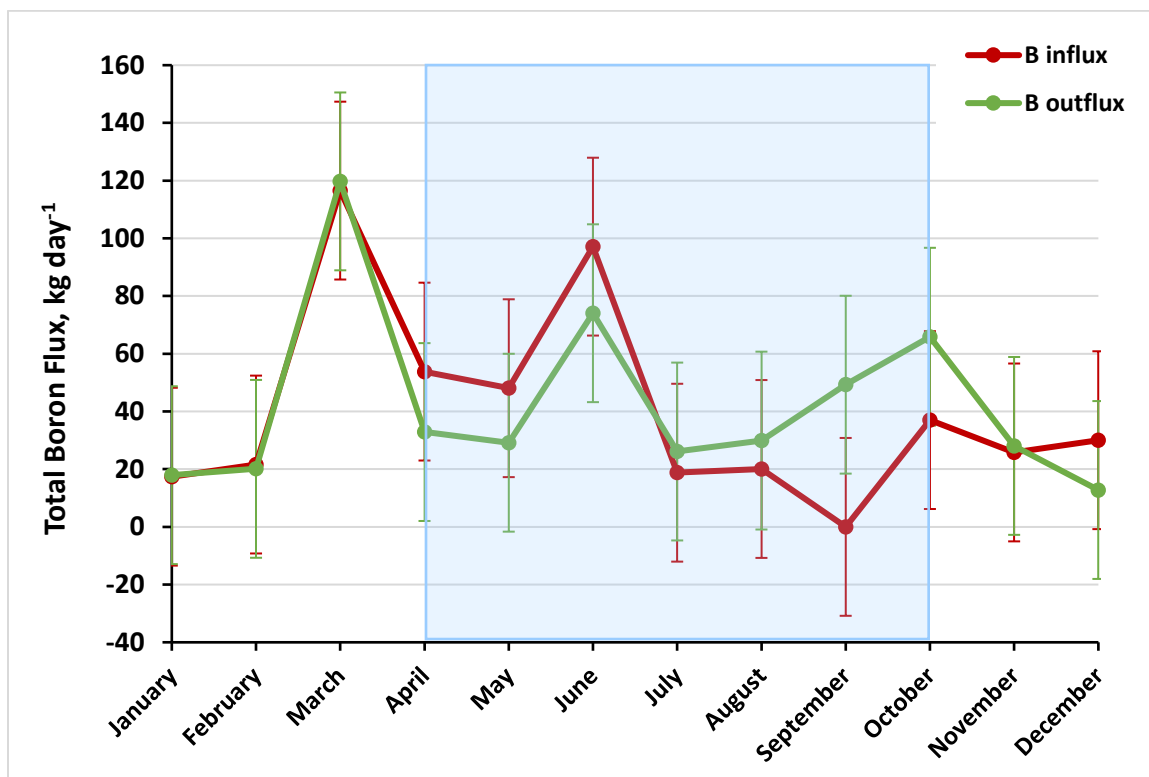


Fig. 2-3. Monthly average B mass flux (2009) calculated using water flow data measured at the UDEQ monitoring stations in the Pariette Wetlands (2008–2009 dataset, Wingert and Adams, 2010). The colored portion on the graph highlights the 2009 irrigation season from April–October.

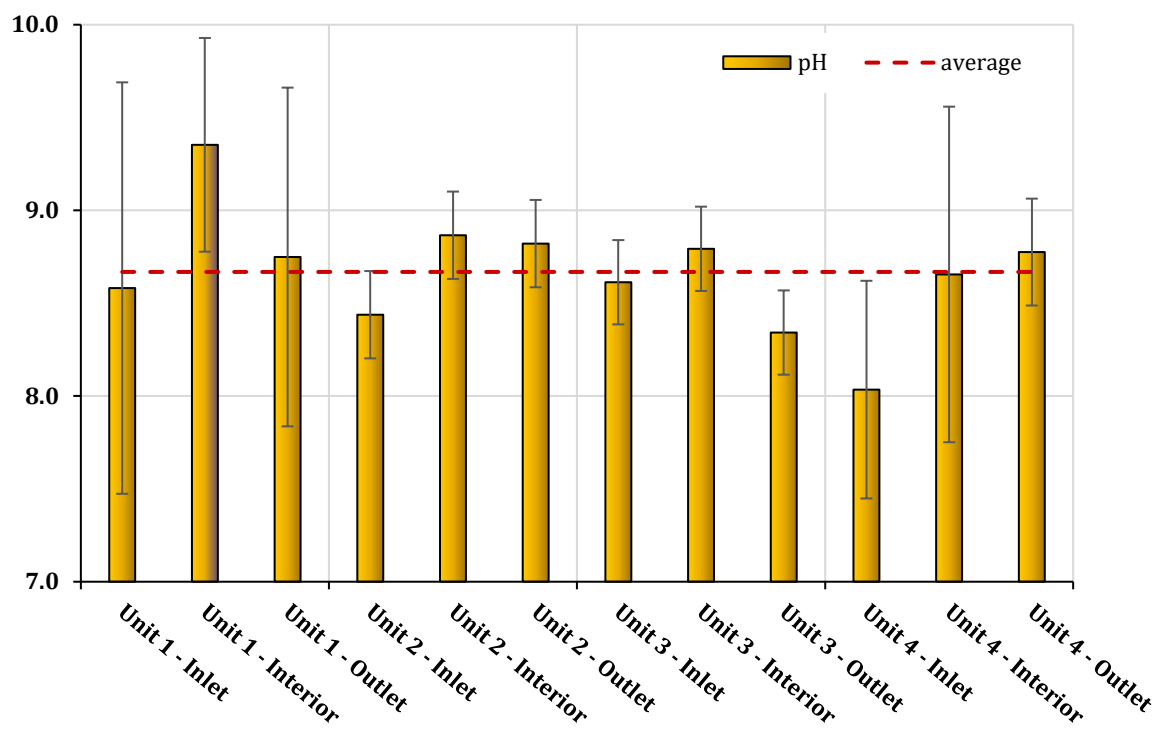


Fig. 2-4a. Bar graph of the water pH calculated for the samples collected at three sampling sites in each unit in the Pariette Wetlands. The dotted line and error bars represent the average pH (8.7 ± 0.6).

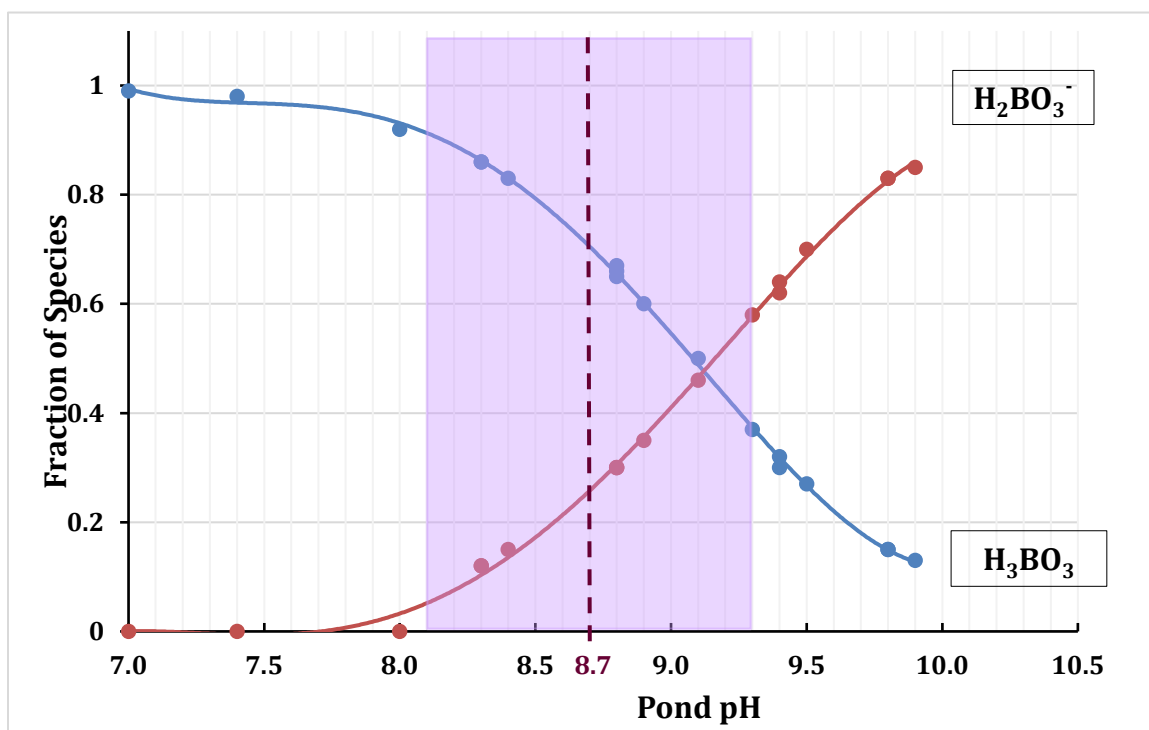


Fig. 2-4b. Speciation diagram for B as a function of pH for two species predicted by the MINTEQ results. The shaded area represents the average pH range (8.7 ± 0.6) for the water samples collected from Pariette Wetlands showing higher concentrations of undissociated boric acid (H_3BO_3).

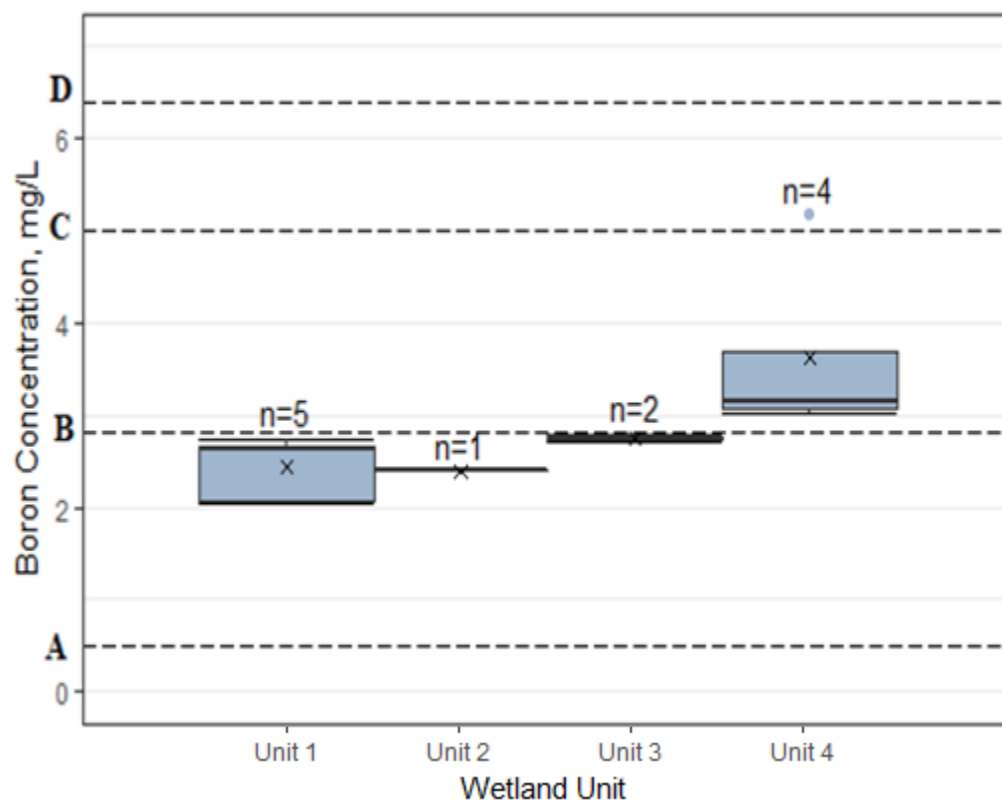


Fig. 2-5. Box and whisker plot of B concentrations in pond water in four units of the Pariette Wetlands. The B levels were measured at $\text{pH} = 8.7 \pm 0.6$, $\text{EC} = 9.1 \text{ mS/cm}$. **A.** observed LOAEL for aquatic plants (0.5 mg L^{-1}), **B.** observed LOAEL for *Crustaceans* (BMI, 2.8 mg L^{-1}), **C.** Maximum acceptable toxicant concentration (MATC) for *Daphnia magna* (6.4 mg L^{-1}), **D.** observed LOAEL for freshwater fish (6 mg L^{-1}). The colored dots, upper and lower whiskers mark data outliers, maximum and minimum concentrations while X = median and n = sample size.

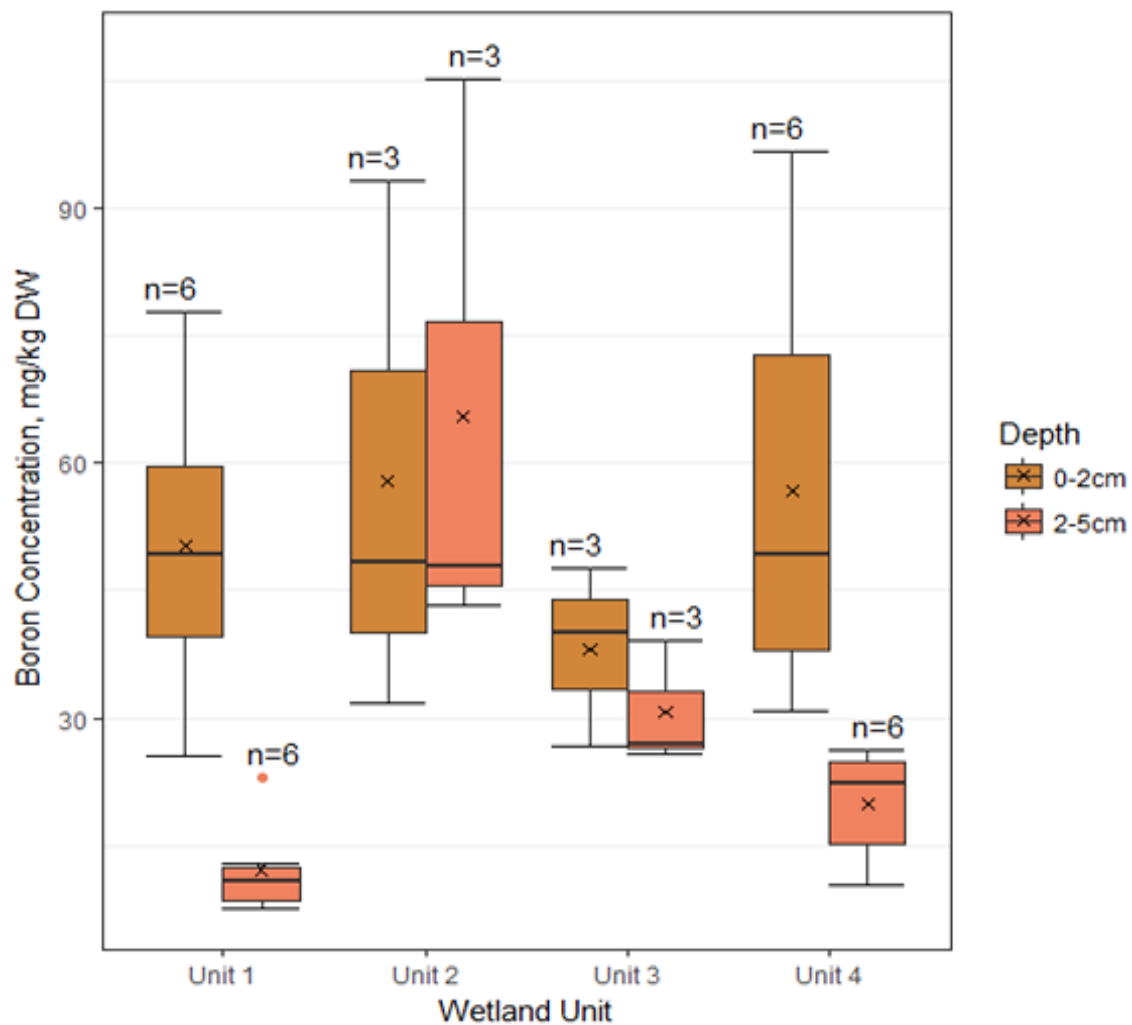


Fig. 2-6. Box and whisker plot comparison of total plant available concentrations of B in the sediment layers at depths 0-2 and 2-5 cm collected from all four pond-units in the Pariette Wetlands. The colored dots, upper and lower whiskers mark data outliers, maximum and minimum concentrations while X = median and n = sample size.

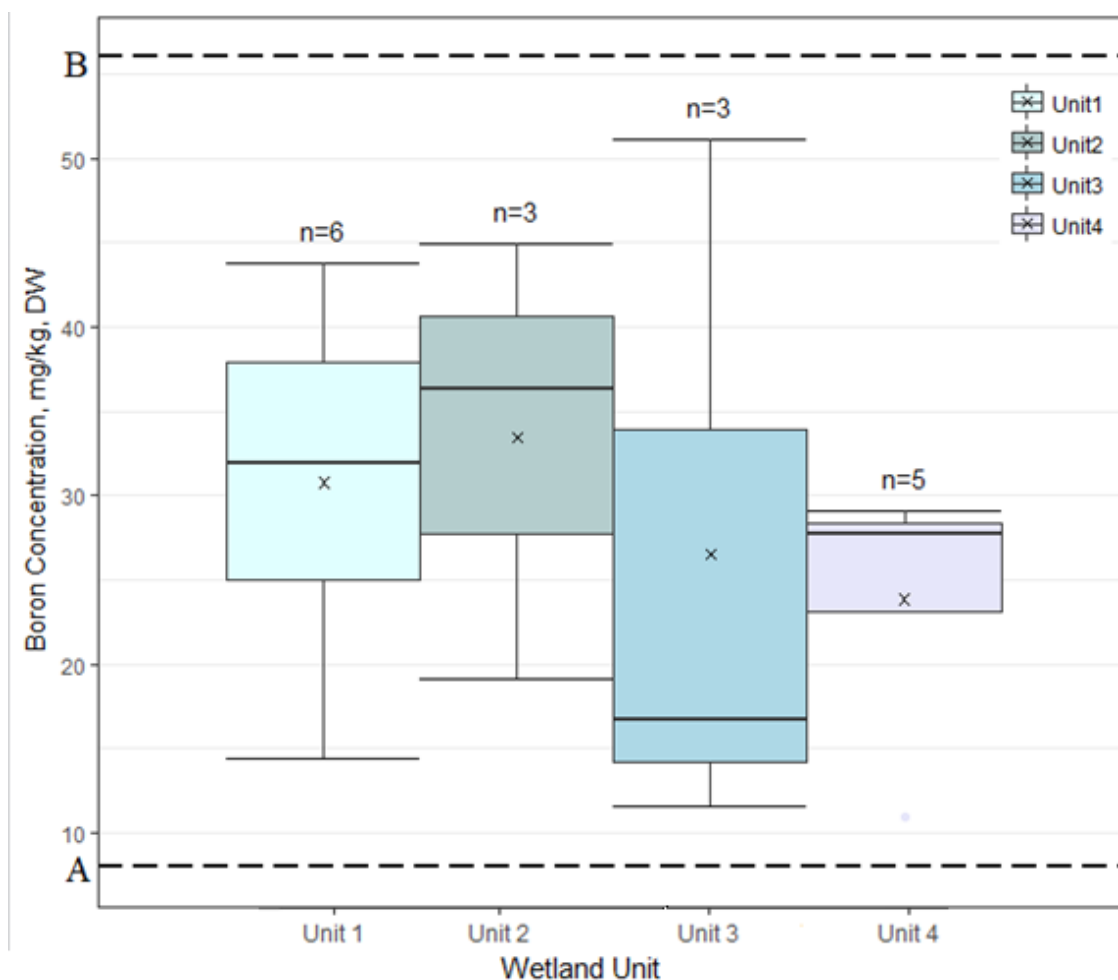


Fig. 2-7. Box and whisker plot of the total B content in BMI samples collected at four pond units in the Pariette Wetlands. The lines mark the dry weight B concentrations in foods observed to reduce weight and weight gain in Mallard ducklings **A.** less than 21 days old (8 mg kg^{-1} , DW); and **B.** all ducklings (56 mg kg^{-1} , DW) (Perry et al., 1994). The colored dots, upper and lower whiskers mark data outliers, maximum and minimum concentrations while X = median and n = sample size.

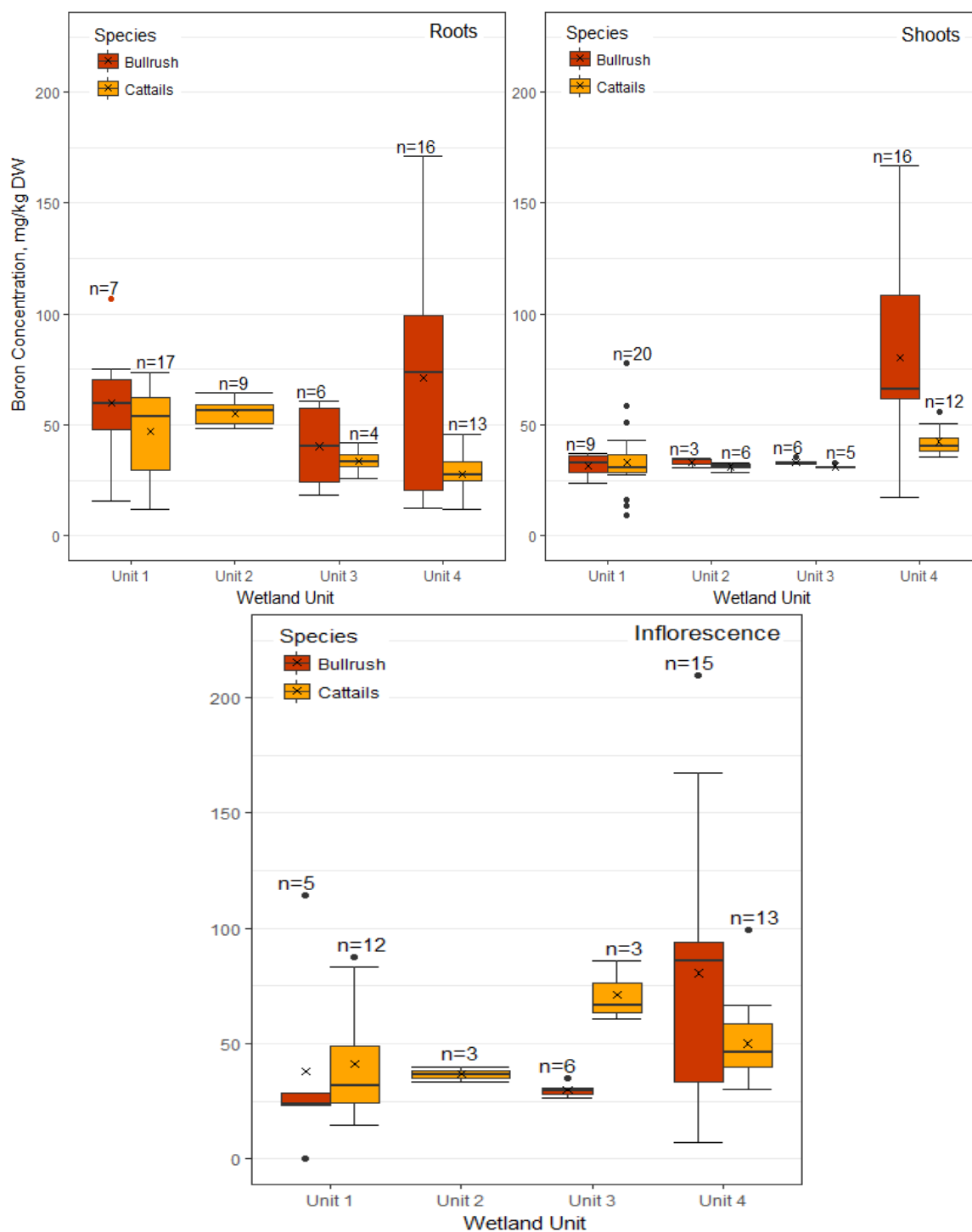


Fig. 2-8. Box and whisker plot comparison of total B content in roots, shoots and inflorescence of Emergent aquatic vegetation species *Cattails* and *Bullrush* collected at four pond-units of the Pariette Wetlands. The black dots, upper and lower whiskers mark data outliers, maximum and minimum concentrations while X = median and n = sample size.

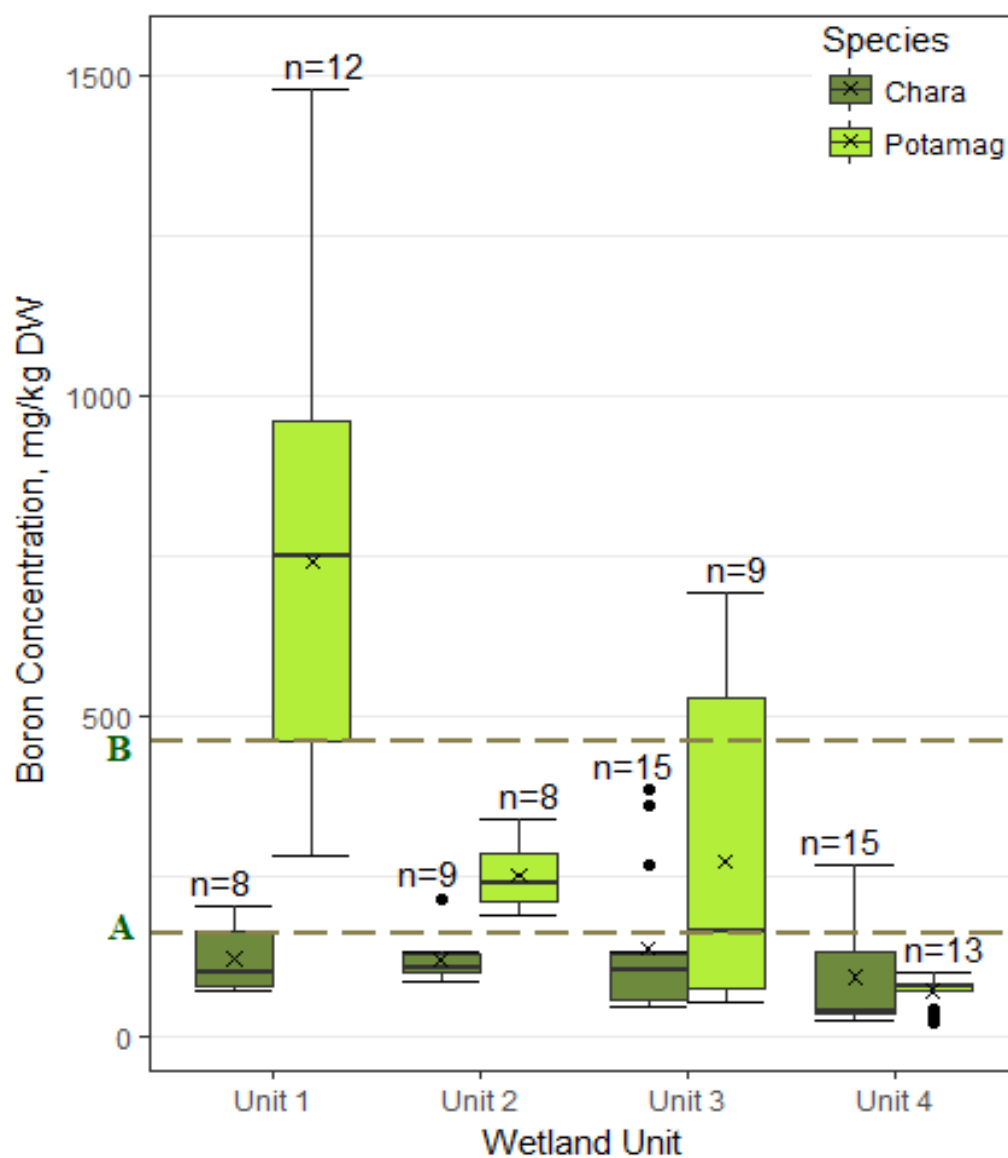


Fig. 2-9. Box and whisker plot comparison of total B content in submerged aquatic vegetation species *Potamageton* and *Chara* collected at the Pariette Wetlands. The lines represent B concentration in *Potamageton* growing **A.** freshwater (160 mg kg^{-1} , DW) and **B.** contaminated irrigation drain water at the Kesterson National Wildlife Refuge, CA (460 mg kg^{-1} , DW) in 1983 (WHO, 1998). The black dots, upper and lower whiskers mark data outliers, maximum and minimum concentrations while X = median and n = sample size.

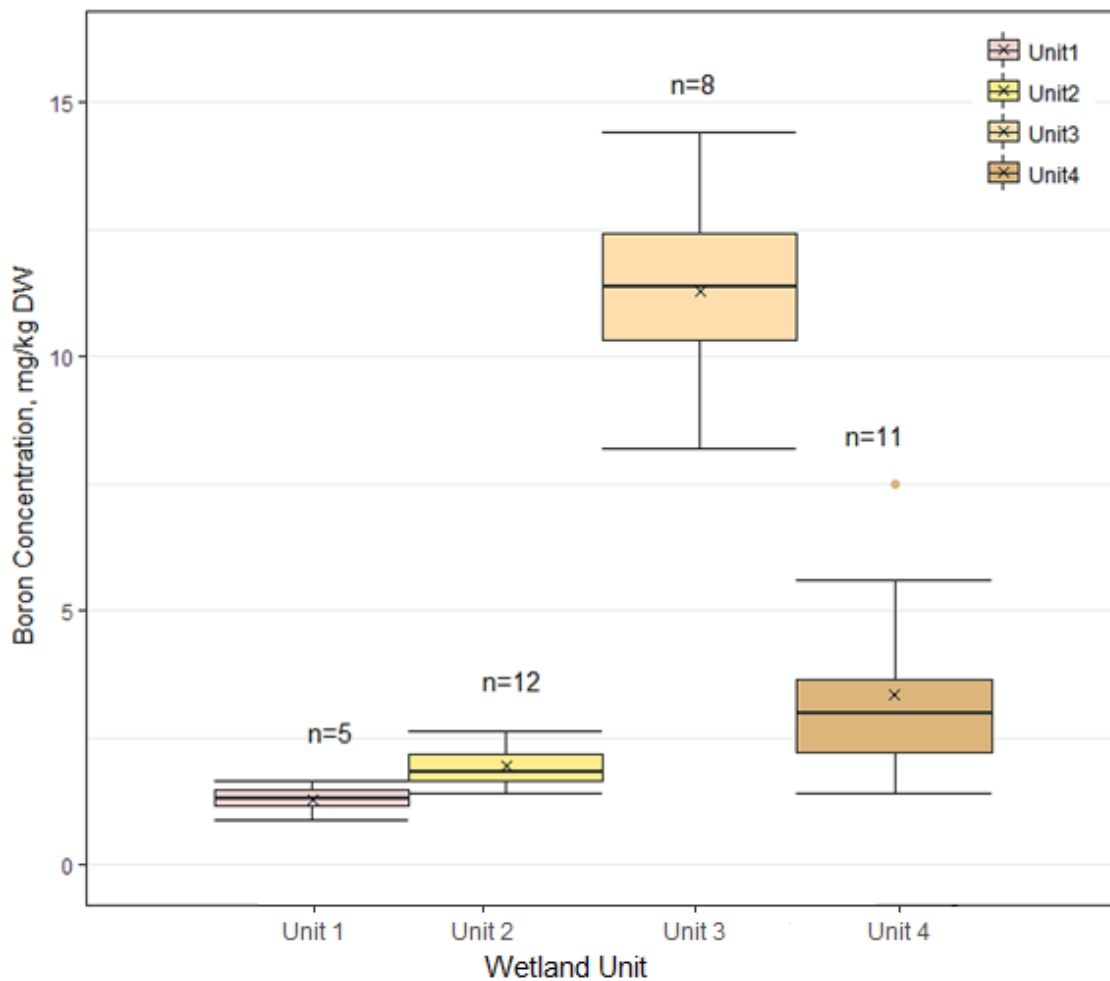


Fig. 2-10. Box and whisker plot displaying total B content in all freshwater fish species collected at the four pond units in the Pariette Wetlands. The colored dots, upper and lower whiskers mark data outliers, maximum and minimum concentrations while X = median and n = sample size.

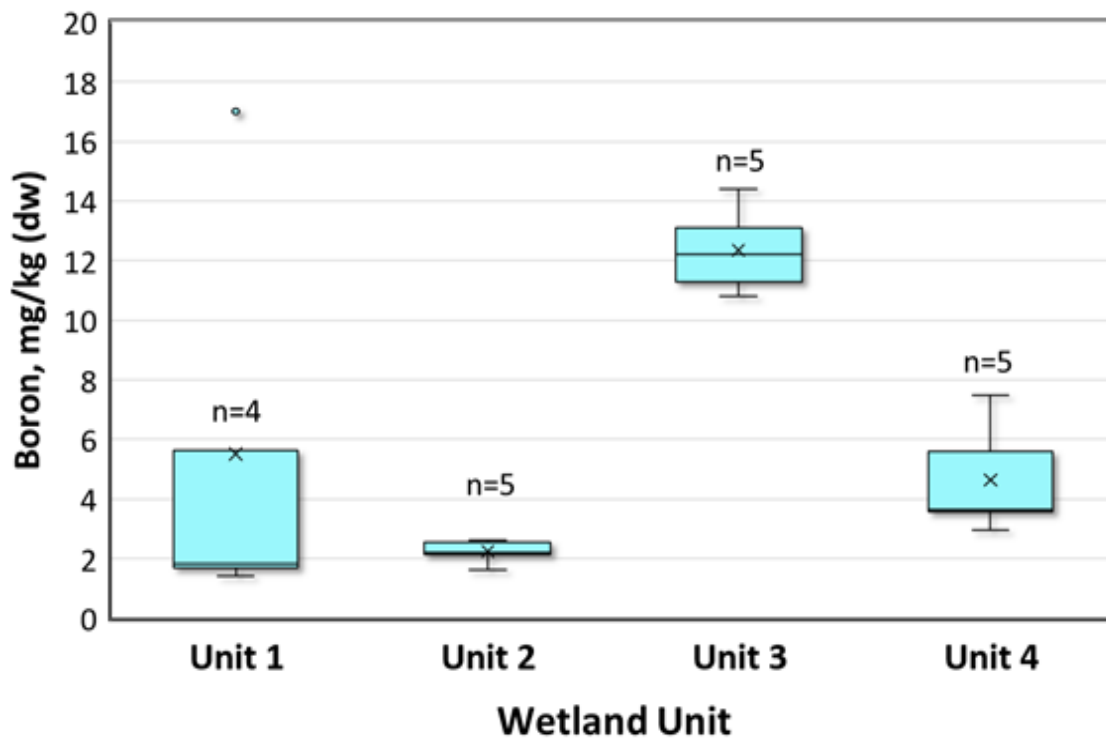


Fig. 2-11. B distribution plotted using a box and whisker plot in Green sunfish, *Lepomis cyanellus* sampled extensively in all four pond-units of the Pariette Wetland complex. The colored dots, upper and lower whiskers mark data outliers, maximum and minimum concentrations while X = median and n = sample size.

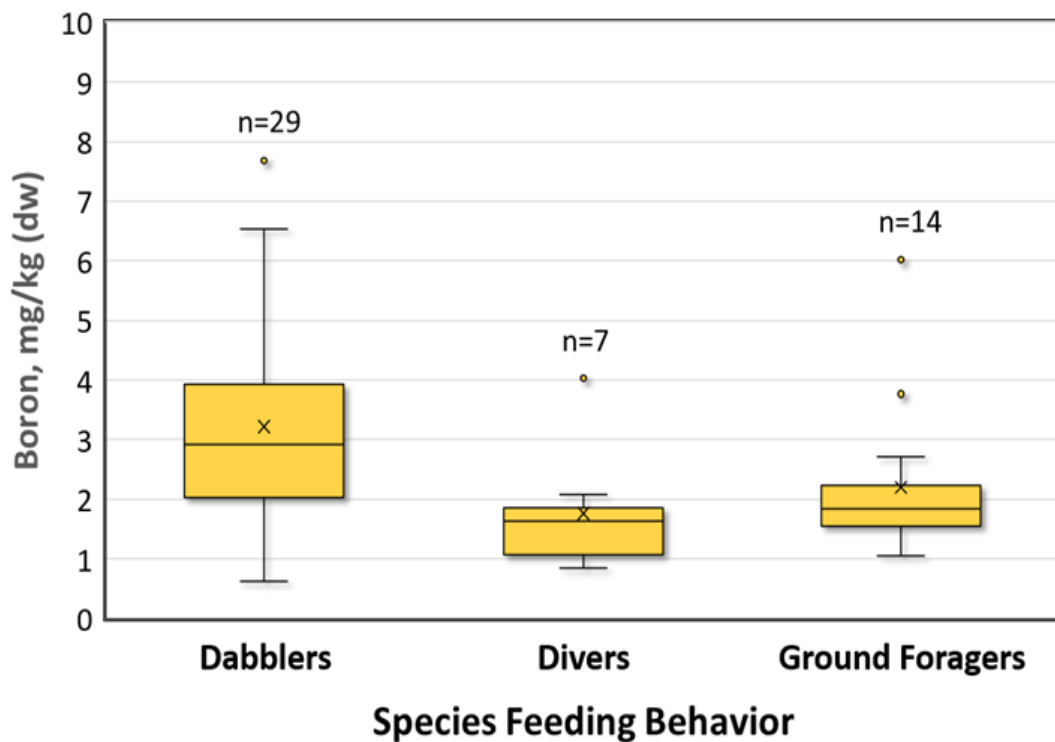


Fig. 2-12. Box and whisker plot demonstrating B distribution in waterfowl eggs collected at sampling sites in all four pond-units at the Pariente Wetlands. The waterfowl species were categorized into three types based on their feeding behavior. The colored dots, upper and lower whiskers mark data outliers, maximum and minimum concentrations while X = median and n = sample size.

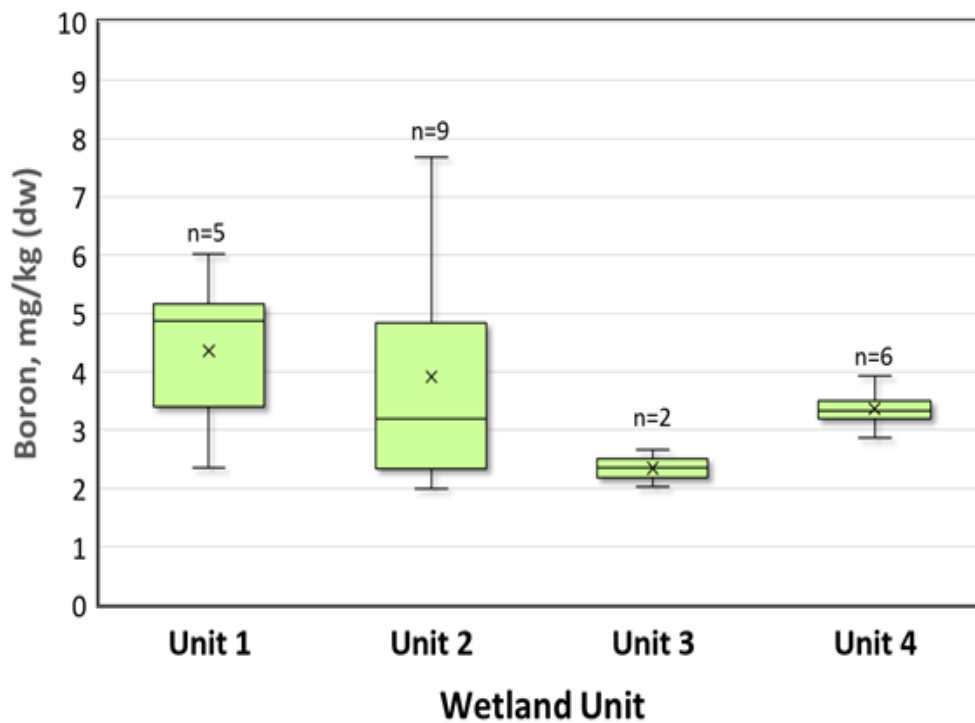


Fig. 2-13. Box and whisker plot displaying B distribution in the dabbler eggs of American Coot, *Fulica Americana*, sampled at sites in all four pond units of the Pariette Wetland complex.

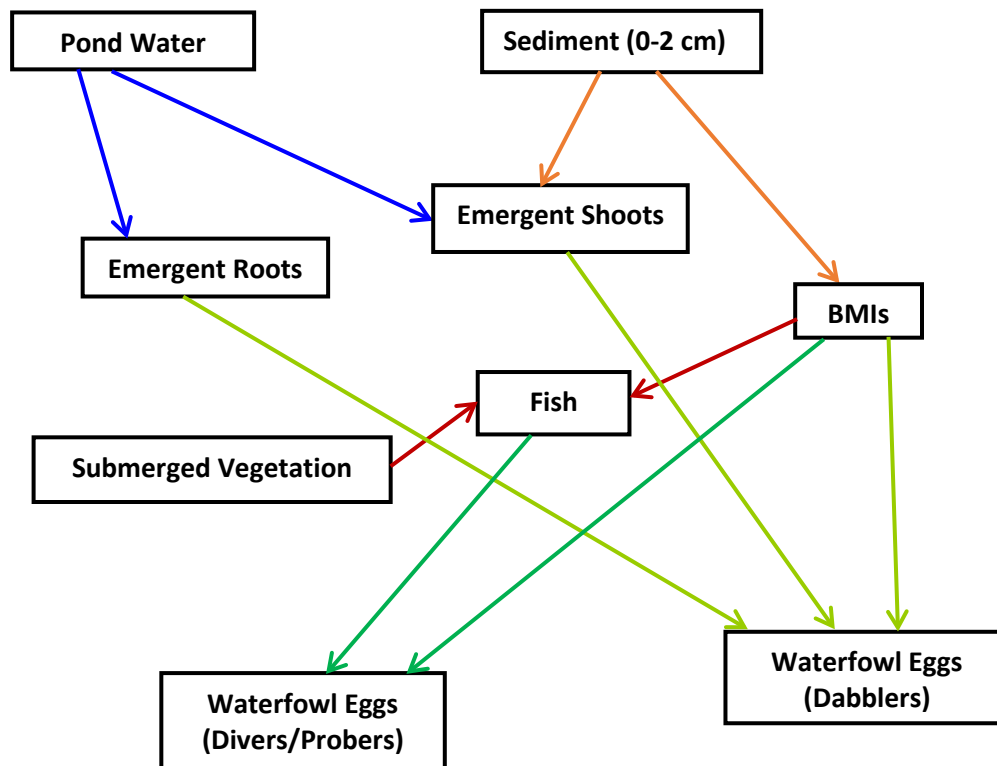


Fig. 2-14. Infographic describing B bioconcentration and bioaccumulation pathways in the Pariette Wetland food web. The colored arrows mark possible exposure routes as suggested by the positive Mantel-r coefficients.

Table 2-1

Water quality characteristics of ponds in Pariette Wetlands from the taxonomic classification of BMI split samples by NAMC

Pond	Diversity Indices		Dominant Family	Hilsenhoff Biotic Index	Tolerant Taxa abundance	USFS Tolerance Quotient
	Shannon	Simpson				
Desilt	1.59	0.75	Corixidae	0.87	53	105
Felters	0.34	0.12	Physidae	0.12	204	103
Big Island	2.28	0.89	Chironomidae	4.16	37	96
Pintail	0.55	0.22	Chironomidae	5.60	158	104
Gadwall	1.51	0.75	Coenagrionidae	5.13	407	94

Table 2-2

Mantel correlations between abiotic and biotic samples collected in Pariette Wetlands. The highlighted rows in red mark the cases where the null hypothesis was rejected.

Correlations	Mantel r	p – val ₁	p–val ₁ > α , Accept H ₀
Water vs Biotic samples			
Water vs BMI	-0.207	0.903	Accept H ₀
Water vs Roots	0.367	0.032	Reject H ₀
Water vs Shoots	0.916	0.002	Reject H ₀
Water vs Submerged Plants	-0.092	0.492	Accept H ₀
Sediments vs Biotic samples			
Sediment vs BMI	0.089	0.288	Accept H ₀
Sediment vs Roots	-0.145	0.741	Accept H ₀
Sediment vs Shoots	0.087	0.275	Accept H ₀
Sediment vs Submerged Plants	-0.220	0.886	Accept H ₀

Null Hypothesis, H₀ = B concentration in biotic samples are significantly similar to B concentrations in abiotic samples at the same sampling site; **Confidence limit, α** = $\pm 5\%$ = 0.10; **One-tailed probability value, p–val₁** = probability of null hypothesis being true; **Mantel coefficient, mantel r** = existing spatial correlation between samples.

Table 2-3

Common and scientific names along with feeding behavior of the 15 waterfowl species for which egg samples were collected at sites in Pariette Wetlands, UT in July, 2014 (<https://www.ducks.org/>).

Feeding Behavior	Common Name	Scientific Name
Diver/Prober	American avocet	<i>Recurvirostra americana</i>
Dabbler	American coot	<i>Fulica americana</i>
Diver/Prober	Black-necked stilt	<i>Himantopus mexianus</i>
Dabbler	Blue-winged teal	<i>Anas discors</i>
Dabbler	Cinnamon teal	<i>Anas cyanoptera</i>
Dabbler	Gadwall	<i>Anas strepera</i>
Ground Forager	Killdeer	<i>Charadrius vociferus</i>
Ground Forager	Marsh wren	<i>Cistothorus palustris</i>
Diver/Prober	Pied-billed grebe	<i>Podilymbus podiceps</i>
Dabbler	Redhead	<i>Aythya americana</i>
Dabbler	Ring-necked duck	<i>Aythya collaris</i>
Ground Forager	Red-winged blackbird	<i>Agelaius phoeniceus</i>
Diver/Prober	Spotted sandpiper	<i>Actitis macularius</i>
Diver Prober	Virginia rail	<i>Rallus limicola</i>
Ground Forager	Yellow-headed blackbird	<i>Xanthocephalus xanthocephalus</i>

Table 2-4a

Site-wise concentrations of ions present in pond water samples (n = 18) collected at Pariette Wetlands analyzed using ICP – AES.

Sampling Site	pH	B	Ca	K	Mg	Na	S	Si
		----- m mol L ⁻¹ -----						
Desilt, Inlet	7.0	0.191	5.69	0.069	5.43	40.1	25.4	0.675
Desilt, Interior	8.8	0.188	3.69	0.077	4.68	43.6	28.1	0.447
Desilt, Outlet	8.3	0.226	3.93	0.161	5.61	46.3	29.0	0.617
Felters, Inlet	9.5	0.243	3.26	0.225	7.55	58.2	37.6	0.066
Felters, Interior	9.8	0.254	3.38	0.229	7.94	60.6	39.3	0.111
Felters, Outlet	9.8	0.246	3.29	0.229	7.88	60.0	38.5	0.026
Big Island, Inlet	8.8	0.258	4.38	0.239	8.27	67.7	42.9	0.349
Big Island, Interior	9.4	0.251	4.17	0.276	8.22	67.7	43.4	0.174
Big Island, Outlet	8.9	0.245	4.27	0.271	8.05	67.7	43.5	0.362
Pintail, Inlet	8.8	0.286	4.31	0.273	9.27	75.4	47.5	0.192
Pintail, Interior	8.0	0.322	5.48	0.226	10.20	82.3	50.7	0.538
Pintail, Outlet	9.3	0.296	4.30	0.274	9.64	76.4	48.4	0.163
Gadwall, Inlet	7.4	0.280	6.37	0.269	9.41	72.2	46.4	0.346
Gadwall, Interior	9.9	0.416	6.75	0.550	12.99	123.4	73.0	0.068
Gadwall, Outlet	9.4	0.478	8.70	0.699	16.23	153.2	90.6	0.153
Redhead, Inlet	8.4	0.216	3.74	0.168	7.49	55.1	35.7	0.017
Redhead, Interior	9.1	0.221	3.54	0.202	7.63	56.3	36.7	0.052
Redhead, Outlet	8.3	0.210	3.51	0.182	7.37	53.6	35.0	0.018

Table 2-4b

Visual MINTEQ (Gustafsson, 2014) results detailing dominant species and their distribution in pond water samples collected at Pariette Wetlands. The highlighted boxes represent species distribution (%) in sites with pH > 9 (blue) and pH < 7.5 (yellow).

Sampling site	H ₃ BO ₃	H ₂ BO ₃ ⁻	K ⁺	Mg	Na	SO ₄ ⁻²	HCO ₃ ⁻
Desilt, Inlet	99	0	95	64 (Mg ⁺²)	96 (Na ⁺)	76	81
Desilt, Interior	67	30	95	48 (Mg ⁺²)	92 (Na ⁺)	85	88
Desilt, Outlet	86	12	94	59 (Mg ⁺²)	95 (Na ⁺)	80	92
Felters, Inlet	27	70	94	71 MgCO ₃ (aq)	57 (Na ⁺)	94	69
Felters, Interior	15	83	91	87 MgCO ₃ (aq)	66 NaCO ₃ ⁻	96	61
Felters, Outlet	15	83	92	87 MgCO ₃ (aq)	66 NaCO ₃ ⁻	96	61
Big Island, Inlet	66	30	93	46 (Mg ⁺²)	90 (Na ⁺)	82	86
Big Island, Interior	32	64	93	62 MgCO ₃ (aq)	66 (Na ⁺)	91	71
Big Island, Outlet	60	35	93	42 (Mg ⁺²)	89 (Na ⁺)	83	84
Pintail, Inlet	65	30	92	46 (Mg ⁺²)	90 (Na ⁺)	81	85
Pintail, Interior	92	0	92	56 (Mg ⁺²)	93 (Na ⁺)	76	91
Pintail, Outlet	37	58	92	53 MgCO ₃ (aq)	73 (Na ⁺)	89	74
Gadwall, Inlet	98	0	93	57 (Mg ⁺²)	94 (Na ⁺)	75	88
Gadwall, Interior	13	85	82	89 MgCO ₃ (aq)	74 NaCO ₃ ⁻	93	57
Gadwall, Outlet	30	62	88	57 MgCO ₃ (aq)	64 (Na ⁺)	83	65
Redhead, Inlet	83	15	94	56 (Mg ⁺²)	94 (Na ⁺)	80	91
Redhead, Interior	50	46	94	36 MgCO ₃ (aq) 33 (Mg ⁺²)	84 (Na ⁺)	87	81
Redhead, Outlet	86	12	94	57 (Mg ⁺²)	94 (Na ⁺)	80	92

APPENDICES

APPENDIX A

Table A1

Input data (B concentrations) used to compute statistical correlations. The B concentrations are in mg L⁻¹ (Water) and mg kg⁻¹, DW (Sediment, BMI, Vegetation – Root, Shoots, Inflorescence (Infl.) and Submerged (Sub.), Fish and Bird eggs (Dabblers, Ground Foragers (GF) and Divers/Probers (D/P)).

Unit	Water	Sediment	BMI	Root	Shoot	Infl.	Sub.	Fish	Dabblers	GF	D/P
1	2.35	51.66	31.90	46.65	30.01	53.96	324.28	1.25	2.60	2.06	NA
1	2.40	49.20	26.20	57.93	35.27	27.52	486.69	1.39	5.16	1.24	NA
1	2.56	49.84	34.21	49.03	33.27	38.08	707.84	1.15	3.81	1.65	0.845
2	2.33	31.85	36.31	60.10	27.51	92.99	158.36	1.69	2.07	2.07	2.07
2	2.39	93.16	44.88	55.29	31.53	NA	178.39	2.24	4.08	4.08	4.08
2	2.28	48.34	19.09	62.97	26.08	30.02	214.68	1.77	3.45	3.45	3.45
3	2.79	40.10	51.07	27.24	31.30	71.00	104.03	9.49	NA	NA	NA
3	2.71	47.64	11.61	23.50	32.72	30.65	196.35	12.63	NA	NA	NA
3	2.65	26.72	16.75	57.30	33.66	29.21	55.64	11.95	0.64	0.64	0.64
4	3.06	37.40	29.08	40.42	30.34	37.86	76.93	2.66	3.17	1.86	1.63
4	3.99	75.62	17.02	73.69	61.13	62.45	100.70	5.22	3.39	NA	NA
4	4.18	57.25	28.07	79.52	67.80	62.20	100.09	4.77	2.56	1.89	NA

APPENDIX B

R Code Used to Perform Simple and Partial Mantel Tests

```

setwd("C:/Users/John Manoha_2/Desktop/PALAK - R_Research")
  ##"C:/Users/A01640632/Documents/RESEARCH_Updated March 24,
  2017/LAB ANALYSIS/R DATA") ##to set the path for R to follow i.e, where
  the files are
getwd()    ##shows path being followed
##### Assuming that sites have the same order for Water and BMIs, create dataframe
Bconc.df<-read.table("Mantel12sites.txt", header = TRUE, na.strings = "EMPTY")
Bconc.df
###-----###
##Load ecodist package from library and Create distance matrices
## using distance() in ecodist package BUT can't deal with "NA"
W.edist <- distance(Bconc.df$Water, "euclidean")
W.edist
Sed.edist <- distance(Bconc.df$Sed, "euclidean")
Sed.edist
R.edist <- distance(Bconc.df$Root, "euclidean")
R.edist
Sh.edist <- distance(Bconc.df$Shoot, "euclidean")
Sh.edist
pHs.w.edist <- distance(Bconc.df$pHs.w, "euclidean")
pHs.w.edist
X=Bconc.df[,c(2)]
Y=Bconc.df[,c(3)]
geo.edist <- distance(cbind(as.vector(X), as.vector(Y)), "euclidean")
geo.edist
##when NA in data
Infl = Bconc.df[,c("Infl")]
Infl.dist=dist(Infl,method="euclidean",diag=FALSE,upper=FALSE)
Infl.dist
BMI = Bconc.df[,c("BMI")]
BMI.dist = dist(BMI,method="euclidean",diag=FALSE,upper=FALSE)
BMI.dist ##one value recorded as "NA"
Sub = Bconc.df[,c("Sub")]
Sub.dist = dist(Sub,method="euclidean",diag=FALSE,upper=FALSE)
Sub.dist ##one value recorded as "NA"
###-----###
          ###-----###

```

ADJUSTING FOR EFFECTS OF GEOGRAPHICAL DISTANCE

```
## 1)Partial Mantel test - Do sites with similar boron concentration in abiotic samples
```

(Water, Sediments) have similar (or dissimilar) boron concentration in biotic samples (Fish, vegetation, bird eggs, BMIs) when adjusting for geographic distance effects?

```
## Water vs biotic samples (BMI,Veg[Roots,Shoots,Sub])
set.seed(15640)
PM_WvsB=mantel(W.edist~BMI.dist+geo.edist, pboot=0.85, cboot=0.90)
PM_WvsB
set.seed(978901)
PM_WvsR=mantel(W.edist~R.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_WvsR
set.seed(152095)
PM_WvsSh=mantel(W.edist~Sh.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_WvsSh
set.seed(95103)
PM_WvsSub=mantel(W.edist~Sub.dist+geo.edist, pboot=0.85, cboot=0.90)
PM_WvsSub
set.seed(981201)
PM_WvsI=mantel (W.edist~Infl.dist+geo.edist, pboot=0.85, cboot=0.90)
PM_WvsI
## Displaying results as a summarised table
Results_PM_WvsBiotic <- as.data.frame
  (rbind(PM_WvsB,PM_WvsR,PM_WvsSh,PM_WvsSub,PM_WvsI))
Results_PM_WvsBiotic

###-----###

## Sediment vs biotic samples (BMI,Veg[Roots,Shoots,Sub])
set.seed(80010)
PM_SvsB2=mantel(Sed.edist~BMI.dist+geo.edist, pboot=0.85, cboot=0.90)
PM_SvsB2
set.seed(71113)
PM_SvsR2=mantel(Sed.edist~R.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_SvsR2
set.seed(32701)
PM_SvsSh2=mantel(Sed.edist~Sh.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_SvsSh2
set.seed(19099)
PM_SvsSub2=mantel (Sed.edist~Sub.dist+geo.edist, pboot=0.85, cboot=0.90)
PM_SvsSub2
set.seed(84273)
PM_SvsI2=mantel (Sed.edist~Infl.dist+geo.edist, pboot = 0.85, cboot=0.9)
PM_SvsI2
## Displaying results as a summarised table
Results_PM_SvsBiotic2 <- as.data.frame
  (rbind(PM_SvsB2,PM_SvsI2,PM_SvsR2,PM_SvsSh2,PM_SvsSub2))
```

```

Results_PM_SvsBiotic2
####-----#####
-----###
## Displaying results for ABIOTIC vs BIOTIC SAMPLES upon adjusting for i) pH
  (summarised table)
Results_PM_AbioticvsBiotic_pH <- as.data.frame (rbind(Results_PM_WvsBiotic,
  Results_PM_SvsBiotic))
Results_PM_AbioticvsBiotic_pH
## Displaying results for ABIOTIC vs BIOTIC SAMPLES upon adjusting for ii)
  geographic distance b/w sites (summarised table)
Results_PM_AbioticvsBiotic_geo.dist <- as.data.frame(rbind(Results_PM_WvsBiotic2,
  Results_PM_SvsBiotic2))
Results_PM_AbioticvsBiotic_geo.dist
####-----#####
## 1) Partial Mantel test - Do sites with similar boron concentration in abiotic samples
  (Water, sediments) have similar (or dissimilar) boron concentration in biotic
  samples (Fish, vegetation, bird eggs, BMIs)when adjusting for pH effects?
## Set seed for random number generator (RNG); setting the seed will nesure that this
  particular number will ALWAYS produce the same result..if you DONT SET the
  seed you will get different answers every time you run a test based on
  permutations
####-----#####
## Water vs biotic samples (BMI,Veg[Roots,Shoots,Infl,Sub]), adjusting for effects of
  pH
set.seed(39805)
PM_WvsB=mantel(W.edist~BMI.dist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_WvsB
set.seed(78901)
PM_WvsR=mantel(W.edist~R.edist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_WvsR
set.seed(52095)
PM_WvsSh=mantel(W.edist~Sh.edist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_WvsSh
set.seed(91032)
PM_WvsSub=mantel(W.edist~Sub.dist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_WvsSub
set.seed(98120)
PM_WvsI=mantel (W.edist~Infl.dist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_WvsI
####-----#####
## Displaying results as a summarised table
Results_PM_WvsBiotic <- as.data.frame
  (rbind(PM_WvsB,PM_WvsI,PM_WvsR,PM_WvsSh,PM_WvsSub))
Results_PM_WvsBiotic
####-----#####

```



```

#####-----#####
## Sediment vs biotic samples (BMI,Veg[Roots,Shoots,Sub]), adjusting for effects of pH
set.seed(48010)
PM_SvsB=mantel(Sed.edist~BMI.dist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_SvsB
set.seed(67113)
PM_SvsR=mantel(Sed.edist~R.edist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_SvsR
set.seed(15012)
PM_SvsSh=mantel(Sed.edist~Sh.edist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_SvsSh
set.seed(90999)
PM_SvsSub=mantel (Sed.edist~Sub.dist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_SvsSub
set.seed(82217)
PM_SvsI=mantel (Sed.edist~Infl.dist+pHs.w.edist, pboot=0.85, cboot=0.90)
PM_SvsI
## Displaying results as a summarised table
Results_PM_SvsBiotic <- as.data.frame
  (rbind(PM_SvsB,PM_SvsI,PM_SvsR,PM_SvsSh,PM_SvsSub))
Results_PM_SvsBiotic
#####-----#####
setwd("C:/Users/John Manoha 2/Desktop/PALAK - R_Research")
  ##"C:/Users/A01640632/Documents/RESEARCH_Updated March 24,
  2017/LAB ANALYSIS/R DATA") ##to set the path for R to follow i.e, where
  the files are
getwd()    ##shows path being followed
##### Assuming that sites have the same order for Water and BMIs, create dataframe
Bconc.df<-read.table("Mantel4sites.txt", header = TRUE, na.strings = "EMPTY")
Bconc.df
#####-----#####
##Load ecodist package from library and Create distance matrices
## using distance() in ecodist package BUT can't deal with "NA"
library(ecodist)
W.edist <- distance(Bconc.df$Water, "euclidean")
W.edist
Sed.edist <- distance(Bconc.df$Sed, "euclidean")
Sed.edist
R.edist <- distance(Bconc.df$Root, "euclidean")
R.edist
Sh.edist <- distance(Bconc.df$Shoot, "euclidean")
Sh.edist
FM.edist <- distance(Bconc.df$Fish.M,"euclidean")
FM.edist
D.P.edist <- distance(Bconc.df$D.P,"euclidean")

```

```

D.P.edist
GF.edist <- distance(Bconc.df$GF,"euclidean")
GF.edist
Dab.M.edist <- distance(Bconc.df$Dab.M,"euclidean")
Dab.M.edist
Sub.edist <- distance(Bconc.df$Sub,"euclidean")
Sub.edist
BMI.edist <- distance(Bconc.df$BMI,"euclidean")
BMI.edist
Infl.edist <- distance(Bconc.df$Infl,"euclidean")
Infl.edist
X=Bconc.df[,c(2)]
Y=Bconc.df[,c(3)]
geo.edist <- distance(cbind(as.vector(X), as.vector(Y)), "euclidean")
geo.edist

##when NA in data
Dab.Am = Bconc.df[,c("Dab.Am")]
Dab.Am.dist = dist(Dab.Am,method="euclidean",diag=FALSE,upper=FALSE)
Dab.Am.dist ##one value recorded as "NA"
Fish.GS = Bconc.df[,c("Fish.GS")]
Fish.GS.dist = dist(Fish.GS,method="euclidean",diag=FALSE,upper=FALSE)
Fish.GS.dist ##one value recorded as "NA"
#####

```

BIRDS EGGS vs FOOD SOURCES

```

#####
## Partial Mantel test - Do sites with similar boron concentration in Bird Eggs (Dabblers,
  GF, DP (divers/probers))) have similar (or dissimilar) boron concentration in their
  food sources (Fish, vegetation, BMIs)?
## Set seed for random number generator (RNG); setting the seed will nesure that this
  particular number will ALWAYS produce the same result..if you DONT SET the
  seed you will get different answers every time you run a test based on
  permutations
#####
## Dabbling Bird Eggs (American Coot)vs Food
  source(BMI&Veg[Roots,Shoots,Infl])adjusting for effects of geographical
  distance
set.seed(29895)
PM_Dab.AmvsB= mantel(Dab.Am.dist~BMI.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_Dab.AmvsB
set.seed(27890)
PM_Dab.AmvsR=mantel(Dab.Am.dist~R.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_Dab.AmvsR
set.seed(35678)

```

```

PM_Dab.AmvsSh=mantel(Dab.Am.dist~Sh.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_Dab.AmvsSh
set.seed(41032)
PM_Dab.AmvsI=mantel(Dab.Am.dist~Infl.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_Dab.AmvsI
set.seed(71234)
PM_Dab.AmvsSub=mantel(Dab.Am.dist~Sub.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_Dab.AmvsSub
###-----###
## Displaying results as a summarised table
Results_PM_Dab.AmvsFood <- as.data.frame
  (rbind(PM_Dab.AmvsB,PM_Dab.AmvsR,PM_Dab.AmvsSh,PM_Dab.AmvsI,PM
    _Dab.AmvsSub))
Results_PM_Dab.AmvsFood
###-----###
###-----###
## Dabber BE (miscellaneous)vs Food source(Veg[Shoots,Submerged])adjusting for
  effects of geographical distance
set.seed(29895)
PM_Dab.MvsSh=mantel(Dab.M.edist~Sh.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_Dab.MvsSh
set.seed(41032)
PM_Dab.MvsSub=mantel(Dab.M.edist~Sub.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_Dab.MvsSub
###-----###
## Displaying results as a summarised table
Results_PM_Dab.MvsFood <- as.data.frame (rbind(PM_Dab.MvsSh,PM_Dab.MvsSub))
Results_PM_Dab.MvsFood
###-----###
###-----###
## Ground Forager Eggs vs Food Sources (BMI,Infl), adjusting for effects of
  gepgraphical distance
set.seed(45678)
PM_GFvsB=mantel(GF.edist~BMI.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_GFvsB
set.seed(67895)
PM_GFvsI=mantel(GF.edist~Infl.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_GFvsI
###-----###
## Displaying results as a summarised table
Results_PM_GFvsFood <- as.data.frame (rbind(PM_GFvsB,PM_GFvsI))
Results_PM_GFvsFood
###-----###
###-----###
## Diver/Prober Eggs vs Food Sources (BMI,Fish - Green Sunfish, Misc.), adjusting for

```

```

effects of geographical distance
set.seed(30000)
PM_D.PvsB=mantel(D.P.edist~BMI.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_D.PvsB
set.seed(79000)
PM_D.PvsFM=mantel(D.P.edist~FM.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_D.PvsFM
set.seed(56890)
PM_D.PvsFish.GS=mantel(D.P.edist~Fish.GS.dist+geo.edist, pboot=0.85, cboot=0.90)
PM_D.PvsFish.GS
###-----###
## Displaying results as a summarised table
Results_PM_D.PvsFood <- as.data.frame
  (rbind(PM_D.PvsB,PM_D.PvsFM,PM_D.PvsFish.GS))
Results_PM_D.PvsFood
###-----###
###-----###
## Displaying results for BIRD EGGS vs FOOD SOURCES (summarised table)
Results_PM_BirdEggsvsFood <- as.data.frame
  (rbind(Results_PM_Dab.AmvsFood,Results_PM_Dab.MvsFood,Results_PM_GF
  vsFood,Results_PM_D.PvsFood))
Results_PM_BirdEggsvsFood

###-----###
###-----###

```

FISH vs FOOD SOURCES

```

## Fish (Green Sunfish) vs Food Sources (BMI), adjusting for effects of geographical
  distance
set.seed(30000)
PM_Fish.GSvsB=mantel(Fish.GS.dist~BMI.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_Fish.GSvsB
set.seed(87123)
PM_Fish.GSvsW=mantel(Fish.GS.dist~W.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_Fish.GSvsW
Results_PM_Fish.GSvsB <- as.data.frame (rbind(PM_Fish.GSvsB,PM_Fish.GSvsW))
Results_PM_Fish.GSvsB
## Plot a partial-Mantel Correlogram for Green Sunfish vs BMI
PMgram_Fish.GSvsB <- pmgram(PM_Fish.GSvsB, geo.edist, resid = FALSE, nperm =
  1000)
plot (PMgram_Fish.GSvsB)
###-----###
## Fish (Misc.- Red Shiner, Fathead Minnow, Black Bullhead catfish) vs Food Sources
  (BMI, submerged veg,sediment), adjusting for effects of geographical distance

```

```

set.seed(79513)
PM_FMvsB=mantel(FM.edist~BMI.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_FMvsB
set.seed (56189)
PM_FMvsSub=mantel(FM.edist~Sub.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_FMvsSub
set.seed (76035)
PM_FMvsSed=mantel(FM.edist~Sed.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_FMvsSed
set.seed(21905)
PM_FMvsW=mantel(FM.edist~W.edist+geo.edist, pboot=0.85, cboot=0.90)
PM_FMvsW
###-----###
## Displaying results as a summarised table
Results_PM_FMvsFood <- as.data.frame
  (rbind(PM_FMvsB,PM_FMvsSub,PM_FMvsSed,PM_FMvsW))
Results_PM_FMvsFood
###-----###
###-----###
## Displaying results for FISH (Green Sunfish & Misc.) vs FOOD SOURCES
  (summarised table)
Results_PM_FishvsFood <- as.data.frame (rbind(Results_PM_Fish.GSvsB,
  Results_PM_FMvsFood))
Results_PM_FishvsFood
###-----###

#### 1) BOX PLOT for Water:
Water.df <- read.table(text="
Unit Bconc
Unit1 2.07
Unit1 2.05
Unit1 2.45
Unit1 2.63
Unit1 2.74
Unit1 2.66
Unit2 2.33
Unit2 2.39
Unit2 2.28
Unit3 2.79
Unit3 2.71
Unit3 2.65
Unit4 3.09
Unit4 3.49
Unit4 3.20
Unit4 3.03

```

Unit4 4.50

Unit4 5.17

```
", header = TRUE)
```

```
Water.df
```

```
summary(Water.df)
```

```
## Load packages:
```

```
library(ggplot2)
```

```
library(reshape2)
```

```
## Reshape dataframe
```

```
Water.df2 <- melt(Water.df)
```

```
Water.df2
```

```
##plot data using grouped boxplots
```

```
Wat <- ggplot(Water.df2, aes(x=variable,y=value,fill=Unit))
```

```
Wat_fun <- function(x){
```

```
  return(data.frame(y=max(x)+0.3, label = paste0("n=", length(x))))
```

```
}
```

```
A <- 0.5
```

```
B <- 2.8
```

```
C <- 5
```

```
D <- 6.4
```

```
Wat + stat_boxplot(geom='errorbar',) +
```

```
geom_boxplot(outlier.color='slategray3', outlier.shape=19) +
```

```
labs(title="Boron Conc. in Water",x="Wetland Unit",y="Boron Concentration, mg/L")+
```

```
scale_fill_manual(values = c("slategray3","slategray3","slategray3","slategray3")) +
```

```
theme_linedraw()+ theme_bw()+ theme(panel.grid.minor.x=element_blank(),
```

```
  panel.grid.major.x=element_blank()) +
```

```
stat_summary(fun.y=mean, geom="point", shape=4, position =
```

```
  position_dodge(width=0.75)) +
```

```
stat_summary(fun.data=Wat_fun, geom="text", position = position_dodge(width =
```

```
  0.75)) +
```

```
scale_x_discrete(breaks=NULL) + ylim(0,7) +
```

```
  geom_hline(aes(yintercept=A),color='black',linetype='longdash',size=0.5)+geom_
```

```
hline(aes(yintercept=B),color='black',linetype='longdash',size=0.5)+geom_hline(a
```

```
es(yintercept=C),color='black',linetype='longdash',size=0.5)+geom_hline(aes(yint
```

```
ercept=D),color='black',linetype='longdash',size=0.5)
```

```
###-----###
```

```
##### 2) BOX PLOT for SEDIMENTS (all depths):
```

```
Sediments.df <- read.table(text="
```

```
Depth Unit1 Unit2 Unit3 Unit4
```

```
0-2cm 77.73 31.85 40.10 43.91
```

```

0-2cm 55.95 93.16 47.64 54.63
0-2cm 60.91 48.34 26.72 35.90
0-2cm 25.60 NA NA 30.90
0-2cm 42.45 NA NA 96.61
0-2cm 38.76 NA NA 78.61
2-5cm 11.01 43.23 39.18 12.94
2-5cm 10.70 105.04 26.88 26.26
2-5cm 22.94 47.96 25.85 22.42
2-5cm 12.97 NA NA 10.26
2-5cm 7.83 NA NA 22.16
2-5cm 7.72 NA NA 25.64
", header = TRUE)
Sediments.df
## Load packages:
library(ggplot2)
library(reshape2)
## Reshape dataframe
Sediments.df2 <- melt(Sediments.df)
Sediments.df2
##plot data using grouped boxplots
Sed <- ggplot(Sediments.df2, aes(x=variable,y=value,fill=Depth))
Sed_fun <- function(x){
  return(data.frame(y=max(x)+3, label = paste0("n=", length(x))))
}

Sed + stat_boxplot(geom='errorbar') +
  geom_boxplot(outlier.color="salmon2", outlier.shape=19) +
  labs(title="Boron Conc. in Sediments",x="Wetland Unit",y="Boron Concentration,
  mg/kg DW")+
  scale_fill_manual(values = c("tan3","salmon2")) +
  theme_linedraw()+ theme_bw()+ theme(panel.grid.minor.x=element_blank(),
  panel.grid.major.x=element_blank()) +
  scale_x_discrete(breaks=c("Unit1","Unit2","Unit3","Unit4"), labels=c("Unit 1","Unit
  2","Unit 3","Unit 4")) +
  stat_summary(fun.y=mean, geom="point", shape=4, position =
  position_dodge(width=0.75)) +
  stat_summary(fun.data=Sed_fun, geom="text", position = position_dodge(width = 1))

####-----###

##### 1) BOX PLOT for BMIs:
BMI.df <- read.table(text="
Unit Bconc
Unit1 37.83
Unit1 37.99

```

```

Unit1 43.76
Unit1 25.97
Unit1 14.41
Unit1 24.65
Unit2 36.31
Unit2 44.88
Unit2 19.09
Unit3 51.07
Unit3 11.61
Unit3 16.75
Unit4 29.08
Unit4 23.14
Unit4 28.37
Unit4 NA
Unit4 10.90
Unit4 27.77
", header = TRUE)
BMI.df
summary(BMI.df)

## Load packages:
library(ggplot2)
library(reshape2)
## Reshape dataframe
BMI.df2 <- melt(BMI.df)
BMI.df2

##plot data using grouped boxplots
BMI <- ggplot(BMI.df2, aes(x=variable,y=value,fill=Unit))
BMI_fun <- function(x){
  return(data.frame(y=max(x)+2, label = paste0("n=", length(x))))
}
A <- 8
B <- 56
BMI + stat_boxplot(geom='errorbar',) +
  geom_boxplot(outlier.color=c("lightcyan","lightcyan3","lightblue","lavender"),
    outlier.shape=19) +
  labs(title="Boron Conc. in BMIs",x="Wetland Unit",y="Boron Concentration, mg/kg,
    DW")+
  scale_fill_manual(values = c("lightcyan","lightcyan3","lightblue","lavender")) +
  theme_linedraw()+ theme_bw()+ theme(panel.grid.minor.x=element_blank(),
    panel.grid.major.x=element_blank()) +
  stat_summary(fun.y=mean, geom="point", shape=4, position =
    position_dodge(width=0.75)) +
  stat_summary(fun.data=BMI_fun, geom="text", position = position_dodge(width =

```



```

0.75)) +
scale_x_discrete(breaks=NULL) +

  geom_hline(aes(yintercept=A),linetype='longdash',size=1)+geom_hline(aes(yinte
rcept=B),linetype='longdash',size=1)

###-----###
### Load package "sfsmisc" from the R directory
###-----###
#### 1) BOX PLOTS for Roots (Cattails VS Bullrush):
Roots.df <- read.table(text="
Species Unit1 Unit2 Unit3 Unit4
Bullrush 46.89 NA 18.47 20.19
Bullrush 15.91 NA 23.01 20.31
Bullrush 106.95 NA 29.01 46.40
Bullrush 59.90 NA 51.44 12.53
Bullrush 49.12 NA 60.79 13.43
Bullrush 74.99 NA 59.68 16.27
Bullrush 65.34 NA NA 84.90
Bullrush NA NA NA 88.82
Bullrush NA NA NA 56.19
Bullrush NA NA NA 67.41
Bullrush NA NA NA 98.55
Bullrush NA NA NA 102.51
Bullrush NA NA NA 79.88
Bullrush NA NA NA 129.76
Bullrush NA NA NA 171.06
Bullrush NA NA NA 128.26
Cattails 12.21 56.63 26.17 33.39
Cattails 17.54 61.06 41.79 27.23
Cattails 73.72 48.39 34.56 33.62
Cattails 62.77 50.69 32.61 35.34
Cattails 56.40 58.99 NA 27.68
Cattails 35.02 50.35 NA 12.85
Cattails 29.58 57.80 NA 12.03
Cattails 29.61 49.53 NA 24.67
Cattails 36.99 64.39 NA 45.93
Cattails 67.37 NA NA 24.77
Cattails 52.23 NA NA 24.37
Cattails 57.26 NA NA 27.44
Cattails 53.97 NA NA 32.37
Cattails 71.50 NA NA NA
Cattails 57.44 NA NA NA
Cattails 62.13 NA NA NA
Cattails 26.54 NA NA NA

```

```

", header = TRUE)
Roots.df
## Load packages:
library(ggplot2)
library(reshape2)
## Reshape dataframe
Roots.df2 <- melt(Roots.df)
Roots.df2
##plot data using grouped boxplots
Root <- ggplot(Roots.df2, aes(x=variable,y=value,fill=Species))
Root_fun <- function(x){
  return(data.frame(y=max(x)+10, label=paste0("n=",length(x))))
}
##plot data using grouped boxplots
Roots_plot <- Root + stat_boxplot(geom='errorbar') +
  geom_boxplot(outlier.color="orangered3", outlier.shape=19) +
  labs(title="Roots",x="Wetland Unit",y="Boron Concentration, mg/kg DW") +
  scale_fill_manual(values = c("orangered3","orange")) +
  theme_linedraw() + theme_bw() + theme(panel.grid.minor.x=element_blank(),
    panel.grid.major.x=element_blank()) +
  scale_x_discrete(breaks=c("Unit1","Unit2","Unit3","Unit4"), labels=c("Unit 1","Unit
    2","Unit 3","Unit 4")) +
  stat_summary(fun.y=mean, geom="point", shape=4, position =
    position_dodge(width=0.75)) +
  stat_summary(fun.data=Root_fun, geom="text", position = position_dodge(width = 1)) +
  ylim(0,225)
R_plot <- Roots_plot+theme(legend.position="none")
R_plot
###-----###

```

2) BOX PLOTS -- Shoots (Cattails VS Bullrush)

```

Shoots.df <- read.table(text="
  Species Unit1 Unit2 Unit3 Unit4
  Bullrush 23.66 30.81 32.34 63.54
  Bullrush 26.42 34.60 33.54 66.30
  Bullrush 28.44 34.26 32.27 62.16
  Bullrush 34.63 NA    32.60 66.39
  Bullrush 33.01 NA    35.55 61.04
  Bullrush 36.64 NA    32.84 64.46
  Bullrush 28.65 NA    NA    70.07
  Bullrush 37.25 NA    NA    17.45
  Bullrush 35.82 NA    NA    21.13
  Bullrush NA    NA    NA    28.21
  Bullrush NA    NA    NA    116.29
  Bullrush NA    NA    NA    157.76

```

```

Bullrush NA NA NA 71.45
Bullrush NA NA NA 148.81
Bullrush NA NA NA 166.74
Bullrush NA NA NA 105.77
Cattails 9.28 30.65 30.85 35.79
Cattails 13.83 33.10 32.99 38.13
Cattails 58.69 30.84 30.62 41.36
Cattails 51.08 32.30 31.15 39.75
Cattails 42.90 31.61 30.89 36.92
Cattails 32.56 28.74 NA 42.16
Cattails 37.24 NA NA 42.41
Cattails 13.70 NA NA 39.01
Cattails 77.74 NA NA 38.37
Cattails 36.42 NA NA 50.39
Cattails 28.96 NA NA 56.12
Cattails 30.13 NA NA 50.27
Cattails 27.47 NA NA NA
Cattails 35.36 NA NA NA
Cattails 30.53 NA NA NA
Cattails 31.11 NA NA NA
Cattails 16.43 NA NA NA
Cattails 30.58 NA NA NA
Cattails 30.66 NA NA NA
Cattails 29.10 NA NA NA
", header = TRUE)
Shoots.df
## Load packages:
library(ggplot2)
library(reshape2)
## Reshape dataframe
Shoots.df2 <- melt(Shoots.df)
Shoots.df2
##plot data using grouped boxplots
Shoot <- ggplot(Shoots.df2, aes(x=variable,y=value,fill=Species))
Shoot_fun <- function(x){
  return(data.frame(y=max(x)+15, label=paste0("n=",length(x))))
}

Shoots_plot <- Shoot + stat_boxplot(geom='errorbar') +
  geom_boxplot(outlier.colour=NULL, outlier.shape=19) +
  labs(title="Shoots",x="Wetland Unit",y="Boron Concentration, mg/kg DW") +
  scale_fill_manual(values = c("orangered3","orange"))+
  theme_linedraw()+ theme_bw() + theme(panel.grid.minor.x=element_blank(),
  panel.grid.major.x=element_blank()) +
  scale_x_discrete(breaks=c("Unit1","Unit2","Unit3","Unit4"), labels=c("Unit 1","Unit

```

```

2", "Unit 3", "Unit 4")) +
stat_summary(fun.y=mean, geom="point", shape=4, position =
  position_dodge(width=0.75)) +
stat_summary(fun.data=Shoot_fun, geom="text", position = position_dodge(width = 1))
+
ylim(0,225)
S_plot <- Shoots_plot + theme(legend.position="none")
S_plot
###-----###

```

3) BOX PLOTS -- Inflorescence (Cattails VS Bullrush)

```

Infl.df <- read.table(text="
Species Unit1 Unit2 Unit3 Unit4
Bullrush 114.21 NA 26.35 22.98
Bullrush 28.45 NA 30.61 14.52
Bullrush 0.35 NA 34.98 7.15
Bullrush 23.27 NA 30.86 90.07
Bullrush 23.51 NA 28.15 97.62
Bullrush NA NA 28.62 89.09
Bullrush NA NA NA 27.95
Bullrush NA NA NA 209.51
Bullrush NA NA NA 84.34
Bullrush NA NA NA 85.94
Bullrush NA NA NA 104.72
Bullrush NA NA NA 87.32
Bullrush NA NA NA 80.56
Bullrush NA NA NA 38.91
Bullrush NA NA NA 167.22
Cattails 30.62 40.06 60.78 35.32
Cattails 27.58 33.61 66.53 30.39
Cattails 32.64 36.85 85.70 39.84
Cattails 22.38 NA NA 48.89
Cattails 14.78 NA NA 41.65
Cattails 25.12 NA NA 40.15
Cattails 83.08 NA NA 58.75
Cattails 87.52 NA NA 61.47
Cattails 72.56 NA NA 49.30
Cattails 41.05 NA NA 46.40
Cattails 34.29 NA NA 99.33
Cattails 21.90 NA NA 66.43
Cattails NA NA NA 32.83
", header= TRUE)
Infl.df
## Load packages:
library(ggplot2)

```

```

library(reshape2)
## Reshape dataframe
Infl.df2 <- melt(Infl.df)
Infl.df2
##plot data using grouped boxplots
Infl <- ggplot(Infl.df2, aes(x=variable,y=value,fill=Species))
Infl_fun <- function(x){
  return(data.frame(y=max(x)+10, label=paste0("n=", length(x))))
}

Infl_plot <- Infl + stat_boxplot(geom='errorbar') +
  geom_boxplot(outlier.color=NULL, outlier.shape=19) +
  labs(title="Inflorescence",x="Wetland Unit",y="Boron concentration, mg/kg DW")+
  scale_fill_manual(values = c("orangered3","orange"))+
  theme_linedraw()+ theme_bw() + theme(panel.grid.minor.x=element_blank(),
  panel.grid.major.x=element_blank()) +
  scale_x_discrete(breaks=c("Unit1","Unit2","Unit3","Unit4"), labels=c("Unit 1","Unit
  2","Unit 3","Unit 4")) +
  stat_summary(fun.y=mean, geom="point", shape=4, position =
  position_dodge(width=0.75)) +
  stat_summary(fun.data=Infl_fun, geom="text", position = position_dodge(width = 1)) +
  ylim(0,225)
I_plot <- Infl_plot+theme(legend.position = "none")
I_plot
####-----###

## Plotting all plots in a single graph
library(gridExtra)
grid.arrange(R_plot,S_plot,I_plot,ncol=2, nrow=2)

####-----###
##### 4) BOX PLOTS -- Submerged Plants (Chara VS Potamageton)
Sub.df <- read.table(text="
Species Unit1 Unit2 Unit3 Unit4
Chara 77.99 85.93 102.48 23.04
Chara 85.58 106.76 100.50 27.62
Chara 111.10 87.15 109.09 34.40
Chara 71.99 215.08 121.76 44.44
Chara 70.68 127.60 132.69 35.54
Chara 158.90 99.08 119.04 35.01
Chara 181.85 103.56 266.21 34.26
Chara 202.42 124.17 385.66 36.96
Chara NA 130.41 361.60 35.11
Chara NA NA 54.98 130.01
Chara NA NA 45.46 131.48

```

```

Chara NA NA 47.59 130.47
Chara NA NA 58.56 228.47
Chara NA NA 71.55 266.71
Chara NA NA 55.69 188.13
Potamag 584.82 188.98 141.35 76.06
Potamag 650.11 257.90 178.99 89.52
Potamag 465.42 196.11 164.29 72.55
Potamag 861.42 215.15 53.77 72.08
Potamag 846.47 217.32 72.38 74.40
Potamag 958.48 339.51 66.66 77.23
Potamag 966.12 272.44 527.81 82.76
Potamag 1479.94 318.00 559.80 97.04
Potamag 990.52 NA 693.02 97.16
Potamag 349.34 NA NA 82.27
Potamag 281.24 NA NA 19.09
Potamag 447.16 NA NA 30.66
Potamag NA NA NA 43.46
", header= TRUE)
Sub.df
## Load packages:
library(ggplot2)
library(reshape2)
## Reshape dataframe
Sub.df2 <- melt(Sub.df)
Sub.df2
##plot data using grouped boxplots
Sub <- ggplot(Sub.df2, aes(x=variable,y=value,fill=Species))
Sub_fun <- function(x){
  return(data.frame(y=max(x)+40, label=paste0("n=", length(x))))
}
A <- 160
B <- 460
Sub + stat_boxplot(geom='errorbar') +
  geom_boxplot(outlier.color="black", outlier.shape=19) +
  labs(title="Boron Conc. in Submerged Plants",x="Wetland Unit",y="Boron
  Concentration, mg/kg DW")+
  scale_fill_manual(values = c("darkolivegreen4","olivedrab2"))+
  theme_linedraw()+ theme_bw() + theme(panel.grid.minor.x=element_blank(),
  panel.grid.major.x=element_blank()) +
  scale_x_discrete(breaks=c("Unit1","Unit2","Unit3","Unit4"), labels=c("Unit 1","Unit
  2","Unit 3","Unit 4")) +
  stat_summary(fun.y=mean, geom="point", shape=4, position =
  position_dodge(width=0.75)) +
  stat_summary(fun.data=Sub_fun, geom="text", position = position_dodge(width = 1)) +
  geom_hline(aes(yintercept=A),color='lightgoldenrod4',linetype='longdash',size=1)+geom

```

```
_hline(aes(yintercept=B),color='lightgoldenrod4',linetype='longdash',size=1)
```

```
#####-----#####
```

```
Fish.df <- read.table(text="
```

```
Unit B.conc
```

```
Unit1 1.63
```

```
Unit1 1.30
```

```
Unit1 1.15
```

```
Unit1 0.88
```

```
Unit1 1.47
```

```
Unit2 1.80
```

```
Unit2 1.87
```

```
Unit2 1.41
```

```
Unit2 2.57
```

```
Unit2 2.16
```

```
Unit2 2.22
```

```
Unit2 1.62
```

```
Unit2 2.64
```

```
Unit2 1.79
```

```
Unit2 1.45
```

```
Unit2 1.67
```

```
Unit2 2.17
```

```
Unit3 11.40
```

```
Unit3 8.90
```

```
Unit3 8.17
```

```
Unit3 12.20
```

```
Unit3 14.40
```

```
Unit3 11.30
```

```
Unit3 10.80
```

```
Unit3 13.10
```

```
Unit4 5.59
```

```
Unit4 2.96
```

```
Unit4 3.64
```

```
Unit4 3.60
```

```
Unit4 7.48
```

```
Unit4 1.71
```

```
Unit4 1.67
```

```
Unit4 2.93
```

```
Unit4 2.99
```

```
Unit4 1.39
```

```
Unit4 2.73
```

```
", header = TRUE)
```

```
Fish.df
```

```
## Load packages:
```

```

library(ggplot2)
library(reshape2)
## Reshape dataframe
Fish.df2 <- melt(Fish.df)
Fish.df2
##plot data using grouped boxplots
Fish <- ggplot(Fish.df2, aes(x=variable,y=value,fill=Unit))
Fish_fun <- function(x){
  return(data.frame(y=max(x)+1, label = paste0("n=", length(x))))
}

Fish + stat_boxplot(geom='errorbar') +
  geom_boxplot(outlier.color=c("mistyrose2","lightgoldenrod1","navajowhite","navajowhite3"), outlier.shape=19) +
  labs(title="Boron Conc. in Fish",x="Wetland Unit",y="Boron Concentration, mg/kg DW")+
  scale_fill_manual(values =
    c("mistyrose2","lightgoldenrod1","navajowhite","navajowhite3")) +
  theme_linedraw()+ theme_bw()+ theme(panel.grid.minor.x=element_blank(),
    panel.grid.major.x=element_blank()) +
  stat_summary(fun.y=mean, geom="point", shape=4, position =
    position_dodge(width=0.75)) +
  stat_summary(fun.data=Fish_fun, geom="text", position = position_dodge(width = 0.7))
  +
  scale_x_discrete(breaks=NULL) + ylim(0,16)
####-----###

```

1) BOX PLOT for Bird Eggs (DABBLERS):

```

BE.df <- read.table(text="
  Types Unit1 Unit2 Unit3 Unit4
Dabblers 2.35 2.14 NA 2.87
Dabblers 6.02 2.00 NA 2.92
Dabblers 5.16 2.94 NA 3.31
Dabblers 3.41 7.68 NA 3.94
Dabblers 6.53 4.08 NA 1.75
Dabblers 4.88 5.30 NA 3.36
Dabblers 1.01 2.67 NA 3.47
Dabblers 2.68 3.45 NA NA
Dabblers NA 2.03 NA NA
Dabblers NA 3.82 NA NA
Dabblers NA 1.28 NA NA
Dabblers NA 5.75 NA NA
Dabblers NA 1.30 NA NA
Dabblers NA 1.40 NA NA
GF 1.56 1.89 3.77 1.90

```



```

GF 2.56 1.84 1.52 1.79
GF 1.24 NA NA 1.88
GF 1.55 NA NA 1.06
GF 1.74 NA NA 2.72
DP 0.85 1.28 4.03 2.09
DP 0.84 NA 1.63 1.63
DP NA NA 1.63 NA
DP NA NA 0.88 NA
", header=TRUE)
BE.df

## Load packages:
library(ggplot2)
library(reshape2)
## Reshape dataframe
BE.df2 <- melt(BE.df)
BE.df2

##plot data using grouped boxplots
BE <- ggplot(BE.df2, aes(x=variable,y=value,fill=Types))
BE_fun <- function(x){
  return(data.frame(y=max(x)+0.25, label = paste0("n=", length(x))))
}
BE_fun
BE + stat_boxplot(geom='errorbar') +
  geom_boxplot(outlier.color="black", outlier.shape=19) +
  labs(title="Boron Conc. in Bird Eggs",x="Wetland Unit",y="Boron Concentration,
  mg/kg DW") +
  scale_fill_manual(values = c("pink","palevioletred", "rosybrown")) +
  theme_linedraw()+ theme_bw()+ theme(panel.grid.minor.x=element_blank(),
  panel.grid.major.x=element_blank()) +
  stat_summary(fun.y=mean, geom="point", shape=4, position = position_dodge(width=
  0.8)) +
  stat_summary(fun.data=BE_fun, geom="text", position = position_dodge(width = 1)) +
  scale_x_discrete(breaks=c("Unit1","Unit2","Unit3","Unit4"), labels=c("Unit 1","Unit
  2","Unit 3","Unit 4"))

BE.df <- read.table(text="
Behavior Bconc
Dabblers 2.35
Dabblers 6.02
Dabblers 5.16
Dabblers 3.41
Dabblers 6.53
Dabblers 4.88

```

Dabblers 2.14
Dabblers 2.00
Dabblers 2.94
Dabblers 7.68
Dabblers 4.08
Dabblers 5.30
Dabblers 2.67
Dabblers 3.45
Dabblers 2.03
Dabblers 3.82
Dabblers 2.87
Dabblers 2.92
Dabblers 3.31
Dabblers 3.94
Dabblers 1.75
Dabblers 3.36
Dabblers 1.01
Dabblers 2.68
Dabblers 1.28
Dabblers 5.75
Dabblers 1.30
Dabblers 1.40
Dabblers 0.64
Dabblers 3.47
GF 1.56
GF 2.56
GF 1.24
GF 1.55
GF 1.74
GF 1.89
GF 1.84
GF 3.77
GF 1.52
GF 1.90
GF 1.79
GF 1.88
GF 1.06
GF 2.72
Diver/Probers 0.85
Diver/Probers 0.84
Diver/Probers 1.28
Diver/Probers 4.03
Diver/Probers 1.63
Diver/Probers 1.63
Diver/Probers 0.88

```

Diver/Probers 2.09
Diver/Probers 1.63
", header=TRUE)
BE.df

## Load packages:
library(ggplot2)
library(reshape2)
## Reshape dataframe
BE.df2 <- melt(BE.df)
BE.df2

##plot data using grouped boxplots
BE <- ggplot(BE.df2, aes(x=variable,y=value,fill=Behavior))
BE_fun <- function(x){
  return(data.frame(y=max(x)+0.25, label = paste0("n=", length(x))))
}
BE_fun
BE + stat_boxplot(geom='errorbar') +
  geom_boxplot(outlier.color=c("pink","palevioletred", "rosybrown"), outlier.shape=19) +
  labs(title="Boron Conc. in Bird Eggs",x="Food behavior",y="Boron Concentration,
  mg/kg DW") +
  scale_fill_manual(values = c("pink","palevioletred", "rosybrown")) +
  theme_linedraw()+ theme_bw()+ theme(panel.grid.minor.x=element_blank(),
  panel.grid.major.x=element_blank()) +
  stat_summary(fun.y=mean, geom="point", shape=4, position = position_dodge(width=
  0.8)) +
  stat_summary(fun.data=BE_fun, geom="text", position = position_dodge(width =0.75 ))
  +

  scale_x_discrete(breaks=c("Dabblers","GF","Divers/Probers"),labels=c("Dabblers",
  "Ground Foragers","Divers & Probers"))

#####-----#####

```

APPENDIX C

Table A2

Visual MINTEQ input parameters and data for calculating the dominant species distribution in the pond water samples collected at Pariette Wetlands.

Partial Pressure, CO₂ = 0.0042 atm

Pond Sampling site	pH	B	Ca	K	Mg	Na	S	Si
		H ₃ BO ₃	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	(SO ₄) ⁻²	H ₄ SiO ₄
		----- mmol L ⁻¹ -----						
Desilt, Inlet	7.0	0.191	5.69	0.069	5.43	40.1	25.4	0.675
Desilt, Interior	8.8	0.188	3.69	0.077	4.68	43.6	28.1	0.447
Desilt, Outlet	8.3	0.226	3.93	0.161	5.61	46.3	29.0	0.617
Felters, Inlet	9.5	0.243	3.26	0.225	7.55	58.2	37.6	0.066
Felters, Interior	9.8	0.254	3.38	0.229	7.94	60.6	39.3	0.111
Felters, Outlet	9.8	0.246	3.29	0.229	7.88	60.0	38.5	0.026
Big Island, Inlet	8.8	0.258	4.38	0.239	8.27	67.7	42.9	0.349
Big Island, Interior	9.4	0.251	4.17	0.276	8.22	67.7	43.4	0.174
Big Island, Outlet	8.9	0.245	4.27	0.271	8.05	67.7	43.5	0.362
Pintail, Inlet	8.8	0.286	4.31	0.273	9.27	75.4	47.5	0.192
Pintail, Interior	8.0	0.322	5.48	0.226	10.20	82.3	50.7	0.538
Pintail, Outlet	9.3	0.296	4.30	0.274	9.64	76.4	48.4	0.163
Gadwall, Inlet	7.4	0.280	6.37	0.269	9.41	72.2	46.4	0.346
Gadwall, Interior	9.9	0.416	6.75	0.550	12.99	123.4	73.0	0.068
Gadwall, Outlet	9.4	0.478	8.70	0.699	16.23	153.2	90.6	0.153
Redhead, Inlet	8.4	0.216	3.74	0.168	7.49	55.1	35.7	0.017
Redhead, Interior	9.1	0.221	3.54	0.202	7.63	56.3	36.7	0.052
Redhead, Outlet	8.3	0.210	3.51	0.182	7.37	53.6	35.0	0.018