

## AN ABSTRACT OF THE THESIS OF

Nicholas T. Dosch for the degree of Master of Science in Water Resources Engineering presented on September 12, 2014.

Title: Spatiotemporal Dynamics and Drivers of Stream pCO<sub>2</sub> in a Headwater Catchment in the Western Cascade Mountains, Oregon

Abstract approved:

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Roy D. Haggerty

We examined the spatial and temporal variability of stream carbon dioxide (CO<sub>2</sub>) and the drivers of these variations in a headwater catchment. To examine temporal variation and drivers, we measured stream and hyporheic pCO<sub>2</sub> at high temporal resolution over 11 months in a 95.9-ha forested headwater catchment in the Western Cascades of Central Oregon, USA. Stream and hyporheic pCO<sub>2</sub> showed high seasonal and event-scale variability with distinct stream and hyporheic dynamics during storm discharge events. Hyporheic exchange flow exported 37.5 kg-C yr<sup>-1</sup> per watershed hectare (confidence interval 4.0–122.3 kg-C ha<sup>-1</sup> yr<sup>-1</sup>) from the riparian zone to the stream. Summing CO<sub>2</sub> evasion and downstream advection suggests that one third of inorganic carbon export originated in the hyporheic zone. Hyporheic exchange flow had greatest influence over stream pCO<sub>2</sub> during low and high baseflow, while CO<sub>2</sub> evasion had greatest influence during storm discharge events. These findings suggest that the hyporheic zone actively participates in carbon cycling in this headwater stream and continuously replenishes stream CO<sub>2</sub>.

To examine spatial variation and drivers, we measured stream CO<sub>2</sub> at monthly intervals from July 2013 through July 2014 at 38 locations across the 6400-ha HJ Andrews Experimental Forest. Stream pCO<sub>2</sub> was consistently supersaturated with respect to atmospheric concentrations. Stream pCO<sub>2</sub> ranged from atmospheric (~400 μatm) to 20 times atmospheric concentrations (8150 μatm) and exhibited strong spatial and temporal variability. The distribution of pCO<sub>2</sub> over the study period was different in small and large streams within the drainage network. At the watershed scale, pCO<sub>2</sub> decreased with distance downstream. At the reach scale, we did not detect clear patterns in the downstream direction. However, individual transects displayed persistent profile shape, with consistent high and low pCO<sub>2</sub> locations. We found negative relationships between stream pCO<sub>2</sub> and stream discharge, mean velocity and the carbon dioxide gas transfer velocity. Stream pCO<sub>2</sub> exhibited changes over short distances, with large changes in pCO<sub>2</sub> over less than 50 m. Longitudinal variability indicates spatial variability of in-stream controls on pCO<sub>2</sub> at this scale. Stream pCO<sub>2</sub> shows generally higher concentrations during the summer and lower concentrations in the winter, with considerable intrannual variability.

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Spatiotemporal Dynamics and Drivers of Stream pCO<sub>2</sub> in a Headwater Catchment in  
the Western Cascade Mountains, Oregon

by  
Nicholas T. Dosch

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Nicholas T. Dosch, Author

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## CONTRIBUTION OF AUTHORS

Manuscript 1: Dr. Roy Haggerty assisted in the development of this project, contributed stream CO<sub>2</sub> evasion data, and provided feedback and insight throughout. Dr. Steve M. Wondzell assisted in the development of the hyporheic DIC export model and provided hyporheic residence time distribution data. Hayley A. Corson-Rikert provided DIC data from the WS01 well network which was used for model calibration.

Manuscript 2: Dr. Roy Haggerty helped in the development of this project and provided guidance and feedback throughout.

# TABLE OF CONTENTS

	<u>Page</u>
1 Introduction .....	1
2 Hyporheic export of inorganic carbon responsible for elevated stream pCO <sub>2</sub> in a temperate forested catchment.....	5
2.1 Abstract.....	5
2.2 Introduction .....	5
2.3 Site Description and Methods.....	7
2.4 Results .....	11
2.5 Discussion.....	15
2.6 Conclusions .....	19
2.7 Acknowledgements .....	19
2.8 References .....	20
3 Drainage network variations in stream pCO <sub>2</sub> within the Lookout Creek watershed .....	24
3.1 Abstract.....	24
3.2 Introduction .....	24
3.3 Site Description .....	26
3.4 Methods .....	33
3.4.1 Field Methods .....	33
3.4.2 Laboratory Methods.....	35
3.4.3 pCO <sub>2</sub> Calculation and Data Processing.....	35
3.4.4 Calculation of Catchment Properties .....	36
3.4.5 Calculation of Physical Variables .....	37
3.4.6 Statistical Analyses .....	38

## TABLE OF CONTENTS (CONTINUED)

	<u>Page</u>
3.5 Results .....	39
3.5.1 Spatial Patterns.....	41
3.5.2 Temporal patterns .....	46
3.5.3 Hydraulic Patterns.....	50
3.6 Discussion.....	52
3.6.1 Spatial Controls on Stream pCO <sub>2</sub> .....	52
3.6.2 Spatial Considerations .....	56
3.6.3 Temporal Controls on pCO <sub>2</sub> .....	57
3.6.4 Assessment of Parameter Uncertainty .....	60
3.7 Conclusions .....	61
3.8 Acknowledgements .....	62
3.9 References .....	62
4 Conclusion.....	68
BIBLIOGRAPHY.....	70
APPENDICES .....	78
Appendix A Monte Carlo Simulation Supporting Information .....	79
Appendix B Additional Figures and Tables Chapter 1 .....	82
Appendix C Vaisala GMM220 CO <sub>2</sub> Module Modification/Implementation Instructions .....	85
Appendix D Additional Figures and Tables Chapter 2 .....	97

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 2.1 – Concentration of hyporheic and stream CO <sub>2</sub> , stream temperature, and stream discharge over the study period from late August, 2013 to July, 2014. ....	12
Figure 2.2 - Hyporheic CO <sub>2</sub> export rate, CO <sub>2</sub> evasion rate and stream pCO <sub>2</sub> over the study period. ....	14
Figure 2.3 - Discharge event response of hyporheic and stream pCO <sub>2</sub> with stream discharge, stream temperature, 5-hour precipitation (ppt) and total precipitation.....	15
Figure 3.1 - Lookout Creek watershed and study site locations with mean pCO <sub>2</sub> . ....	31
Figure 3.2 – Linear regressions of site average pCO <sub>2</sub> with site downstream distance, site elevation, site contributing drainage area, and reach slope .....	42
Figure 3.3 – Longitudinal pCO <sub>2</sub> profile variability and contributing transect drainage area .....	44
Figure 3.4 – Persistent spatial trends in longitudinal pCO <sub>2</sub> in W1 .....	45
Figure 3.5 – Variogram of mean pCO <sub>2</sub> measurements in Watershed 1 .....	45
Figure 3.6 - Temporal variations in pCO <sub>2</sub> at each site over the study period, separated by sample collection run .....	48
Figure 3.7 – Annual variation in calculated stream pCO <sub>2</sub> and stream temperature in the Lookout Creek drainage network.....	49
Figure 3.8 – Linear regression of Arrhenius temperature and the logarithm of stream minus atmospheric pCO <sub>2</sub> . ....	50
Figure 3.9 – Linear regressions of excess stream pCO <sub>2</sub> with, log discharge, mean velocity, log carbon dioxide transfer velocity.....	51

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 2.1 - Summary of measured properties and Pearson Correlation Coefficients.....	13
Table 3.1 – Study watersheds within HJA with physical information and management history .....	30
Table 3.2 – Sample site locations within HJA, and associated physical properties .....	32
Table 3.3 – Summary of average pH, temperature, alkalinity, and pCO <sub>2</sub> for each sample site.....	40
Table 3.4 – Watershed Average pCO <sub>2</sub> for each sample run and percent change from the previous month.....	47

## LIST OF APPENDIX FIGURES

<u>Figure</u>	<u>Page</u>
Figure A.1 - Monte Carlo simulation results for 10,000 iterations.....	81
Figure B.1 – Rate of recovery in stream pCO <sub>2</sub> following fall/winter storms .....	83
Figure B.2 - Modeled and Measured Excess hyporheic DIC with respect to travel time. Results of model calibration to lowest RMSE.....	84
Figure B.3 – Model calibration results, modeled as a function of measured excess hyporheic DIC.....	84
Figure C.1 - Overview of the Vaisala GMM 220 CO <sub>2</sub> probe pre-modification .....	85
Figure C.2 - Close-up view of the CO <sub>2</sub> probe.....	86
Figure C.3 - PTFE fabric used for the modification from International Polymer Engineering, Inc.....	86
Figure C.4 - PTFE sleeve adjacent to Vaisala pCO <sub>2</sub> probe .....	87
Figure C.5 - CO <sub>2</sub> probe modification 1.....	88
Figure C.6 - Probe modification 2 .....	89
Figure C.7 - CO <sub>2</sub> probe modification 3.....	90
Figure C.8 - CO <sub>2</sub> probe modification 4.....	91
Figure C.9 - CO <sub>2</sub> probe modification 5.....	92
Figure C.10 - Schematic wiring diagram to connect a Vaisala GMM 220 pCO <sub>2</sub> probe to a Campbell C200 series data logger .....	93
Figure C.11 - Data logger and GMM 220 deployed in the field.....	94
Figure C.12 - GMM deployed in the field .....	95
Figure D.1 - Longitudinal pCO <sub>2</sub> profile variability and contributing transect drainage area of Watershed 2 transect.....	97

## LIST OF APPENDIX FIGURES (CONTINUED)

<u>Figure</u>	<u>Page</u>
Figure D.2 - Longitudinal pCO <sub>2</sub> profile variability and contributing transect drainage area of Mack Creek transect .....	98
Figure D.3 - Longitudinal pCO <sub>2</sub> profile variability and contributing transect drainage area of McRae Creek transect.....	99
Figure D.4 - Box plots of measured pCO <sub>2</sub> in the 5 longitudinal transects.....	100
Figure D.5 - Linear regression of Arrhenius temperature and the log mean site stream pCO <sub>2</sub> minus atmospheric pCO <sub>2</sub> . .....	101
Figure D.6 - Linear regression of Arrhenius temperature and carbonate alkalinity .....	102
Figure D.7 – Regression between the log of specific discharge and excess stream pCO <sub>2</sub> .....	103
Figure D.8 - Annual variation in stream carbonate alkalinity from the Lookout Creek drainage network from July 2013 to July 2014 .....	104
Figure D.9 - Annual variation in stream pH and from the Lookout Creek drainage network from July 2013 to July 2014 .....	105
Figure D.10 - Alkalinity time sensitivity regression.....	106
Figure D.11 - Directly measured pCO <sub>2</sub> and pCO <sub>2</sub> calculated with CO2SYS regression.....	107

## LIST OF APPENDIX TABLES

<u>Table</u>	<u>Page</u>
Table A.1 – Hyporheic DIC model parameter confidence intervals (CI).....	80
Table A.2 - Monte Carlo simulation results of hyporheic DIC export, 10,000 iterations .....	81
Table A.3 - Monte Carlo simulation results of the percentage of total Watershed 1 DIC export originating from the hyporheic zone, 1000 iterations.....	81
Table B.1 - Recovery in stream pCO <sub>2</sub> following fall/winter storms.....	82
Table C.1 - Material list for modified stream pCO <sub>2</sub> probe .....	96
Table C.2 - Additional items for probe modification .....	96
Table D.1 - Time sensitivity error analysis in laboratory determination of carbonate alkalinity .....	106

## 1 Introduction

Recent work has established that streams and rivers play a disproportionately large role in the global carbon cycle relative to their size on the landscape [e.g., *Richey et al.*, 2002; *Raymond et al.*, 2008; *Tranvik et al.*, 2009]. Despite making up only ~1% of terrestrial surface area, carbon fluxes per unit area in streams and rivers often surpass that of the landscape that makes up their watershed [*Cole et al.*, 2007; *Aufdenkampe et al.*, 2011]. Headwater streams in particular may play an important role because they are a major component of terrestrial drainage networks. First and second order streams make up ~75% total river length and ~30% of total stream and river surface area worldwide [*Leopold et al.*, 1964; *Downing et al.*, 2012].

Inputs of terrestrial organic matter to headwater streams from adjacent ecosystems fuel high rates of microbial respiration that exceed in-stream production, causing most headwater systems to be heterotrophic [*Vannote et al.*, 1980; *Dawson et al.*, 2001]. This high metabolic rate is driven by the delivery of organic matter, nutrients, and oxygen to subsurface microbial communities via hyporheic exchange, which occurs at proportionally higher rates in headwater streams than in larger streams and rivers [*Battin et al.*, 2008; *Wondzell*, 2011]. Because headwater streams are typically heterotrophic, they are often supersaturated with carbon dioxide (CO<sub>2</sub>) with respect to atmospheric concentrations [e.g., *Cole and Caraco*, 2001; *Richey et al.*, 2002; *Humborg et al.*, 2010; *Butman and Raymond*, 2011].

Annually, ~0.9 Pg of carbon are advected downstream by rivers and delivered to the ocean [*Cole et al.*, 2007; *Battin et al.*, 2009; *Stets and Striegl*, 2012]. However, a

large fraction of stream dissolved carbon does not reside in streams long enough to be transported to the ocean. Excess CO<sub>2</sub> has a short residence time and is quickly evaded from the stream surface [*Fiedler et al.*, 2006; *Davidson et al.*, 2010]. A recent global estimate reported as much as ~2.1 Pg C evades from stream surfaces annually [*Raymond et al.*, 2013]. The abundance of geomorphic features that influence this gaseous flux of CO<sub>2</sub> can vary between geographic regions and within watersheds [*Butman and Raymond*, 2011; *Raymond et al.*, 2012]. Rates of evasion scale with stream turbulence, the ratio of surface to cross-sectional area, and the CO<sub>2</sub> concentration gradient across the stream surface – all of which tend to be greatest in low-order streams [*Wallin et al.*, 2010; *Raymond et al.*, 2012]. Nonetheless, research on small streams has shown that many are able to sustain elevated partial pressures of carbon dioxide (pCO<sub>2</sub>) on both daily and seasonal time scales despite continual CO<sub>2</sub> loss from evasion fluxes [*Jones and Mulholland*, 1998; *Öquist et al.*, 2009; *Wallin et al.*, 2013]. Sustained stream CO<sub>2</sub> evasion requires continual CO<sub>2</sub> input. The hydrologic and ecosystem patterns and sources of that CO<sub>2</sub> input are not yet known [*Dinsmore et al.*, 2013; *Crawford et al.*, 2014].

The supply of CO<sub>2</sub> to headwater streams has been attributed primarily to inputs of CO<sub>2</sub>-rich ground- and soil-water. However, interactions between headwater streams and adjacent riparian zones through hyporheic exchange may also represent an important mechanism for CO<sub>2</sub> delivery to headwater streams [*Peter et al.*, 2014]. Headwater streams support high rates of hyporheic exchange, a process where water leaves and reenters the stream after following short (minutes to hours) or long (days) subsurface flowpaths [*Valett et al.*, 1993; *Bencala*, 2011; *Boano et al.*, 2014]. Stream water may enter the hyporheic repeatedly along a reach of headwater stream [*Wondzell*, 2011]. This

exchange delivers organic material, nutrients and oxygen to active subsurface microbial communities, generating a hotspot of microbial respiration [e.g., *Grim and Fisher*, 1984; *Findlay et al.*, 1993; *Sobczak and Findlay*, 2002]. The continual cycling of stream water through these zones may replenish stream CO<sub>2</sub> concentrations.

Research on CO<sub>2</sub> dynamics in stream ecosystems has demonstrated that the spatial distribution of CO<sub>2</sub> in streams is not uniform. In order to characterize spatial variability in stream pCO<sub>2</sub>, studies have collected measurements at various scales. Many studies have sampled within regions, along transects or at points in a stream [e.g., *Jones and Mulholland*, 1998b; *Hope et al.*, 2001; *Striegl et al.*, 2012]. Studies focusing on regional or larger spatial scales have observed general decreasing trends in stream pCO<sub>2</sub> with distance downstream [e.g., *Humborg et al.*, 2010; *Butman and Raymond*, 2011]. However, studies of stream pCO<sub>2</sub> at smaller scales with higher spatial resolution report strong spatial stream pCO<sub>2</sub> variability, with no consistent downstream trend [e.g., *Dawson et al.*, 2001; *Crawford et al.*, 2014]. The spatial resolution of stream pCO<sub>2</sub> measurements appears to be important, with fine-scale measurements revealing patterns in stream CO<sub>2</sub> not discernable from coarse sampling [*Crawford et al.*, 2013]. The degree of spatial variability across a watershed and the factors that influence this variability remain uncertain.

In response to these issues, we sought to address the following research questions:

1. How does stream pCO<sub>2</sub> vary across a headwater drainage network and what factors influence variability?
2. What are the scales and magnitudes of temporal and spatial variability of stream pCO<sub>2</sub>?

3. Does hyporheic exchange influence stream  $p\text{CO}_2$  and overall inorganic carbon export in a headwater ecosystem?

In our first paper, *Hyporheic export of inorganic carbon responsible for elevated stream  $p\text{CO}_2$  in a temperate forested catchment*, we investigated stream and hyporheic  $p\text{CO}_2$  dynamics, and modeled the contribution of dissolved inorganic carbon to a headwater stream from the hyporheic zone. In the second paper, *Drainage network variations in stream  $p\text{CO}_2$  within the Lookout Creek watershed*, we examined the magnitude and spatial scale of stream  $p\text{CO}_2$  variability across a headwater drainage network in order to identify features and processes that drive changes in stream  $\text{CO}_2$  concentrations.

## 2 Hyporheic export of inorganic carbon responsible for elevated stream pCO<sub>2</sub> in a temperate forested catchment

Nicholas T. Dosch, Roy Haggerty, Hayley A. Corson-Rikert, Steve M. Wondzell

For Submission to *Geophysical Research Letters*

### 2.1 Abstract

We measured stream and hyporheic pCO<sub>2</sub> at high temporal resolution over 11 months in a 95.9-ha forested headwater catchment in the Western Cascades of Central Oregon, USA. Stream and hyporheic pCO<sub>2</sub> showed high seasonal and event-scale variability with distinct stream and hyporheic dynamics during storm discharge events. Hyporheic exchange flow exported 37.5 kg-C yr<sup>-1</sup> per watershed hectare (confidence interval 4.0–122.3 kg-C ha<sup>-1</sup> yr<sup>-1</sup>) from the riparian zone to the stream. Summing CO<sub>2</sub> evasion and downstream advection suggests that one third of inorganic carbon export originated in the hyporheic zone. Hyporheic exchange flow had greatest influence over stream pCO<sub>2</sub> during low and high baseflow, while CO<sub>2</sub> evasion had greatest influence during storm discharge events. These findings suggest that the hyporheic zone actively participates in carbon cycling in this headwater stream and continuously replenishes stream CO<sub>2</sub>.

### 2.2 Introduction

Headwater streams may play an important role in global carbon cycling because they are a major component of terrestrial drainage networks, removing both water and carbon. First- and second-order streams make up ~75% total river length and ~30% of total stream and river surface area worldwide [*Leopold et al.*, 1964; *Downing et al.*,

2012]. Inputs of terrestrial organic matter to headwater streams from adjacent ecosystems fuel high rates of microbial respiration that exceed in-stream production, causing most headwater systems to be heterotrophic [Vannote *et al.*, 1980; Dawson *et al.*, 2001]. High metabolic rates in subsurface microbial communities are maintained by the delivery of organic matter, nutrients, and oxygen via hyporheic exchange, which occurs at proportionally higher rates in headwater streams than in larger streams and rivers [Battin *et al.*, 2008; Wondzell, 2011].

Headwater streams are typically heterotrophic and are often supersaturated with carbon dioxide (CO<sub>2</sub>), with respect to atmospheric concentrations [e.g., Cole and Caraco, 2001; Richey *et al.*, 2002; Humborg *et al.*, 2010; Butman and Raymond, 2011]. This excess CO<sub>2</sub> has a short residence time in streams and is quickly evaded from the stream surface [Fiedler *et al.*, 2006; Davidson *et al.*, 2010]. Rates of evasion scale with stream turbulence, the ratio of surface to cross-sectional area, and the CO<sub>2</sub> concentration gradient across the stream surface – all of which tend to be greatest in low order streams [Wallin *et al.*, 2010; Raymond *et al.*, 2012]. Nonetheless, research on small streams has shown that many are able to sustain elevated partial pressures of carbon dioxide (pCO<sub>2</sub>) on both daily and seasonal time scales despite continuous CO<sub>2</sub> loss from evasion fluxes [Jones and Mulholland, 1998; Öquist *et al.*, 2009; Wallin *et al.*, 2013]. Sustained stream CO<sub>2</sub> evasion requires continual CO<sub>2</sub> input. The hydrologic and biologic patterns and sources of that CO<sub>2</sub> input are not yet known [Dinsmore *et al.*, 2013; Crawford *et al.*, 2014].

The supply of CO<sub>2</sub> to headwater streams has been attributed primarily to inputs of CO<sub>2</sub>-rich ground- and soil-water. However, interactions between headwater streams and adjacent riparian zones through hyporheic exchange may also represent an important

mechanism for CO<sub>2</sub> delivery to headwater streams [Peter *et al.*, 2014]. Headwater streams support high rates of hyporheic exchange, a process where water leaves and reenters the stream following along short (minutes to hours) or long (days) subsurface flowpaths [Valett *et al.*, 1993; Bencala, 2011; Boano *et al.*, 2014]. Stream water may enter the hyporheic zone repeatedly along a reach of headwater stream [Wondzell, 2011]. This exchange delivers organic material, nutrients and oxygen to active subsurface microbial communities, generating hotspots of microbial respiration [e.g., Grim and Fisher, 1984; Findlay *et al.*, 1993; Sobczak and Findlay, 2002]. The continual cycling of stream water through these zones may replenish stream CO<sub>2</sub> concentrations.

We sought to examine the dynamics of stream and hyporheic pCO<sub>2</sub> in a headwater stream with high temporal resolution at seasonal and event scales. We investigated the relative stream-hyporheic dynamics and timescales at which hyporheic exchange flow influences the stream water pCO<sub>2</sub>. We did this by measuring and modeling hyporheic DIC and estimating the rate and magnitude of DIC contributed to a headwater stream from the hyporheic zone.

### ***2.3 Site Description and Methods***

The study was conducted in within a second-order stream reach of Watershed 1 (WS01) in the HJ Andrews Experimental Forest (HJA) (44°12'28.0''N, 122°15'30.0''W), in the Western Cascades of Central Oregon, USA. WS01 is a steep catchment draining 95.9 ha of temperate, second-growth conifer forest. The catchment is underlain by bedrock of exclusively volcanic origin, largely tuffs and breccias, and is free of carbonates [Swanson and James, 1975]. Weathering in WS01 has led to locally steep

valley walls while the valley floor is filled by colluvial deposits that rarely exceed 2 m in depth [Wondzell, 2006]. The climate consists of warm, dry summers and cool, mild winters with total annual precipitation of 2200-2600 mm, dominated by rainfall in November – March. The hydrology of surface and groundwater in WS01 has been well studied. The study reach contains a well network that has been used to observe hydraulic gradients and exchange fluxes [e.g., Wondzell, 2006; Ward *et al.*, 2013]. Results from these studies suggest that the WS01 hyporheic zone receives essentially all water from the stream, is dominated by down-valley gradients with no significant changes in lateral or downslope hydraulic gradients from low to high baseflow or during storms, and has a water uptake length of ~130m with all stream water cycled through the hyporheic over this distance [Kasahara and Wondzell, 2003; Wondzell, 2006; Voltz *et al.*, 2013; Ward *et al.*, 2013].

Stream and hyporheic pCO<sub>2</sub> were observed over 11 months from 27 August 2013 to 10 July 2014. CO<sub>2</sub> measurements were made using GMM220 series CO<sub>2</sub> probes following the method in Johnson *et al.* [2010]. Probes were sealed in gas permeable PTFE sleeves and connected to external data loggers where mole fraction pCO<sub>2</sub> (ppmv) was measured at 5-min intervals, averaged and recoded at 30-min intervals, and converted to partial pressure ( $\mu\text{atm}$ ) by multiplying by atmospheric pressure. One probe was placed in the WS01 stream attached to a styrofoam float at a depth of 6 cm and another in a riparian well located 0.4 m from the stream edge at a depth of 65 cm below the water table. The median travel time to this well was determined to be 64.2 hours from a 5-day salt tracer study [Wondzell, unpublished data]. Stream temperature and discharge were recorded at 15-min intervals at the WS01 gauge station located 75 m downstream.

Independent measurements of hyporheic temperature, and water level were measured at monthly intervals. Synoptic measurements of stream and hyporheic DIC, pH and alkalinity were performed between June and December 2013 at monthly intervals. We used a 1 m LIDAR-based digital elevation model to create a flow accumulation raster and delineate stream length.

We delineated 13 storm discharge events from the hydrograph with flows in the 90<sup>th</sup> percentile or greater of all observed discharge measurements ( $> 128.3 \text{ L s}^{-1}$ ). These events were produced by precipitation, snowmelt, or a combination thereof. We defined the onset of storms as the first hour of an increasing hydrograph following baseflow. For the purpose of quantifying response times and magnitudes, two storms with clean event hydrographs and  $\text{pCO}_2$  response were selected for this analysis. Other storms, with more complex hydrographs, displayed similar but more complex responses, and were therefore not included in this analysis.

To gauge the relative importance of hyporheic exchange flow in WS01, we modeled the difference between stream and hyporheic DIC concentrations over the study period. We chose to model DIC because it accounts for carbonate species change between the stream and hyporheic zone. This excess hyporheic DIC was modeled as a function of hyporheic travel time ( $\tau$ ; hr) and stream temperature ( $T_s$ ; °K).

$$DIC_H(\tau, T_s) = DIC_{max} \left\{ 1 - \exp \left[ -\tau \lambda_0 \exp \left( \frac{E_R}{k T_c} - \frac{E_R}{k T_s} \right) \right] \right\} \quad (1)$$

where  $DIC_H$  is the modeled 30-minute concentration of hyporheic excess DIC at a given temperature and travel time ( $\text{g-C L}^{-1}$ ).  $DIC_{max}$  ( $\text{g-C L}^{-1}$ ), a model parameter representing the maximum hyporheic excess DIC, and  $\lambda_0$  ( $\text{hr}^{-1}$ ), a reaction rate constant, are fitting

parameters set to minimize model root-mean-square error (RMSE) with observed excess DIC. Stream temperature ( $T_c$ ) was normalized to its mean of 281.75°K using the Boltzmann-Arrhenius relationship where  $E_R$  is the apparent activation energy for respiration in stream ecosystems, here selected to be 0.58 eV [Yvon-Durocher *et al.*, 2012]. The term  $k$  is the Boltzmann constant ( $8.62 \times 10^{-5}$  eV K<sup>-1</sup>), reference and stream temperature (1) are in K. The model was calibrated using results from our 7-month dataset of hyporheic and stream DIC, water temperature, and experimentally determined travel times within the WS01 well network [Wondzell, unpublished data].

Export of hyporheic DIC is a function of the concentration difference between the stream and the hyporheic zone, the residence time distribution of hyporheic water, and hyporheic discharge henceforth referred to as hyporheic exchange flow ( $Q_{hef}$ ). The total mass of DIC exported from the hyporheic zone in WS01 was calculated as follows:

$$Q_{hef} = 0.47 Q_s^{0.87} \quad (2)$$

$$M_{DIC} = \frac{L}{100 \text{ m}} \int_0^{1 \text{ yr}} Q_{hef}(t) \int_0^{125 \text{ h}} f(\tau) DIC_H(\tau, t) d\tau dt \quad (3)$$

Equation 2, applied here to calculate  $Q_{hef}$  (m<sup>3</sup> s<sup>-1</sup>) in WS01, was established from a synthesis of well network and streamflow data throughout the HJA and defines  $Q_{hef}$  as a function of  $Q_s$  per 100 meters of stream [Wondzell, 2012]. The mass exported was calculated according to (3), where  $f(\tau)$  is the hyporheic exchange flow residence time distribution function in the WS01 well network determined by Kasahara and Wondzell [2003].  $DIC_H$  in (3) is modeled hyporheic excess DIC from (1). These two terms are integrated over travel times of 0 to 125 hours, with negligible amounts of flow experiencing travel times greater than 125 h, to calculate average flux-averaged

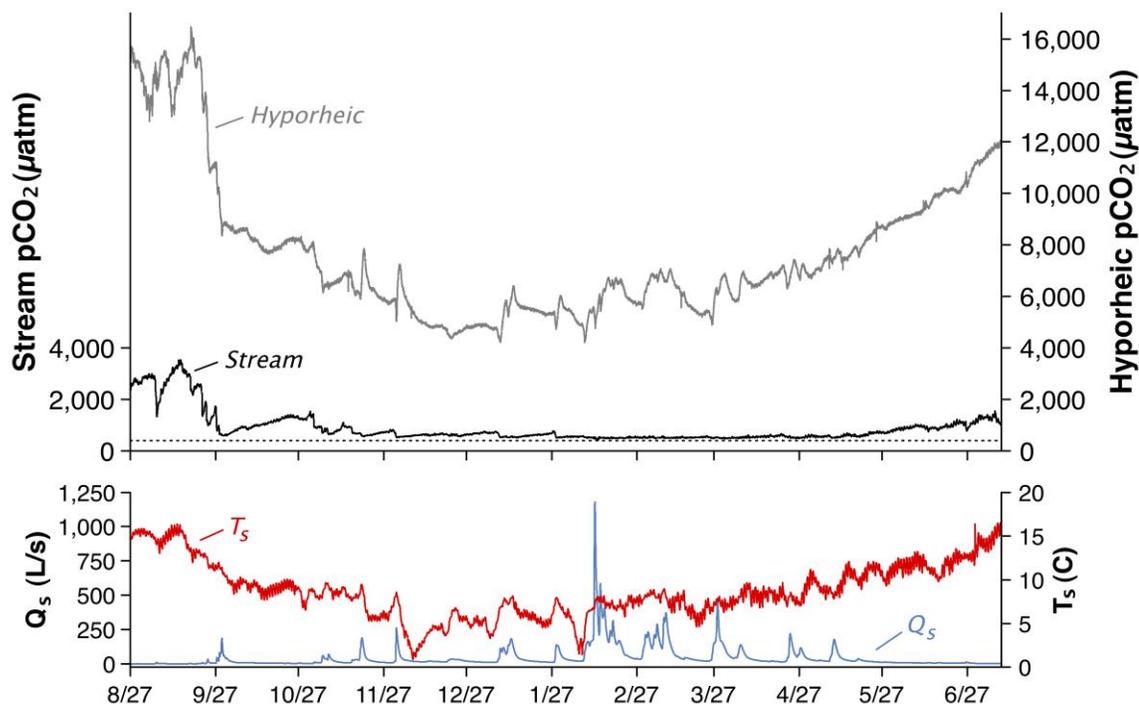
hyporheic DIC concentration. To determine WS01 hyporheic DIC export rate for each time step, the representative concentration is multiplied by  $Q_{hef}$  and is scaled to the WS01 by multiplying by the number of 100 m segments of stream in WS01, where  $L$  is the length of stream ( $L = 2361\text{m}$ ). The total annual mass of DIC exported from the hyporheic zone in WS01 is calculated by integrating hyporheic export rate over 1 year (3).

We performed a Monte Carlo simulation (10,000 iterations) to constrain the total uncertainty of our estimate. We calculate the mean value of the model output and the 90 percent confidence intervals (5 and 95 percentile of Monte Carlo simulations) based on ranges of parameter uncertainty and error distribution. Confidence intervals for nonlinear terms  $DIC_{max}$  and  $\lambda_o$  were calculated with a first-order approximation to the parameter covariance matrix, using the sensitivity of model output to parameter estimates and model RMSE [e.g., Bard, 1974; Draper and Smith, 1981; Haggerty et al., 2001]. Parameter values and 95% confidence intervals for the Monte Carlo simulations are given in Table A.1 of Appendix A.

## 2.4 Results

In the monitored locations Stream and hyporheic water were supersaturated with  $\text{CO}_2$  with respect to atmospheric concentrations at all times, with hyporheic concentrations ranging from 4 to 15 times greater than stream concentrations over the study period (Figure 1). Stream and hyporheic  $\text{pCO}_2$  displayed different seasonal patterns between summer and winter. Changeover from the summer baseflow period to winter higher flows occurred after an early October storm, delineating a shift in the hydraulic

regime. Stream hyporheic pCO<sub>2</sub> were greater during summer months (Aug–Sep; Jun–Jul) and lower during winter months (Oct–May) (Figure 2.1).



**Figure 2.1** – Concentration of hyporheic and stream CO<sub>2</sub> (top), stream temperature and stream discharge (bottom) over the study period from late August, 2013 to July, 2014. The dotted line in the top portion shows atmospheric pCO<sub>2</sub>.

Maximum pCO<sub>2</sub> occurred at the end of the summer baseflow period in late September 2013 with pCO<sub>2</sub> of 3,550 µatm in the stream and 16,480 µatm in the hyporheic zone. Decreases in pCO<sub>2</sub> in both locations occurred into the fall, with the largest drop from September to October when monthly averages of stream pCO<sub>2</sub> decreased 55% and hyporheic pCO<sub>2</sub> decreased 41%. Sustained lower pCO<sub>2</sub> occurred during winter months, with average stream pCO<sub>2</sub> of 665 µatm and average hyporheic pCO<sub>2</sub> of 6,444 µatm (Table 2.1). Beginning in late May, stream and hyporheic pCO<sub>2</sub> steadily recovered from low winter concentrations. This recovery coincided with

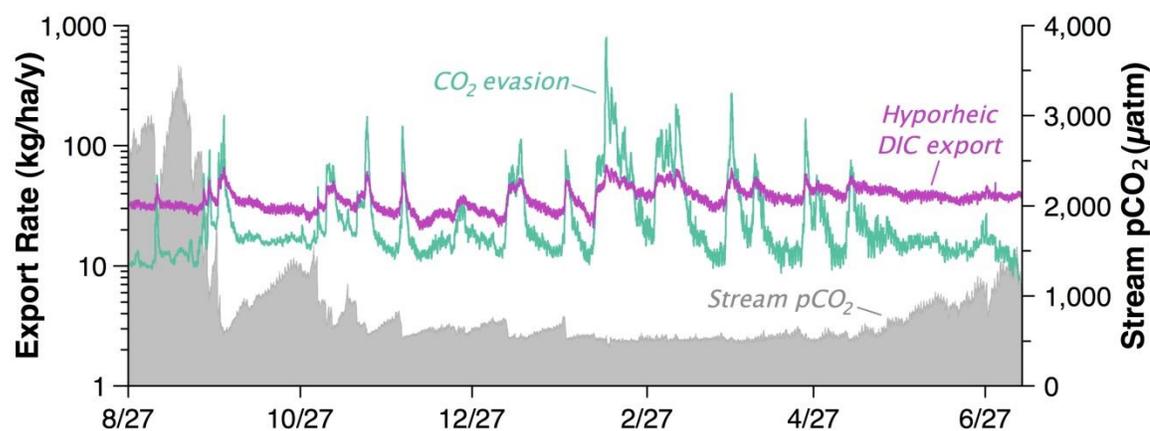
increasing stream temperature and decreasing discharge, and continued through the end of the study period in July, with stream  $p\text{CO}_2$  increasing 89% and hyporheic  $p\text{CO}_2$  increasing 40%.

**Table 2.1** - Summary of measured properties and Pearson Correlation Coefficients

Property		Annual	Summer	Winter
Mean Stream $p\text{CO}_2$ ( $\mu\text{atm}$ )		889	1634	665
Mean Hyporheic $p\text{CO}_2$ ( $\mu\text{atm}$ )		7715	11896	6444
Mean Discharge (L/s)		44.8	7.0	56.3
Mean Stream Temperature ( $^{\circ}\text{C}$ )		8.7	13.2	7.0
Correlation Coefficient ( $r$ ) $p\text{CO}_2$ and Discharge	Stream	-0.29	-0.34	-0.36
	Hyporheic	-0.23	-0.35	-0.12
Correlation Coefficient ( $r$ ) $p\text{CO}_2$ and Stream Temp.	Stream	0.73	0.73	0.26
	Hyporheic	0.89	0.72	0.80
Correlation Coefficient ( $r$ ) between Stream and Hyporheic $p\text{CO}_2$		0.89	0.90	0.47

Hyporheic DIC export is relatively constant through the year compared with  $p\text{CO}_2$ , temperature and discharge (Figure 2.2). Although excess hyporheic DIC concentrations exhibit seasonal change, the overall export rate is moderated and largely controlled by  $Q_{hef}$ . Mean  $Q_{hef}$  was  $2.4 \text{ L s}^{-1}$ , ranging from  $1.3 - 4.8 \text{ L s}^{-1}$ , experiencing fluctuations proportionally smaller than those in  $Q_s$ . The hyporheic zone exports  $37.5 \text{ kg-C yr}^{-1}$  per watershed hectare ( $\text{kg-C ha}^{-1} \text{ yr}^{-1}$ ), with confidence interval (CI) of  $4.0 - 122.3 \text{ kg-C ha}^{-1} \text{ yr}^{-1}$ . This represents 35% (CI = 3.6-100%) of the inorganic carbon evaded as

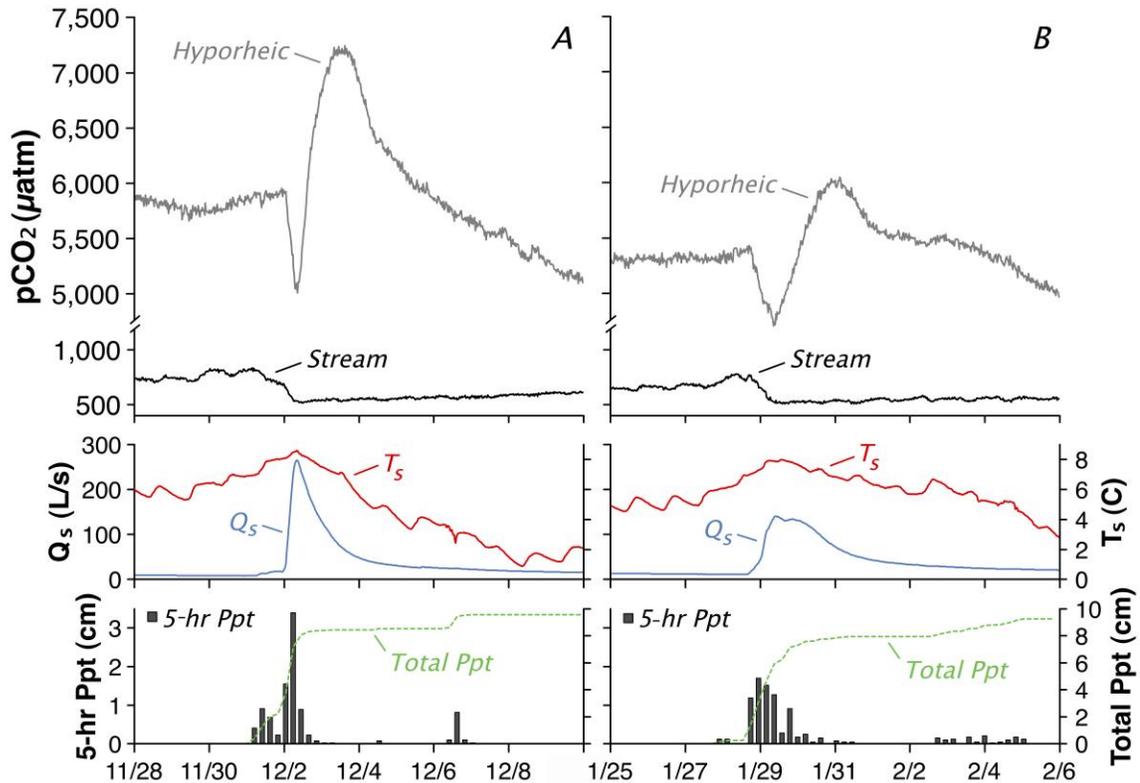
CO<sub>2</sub> or exported downstream as DIC by WS01 [based partly on data from *Argerich et al.*, manuscript in preparation, 2014].



**Figure 2.2** - Hyporheic CO<sub>2</sub> export rate, CO<sub>2</sub> evasion rate from Argerich et al., [manuscript in preparation, 2014] and stream pCO<sub>2</sub> over the study period.

Stream and hyporheic pCO<sub>2</sub> concentrations show a distinct response to storm discharge events (Figure 2.3). Each location responds rapidly, though distinctly, to changes in discharge. Stream pCO<sub>2</sub> exhibits a negative discharge-concentration relationship, with stream concentrations decreasing sharply, with no lag following storm onset, to near atmospheric concentrations (average = 520 µatm) through the peak of the storm hydrograph. Recovery of stream pCO<sub>2</sub> changes from fall to winter to spring. In the late summer early fall, stream pCO<sub>2</sub> recovers quickly following discharge events, with an average recovery of 41.8 µatm day<sup>-1</sup> (Figure 2.1). In the late fall and early winter, the rate of stream pCO<sub>2</sub> recovery decreases to 9.4 µatm day<sup>-1</sup>. No identifiable recovery occurred following discharge events from February to May 2014. Hyporheic pCO<sub>2</sub> also responds strongly to discharge but the response is distinct from the stream. Hyporheic pCO<sub>2</sub> initially drops then increases sharply through the peak and falling limb of the storm

hydrograph. Hyporheic response times lag stream pCO<sub>2</sub> response, but only just, with the initial response lagging storm onset by an average of 2.5 hours.



**Figure 2.3** - Discharge event response: hyporheic and stream pCO<sub>2</sub>, stream discharge, stream temperature, 5-hour precipitation (ppt) and total precipitation during (A) late November 2013 storm and (B) late January 2014 storms.

## 2.5 Discussion

Both stream and hyporheic pCO<sub>2</sub> follow seasonal patterns that reflect changes in local discharge and temperature. Changeover from summer baseflow to winter highflow has a strong influence on stream and hyporheic pCO<sub>2</sub>. At seasonal timescales, both locations exhibit slight negative concentration-discharge correlation (Table 2.1), with lower concentrations occurring in winter when average flows were higher and storm events were frequent. Variations in stream flow affect stream-atmosphere gas transfer

rate and hydraulic flow paths through the catchment, thereby changing patterns of CO<sub>2</sub> delivery and export within the system [Jones and Mulholland, 1998]. Seasonal changes in temperature also appear to be important, with stream temperatures explaining 53 percent of the variance in stream pCO<sub>2</sub> and 79 percent of the variance in hyporheic pCO<sub>2</sub>.

Observed seasonal changes agree with the findings of Peter *et al.* [2014], where strong seasonal variability in stream and hyporheic pCO<sub>2</sub> were observed, and with those of Dinsmore *et al.* [2013], where seasonal variations were observed in an intermittent headwater stream in the Fraser Lowland of British Columbia, Canada. It is worth noting that despite concentration and seasonal differences, stream and hyporheic pCO<sub>2</sub> have a strong positive correlation ( $r^2 = 0.78$ ) over the study period, which suggests interdependence between stream and hyporheic pCO<sub>2</sub>. This relationship, however, is stronger in summer than winter, indicating a seasonal change in stream-hyporheic exchange dynamics.

Comparison of modeled hyporheic DIC export rate and CO<sub>2</sub> evasion rate from Argerich *et al.* [manuscript in preparation, 2014] reveals a strongly coupled relationship between processes, with an interplay that drives stream pCO<sub>2</sub> (Figure 2.2). Stream pCO<sub>2</sub> tends to increase when hyporheic export rate is greater than the rate of CO<sub>2</sub> evasion while stream pCO<sub>2</sub> tends to decrease when the hyporheic export rate is less than the rate of CO<sub>2</sub> evasion. It appears that hyporheic exchange and CO<sub>2</sub> evasion alternate periods of control and, with changes in stream hydraulics, collectively drive stream pCO<sub>2</sub> in this system. Hyporheic exchange flow is proportionally less influential during high flows because the ratio of Q<sub>HEF</sub> to Q<sub>S</sub> decreases [Findlay, 1995] and rates of CO<sub>2</sub> efflux from the stream surface increase. Our model suggests that hyporheic exchange flow is most important in

driving stream pCO<sub>2</sub> during baseflow while CO<sub>2</sub> efflux is most important in driving stream pCO<sub>2</sub> during storm events.

Monte Carlo simulation results indicate considerable uncertainty in our estimates of hyporheic DIC export and the percent of total stream DIC export originating in the hyporheic zone. In the Monte Carlo simulations, we accounted for uncertainty in the derived model parameters and the modeled relationship between  $Q_{hef}$  and  $Q_s$  (Appendix A). Although we limited our error simulation to these terms, additional error may also be introduced by other components of the model analysis. We expect that temporal variations in hyporheic travel times within the watershed are not a large source of error to the model, as riparian hydraulic gradients are stable through the year and during storm events [Kasahara and Wondzell, 2003; Ward *et al.*, 2013; Voltz *et al.*, 2013]. Spatial variation in hyporheic travel times may be a larger source of error. For this analysis, we assume that the residence time distribution observed in the well network at the base of the watershed is representative of riparian exchange along the full length of the Watershed 1 channel. However, the residence time distribution may vary longitudinally, due to changes in the morphology of the stream channel. We currently have no way to estimate this variation. Further work is needed to better constrain our assumptions and the values of model parameters.

Ultimately, although error bounds on our estimates are large, we are confident that the mean values generated by the Monte Carlo simulations provide a reasonable estimate of hyporheic DIC export in the Watershed 1 system. Our result of 37.5 kg-C ha<sup>-1</sup> yr<sup>-1</sup> agrees well with an estimate of lateral DIC export of 32 (±1) kg-C ha<sup>-1</sup> yr<sup>-1</sup> in a boreal headwater stream in Sweden [Öquist *et al.*, 2009].

Storm discharge events strongly influenced  $p\text{CO}_2$  and rates of inorganic carbon export within this system. During storm discharge events, stream and hyporheic  $p\text{CO}_2$  were dynamic and exhibited very different responses to changes in flow. We hypothesize that the sharp drop in stream  $p\text{CO}_2$  following the onset of storm events is due to either increased evasion under turbulent flow conditions or a dilution of stream  $\text{CO}_2$  concentrations by storm runoff [Crawford et al., 2013]. The multistage hyporheic response, however, is more difficult to interpret. It has been shown in this and other streams that the rising limb of discharge events can have highly elevated DOC concentrations that recede through the peak of the storm [Hood et al., 2006; Raymond and Saiers, 2010; Corson-Rikert, unpublished data, 2014]. However, it is unlikely that the spike increase in hyporheic  $p\text{CO}_2$  following the initial drop is the result of lagged respiration from a pulse of DOC-rich stream water to the hyporheic, as the response peak for storm A and B, of 36 and 30 hours, is faster than the 62-hour hyporheic travel time to this well.

We suggest that the  $p\text{CO}_2$  response in the hyporeic zone during storm events is triggered by dissolved organic carbon (DOC) transported to the hyporheic zone by vertical infiltration of storm precipitation. The initial drop in hyporheic  $p\text{CO}_2$  following the onset the storm event is likely due to dilution from vertically infiltrating water that is low in  $\text{CO}_2$ . Although it is low in  $\text{CO}_2$ , we suggest that the infiltrating water transports DOC leached from terrestrial organic material to the hyporeic zone. The subsequent respiration of this DOC may account for the production of and observed increase in hyporeic zone  $p\text{CO}_2$  following the peak of the storm hydrograph and during the first portion of the receding limb. As stream discharge continued to fall, observed hyporeic

pCO<sub>2</sub> concentrations peaked and then decreased and eventually fell below pre-storm concentrations. It is possible that the CO<sub>2</sub> production fueled by the terrestrial DOC is short-lived, and that hyporeic pCO<sub>2</sub> begins to decrease as the majority of this DOC is consumed and precipitation ceases. However, during this period stream pCO<sub>2</sub> was also below pre-storm concentrations. We expect that laterally infiltrating stream water also contributes to the decline in hyporeic pCO<sub>2</sub>.

## **2.6 Conclusions**

The processes that drive the temporal dynamics of pCO<sub>2</sub> and support sustained supersaturation are important for scaling CO<sub>2</sub> fluxes at local and larger scales. Our results suggest that hyporeic exchange flow may be an important control on stream pCO<sub>2</sub>, and on watershed inorganic carbon export. The hyporeic zone contributes 37.5 kg-C ha<sup>-1</sup> yr<sup>-1</sup> (confidence interval 4.0–122.3 kg-C ha<sup>-1</sup> yr<sup>-1</sup>) to the stream, which is equal to approximately one third of the inorganic carbon evaded or exported downstream by WS01 each year. Hyporeic exchange flow serves to actively replenish stream pCO<sub>2</sub> and is most influential during low and high baseflow conditions.

## **2.7 Acknowledgements**

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publically available through the HJ Andrews data catalog

<http://andrewsforest.oregonstate.edu/lter/data.cfm?frameURL=173>

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### **3 Drainage network variations in stream pCO<sub>2</sub> within the Lookout Creek watershed**

#### **3.1 Abstract**

We measured stream carbon dioxide (CO<sub>2</sub>) at monthly intervals from July 2013 through July 2014 across a forested headwater drainage network in the Western Cascades of Oregon. At a large majority of observations, stream CO<sub>2</sub> partial pressure (pCO<sub>2</sub>) was supersaturated with respect to atmospheric concentrations. Stream pCO<sub>2</sub> ranged from atmospheric (~400 μatm) to 20 times atmospheric concentrations (8150 μatm) and exhibited strong spatial and temporal variability. At the watershed scale, pCO<sub>2</sub> decreased with distance downstream. At the reach scale, we did not detect clear patterns in the downstream direction. However, individual transects displayed persistent profile shape, with consistent high and low pCO<sub>2</sub> locations. We found negative relationships between stream pCO<sub>2</sub> and stream discharge, mean velocity and the carbon dioxide gas transfer velocity ( $k_{CO_2}$ ). Stream pCO<sub>2</sub> exhibited changes over short distances, with large changes in pCO<sub>2</sub> over 50 m. Longitudinal variability indicates spatial nonuniformity of in-stream controls on pCO<sub>2</sub> at this scale. Stream pCO<sub>2</sub> shows generally higher concentrations during the summer and lower concentrations in the winter, with considerable intrannual variability. The distribution of pCO<sub>2</sub> over the study period was significantly different in small and large streams within the drainage network.

#### **3.2 Introduction**

Recent work has established that streams and rivers play a disproportionately large role in the global carbon cycle relative to their size on the on the landscape [e.g., *Cole et al., 1994; Richey et al., 2002; Raymond et al., 2008; Tranvik et al., 2009*].

Despite making up only ~1% of terrestrial surface area, carbon fluxes per unit area in streams and rivers often surpass that of the landscape that makes up their watershed [Cole *et al.*, 2007]. Streams receive, transport, process, and emit large quantities of terrestrially derived carbon [Aufdenkampe *et al.*, 2011; Bianchi *et al.*, 2013]. Annually, ~0.9 Pg of carbon are exported by rivers downstream and delivered to the ocean [Cole *et al.*, 2007; Battin *et al.*, 2009; Stets and Striegl, 2012]. However, a large fraction of the carbon that enters streams and rivers does not reside in streams long enough to be transported to the ocean and is emitted in the form of carbon dioxide (CO<sub>2</sub>) from the stream surface. A recent global estimate reported as much as ~2.1 Pg C evades from stream surfaces annually [Raymond *et al.*, 2013].

Streams are typically supersaturated with CO<sub>2</sub>, with partial pressures of carbon dioxide (pCO<sub>2</sub>) that can far surpass atmospheric concentrations [e.g., Jones *et al.*, 2003; Butman and Raymond, 2011]. The pCO<sub>2</sub> concentration gradient across the stream-atmosphere interface can lead to CO<sub>2</sub> outgassing. Factors that influence the gaseous flux of CO<sub>2</sub> can vary between geographic regions and within watersheds [Raymond *et al.*, 2012]. Small headwater streams have been shown to have particularly high concentrations of pCO<sub>2</sub>, and lose CO<sub>2</sub> to the atmosphere at higher rates than larger systems – a result that makes headwater streams quantitatively important in the global carbon cycle [Jones and Mulholland, 1989a; Johnson *et al.*, 2008; Butman and Raymond, 2011].

Studies have characterized spatial variability in stream pCO<sub>2</sub> at various scales. Many studies have sampled within regions, along transects or at points in a stream [e.g., Jones and Mulholland, 1998b; Hope *et al.*, 2001; Striegl *et al.*, 2012]. Studies at regional

or larger spatial scales tend to observe general decreasing trends in stream pCO<sub>2</sub> with distance downstream [e.g., *Humborg et al.*, 2010; *Butman and Raymond*, 2011]. However, studies of stream pCO<sub>2</sub> at smaller scales with higher spatial resolution, report strong spatial stream pCO<sub>2</sub> variability, with no consistent downstream trend [e.g., *Dawson et al.*, 2001; *Crawford et al.*, 2014]. The spatial resolution of stream pCO<sub>2</sub> measurements appears to be important, with fine scale measurements revealing patterns in stream CO<sub>2</sub> not discernable from coarse sampling [*Crawford et al.*, 2013]. The degree of spatial variability across a watershed and the factors that influence this variability remain uncertain.

In this study, we assessed the magnitude and spatial scale of stream pCO<sub>2</sub> variability in a headwater catchment in order to identify features and processes that drive changes in stream CO<sub>2</sub> concentrations. To do so, we calculated pCO<sub>2</sub> at 38 sites at monthly intervals over one year. We selected the sites to capture a range of spatial resolutions and to represent the physical variability of the catchment.

### **3.3 Site Description**

This study was conducted within HJ Andrews Experimental Forest (HJA) (44°14'N, 122°11'W), in the Western Cascades of Central Oregon, USA. The boundary of HJA is delineated by the Lookout Creek watershed, a 64 km<sup>2</sup> drainage basin ranging in elevation from 410 m to 1630 m. Lookout Creek drains a network of forested headwater streams and is a tributary of Blue River and the McKenzie River. The HJA is underlain by bedrock of volcanic origin, Oligocene to Lower Miocene in age, and is free of carbonates. Low elevation areas are largely composed of tuffs, breccias and stream

deposited alluvium while higher areas are composed basalt and andesite flows of Miocene age and of younger, High Cascade rock [Swanson and James, 1975]. Weathering and glaciation within the Lookout Creek drainage basin has led to locally steep topography and well-defined subbasins within the Lookout Creek drainage network [Swanson and James, 1975]. Soils across HJA are mainly sandy or gravelly loam inceptisols, developed from parent bedrock. The climate of the Western Cascades consists of warm, dry summers and cool, wet winters. Snow and rainfall typically begin in November and continue through June, with a transient snowline mid-elevation of HJA. Mean annual precipitation is 2200-2600 mm.

Forests of the HJA are dominated by Douglas-fir (*Pseudotsuga menziesii*), western hemlock (*Tsuga heterophylla*), and red cedar (*Thuja plicata*) with pacific yew (*Taxus brevifolia*) common in the understory [Rothacher et al., 1967]. When the HJA was established, much of the area was covered by old-growth (> 400 years), and mature (100-150 years) forest. Beginning in the early 1950s portions of HJA forest were manipulated (clear cutting, burning, replanting treatments, and thinning) to establish a series of experimental watersheds within the HJA. These experimental watersheds have been subject to long-term studies of basin hydrology, ecology and biogeochemistry, an initiative to better understand and quantify the influence of forest management history on ecosystem and hydrologic processes [Dyrness, 1969].

38 sample sites at were established across the Lookout Creek drainage network were at a variety of sites that captured the diverse natural and managed landscape of the HJA. Sample sites were chosen to ensure they included streams from a range of basin sizes, elevations, discharge regimes, subclimates and forest management histories.

Multiple sample sites were placed along Lookout Creek and its major tributaries and were sampled as longitudinal transects from the highest upstream point to the lowest downstream point accessible by truck. Samples were collected at all gauge stations and from all experimental watersheds. Major confluences were included in sampling design, with sample sites placed above and below these locations.

These 38 sampling locations were located along 13 streams, including Lookout Creek (LO) and twelve of its major tributaries within HJA. Information regarding stream and associated watershed properties is detailed in Table 3.1. The major tributaries include: Watershed 1 (W1), Watershed 2 (W2), Watershed 3 (W3), Watershed 6 (W6), Watershed 7 (W7), Watershed 8 (W8), Watershed 9 (W9), Watershed 10 (W10), MacRae Creek (MR), Mack Creek (MK), Cold Creek (CC) and an unnamed stream referred to here as No Name Creek (NN). Each sample site was assigned a four or five character title for identification. Each title is composed of two stream identification characters (with the exception of Watershed 10, which was assigned 3 characters), in parentheses above, followed by two transect order identification numbers. Sites that were the highest elevation sites on a given transect, i.e., the closest point to the stream origin, were given the transect order identification numbers of “01”. The next downstream sampled site, i.e., the site second closest to the stream origin, was given the numbers “02”, and so on to the lowest sample site along a given stream transect. For example, the highest elevation sample site in Watershed 1 was titled W101 and the third downstream site along the Lookout Creek transect was titled LO03. Several streams were only accessible in one location and were not sampled as transects. These sites were simply assigned the number “01”. For example, Watershed 6 is not part of a sampling transect, thus, the only site was

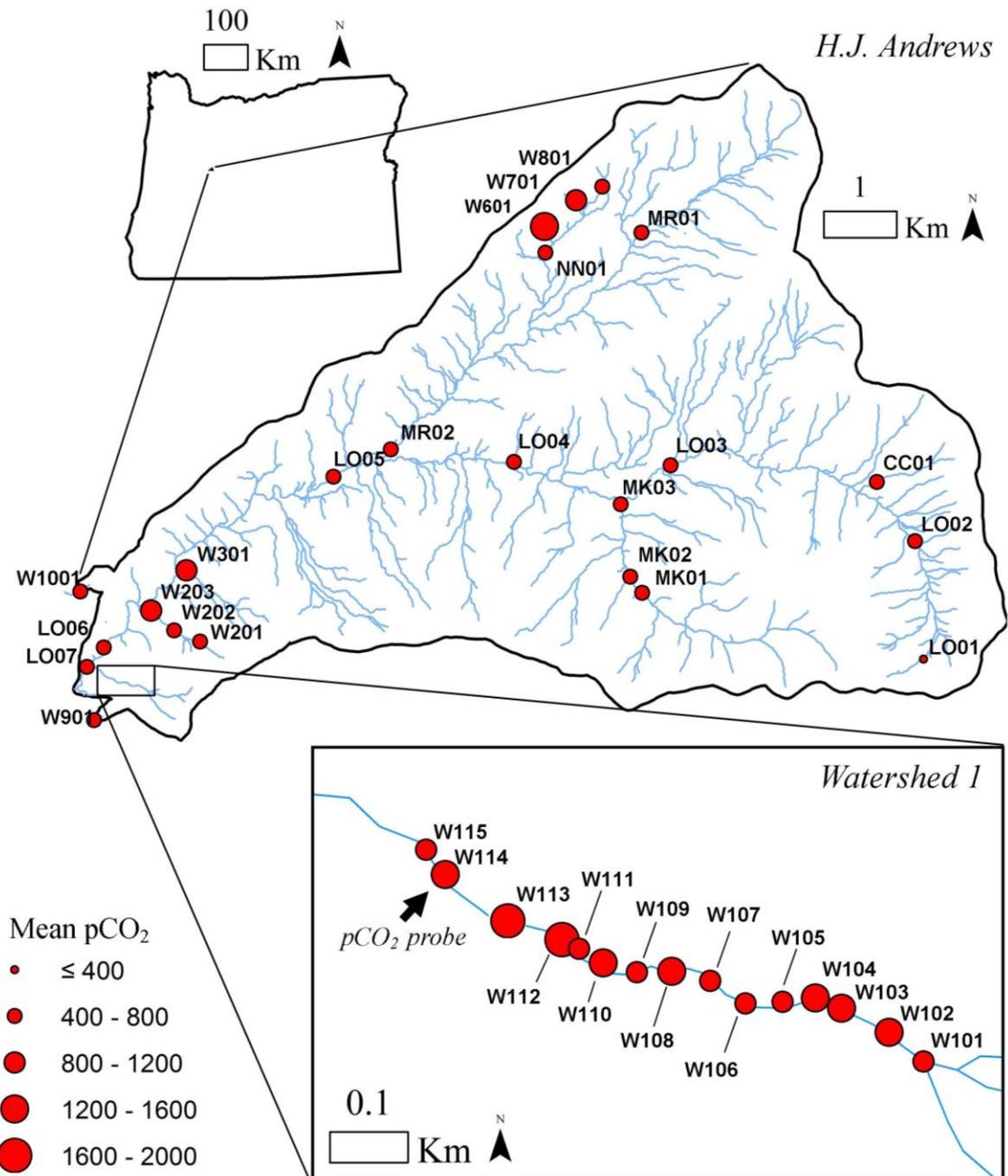
titled W601. A list of sample collection sites and site specific physical properties are outlined in (Table 3.2). The location of HJA and the sample sites within the LO drainage network are illustrated in (Figure 3.1).

The longitudinal distance between sample sites was also considered in sample design. To address this variable, a dense sampling array was set up along the W1 transect, with samples collected every 50m downstream along the entirety of the second order portion of W1 to its confluence with LO. In contrast, average longitudinal spacing between sampling sites along the LO transect was 2.9 km. The density of longitudinal sampling is of primary interest in this study, as the scales at which pCO<sub>2</sub> variability occurs within streams remains poorly quantified [*Hope et al.*, 2004; *Wallin et al.*, 2010; *Striegl et al.*, 2012]. The magnitude of pCO<sub>2</sub> variability at the 50m scale implemented in W1 may be instructive in interpreting larger scale variability observed across the HJA.

**Table 3.1** – Study watersheds within HJA with physical information and management history

<b>Stream</b>	<b>Basin Area (km<sup>2</sup>)</b>	<b>Elevation (m)</b>	<b>Basin Slope %</b>	<b>Aspect (Degrees)</b>	<b>Soil</b>	<b>Forest Management History</b>
Watershed 1	0.96	450-1027	59.35	286	Gravel Clay Loam	100% clearcut, 1962-66; prescribed burned in 1967
Watershed 2	0.20	476-1079	53.19	318	Gravel Loam	Control; Old-Growth and Mature
Watershed 3	0.97	475-1080	52.39	313	Gravel Loam	1.5 km (6%) roads, 1959; 25% clearcut in 3 patches, 1963
Watershed 6	0.12	893-1029	25.19	165	Gravel Clay Loam	100% clearcut in 1974
Watershed 7	0.17	931-1102	33.68	158	Gravelly Loam	50% selective canopy removal, 1974; remaining canopy removed 1984; 12% thin 2001
Watershed 8	0.20	968-1182	25.78	165	Gravel Sandy Loam	control; old-growth and mature
Watershed 9	0.09	438-731	58.36	247	Gravel Clay Loam	control; old-growth and mature
Watershed 10	0.10	679-471	58.12	250	Gravel Loam	100% clearcut, 1975
Lookout Creek	63.35	434-1627	40.28	267	Gravel Sandy Loam	mature and old-growth, 25% plantations <50 yrs
Mack Creek	8.64	671-1626	48.41	306	Gravel Sandy Loam	control; old-growth and mature
McRae Creek	15.46	555-1570	42.55	242	Gravel Sandy Loam	patch cut
Cold Creek	0.64	980-1495	46.21	208	Gravel Sandy Loam	patch cut
No Name	1.23	809-1182	25.20	120	Gravel Sandy Loam	patch cut

\*Basin size and basin slope reported here may be different than reported by H.J. Andrews. These values are based off this study's analysis of geospatial data



**Figure 3.1** - (Top) Location of H.J. Andrews Experimental Forest within Oregon. (Middle) H.J. Andrews and (Bottom) Watershed 1 with sample site locations detailed ( $n = 38$ ). Size of location dots proportional to mean  $p\text{CO}_2$  (given in Table 3.3). The  $p\text{CO}_2$  probes from Chapter 2 are located at W114 near the base of the W1 transect (labeled).

**Table 3.2** – Sample site locations within HJA, and associated physical properties

Site ID	Watershed	Latitude	Longitude	Elevation	Drainage Area	Distance Downstream	Slope
		N (decimal)	W (decimal)	m	km <sup>2</sup>	m	%
W101	Watershed 1	44.20451	122.24989	563	0.62	555	24.4
W102	Watershed 1	44.20504	122.25018	554	0.63	605	19.9
W103	Watershed 1	44.2052	122.25105	544	0.68	655	11.7
W104	Watershed 1	44.20507	122.25131	537	0.72	705	13.1
W105	Watershed 1	44.2053	122.25191	528	0.74	755	20.6
W106	Watershed 1	44.20534	122.25253	519	0.74	805	19.5
W107	Watershed 1	44.20565	122.25302	510	0.78	855	20.6
W108	Watershed 1	44.20575	122.25368	503	0.83	905	11.8
W109	Watershed 1	44.20574	122.25423	496	0.85	955	14.6
W110	Watershed 1	44.20581	122.25482	486	0.86	1005	18.0
W111	Watershed 1	44.20609	122.25514	481	0.88	1055	10.6
W112	Watershed 1	44.20612	122.25539	477	0.89	1105	18.8
W113	Watershed 1	44.20636	122.25632	466	0.91	1155	17.0
W114	Watershed 1	44.20704	122.25713	452	0.94	1245	9.2
W115	Watershed 1	44.20704	122.25768	444	0.95	1295	24.9
W201	Watershed 2	44.20164	122.24097	664	0.20	455	37.4
W202	Watershed 2	44.21201	122.24522	543	0.61	903	25.6
W203	Watershed 2	44.21427	122.2493	476	0.74	1488	17.9
W301	Watershed 3	44.21953	122.24294	475	0.97	1552	19.5
W601	Watershed 6	44.26149	122.18079	878	0.12	211	26.2
W701	Watershed 7	44.26469	122.17537	919	0.17	184	26.3
W801	Watershed 8	44.26632	122.17097	962	0.20	412	20.1
W901	Watershed 9	44.20147	122.25894	423	0.09	201	31.5
W1001	Watershed 10	44.21702	122.26109	459	0.10	255	19.7
LO01	Lookout Creek	44.20756	122.11718	1224	0.05	692	29.4
LO02	Lookout Creek	44.2222	122.11781	1012	3.03	2877	11.1
LO03	Lookout Creek	44.23187	122.15955	723	15.58	7422	8.4
LO04	Lookout Creek	44.23258	122.18631	607	30.89	9626	4.4
LO05	Lookout Creek	44.23089	122.21742	532	51.54	12523	11.8
LO06	Lookout Creek	44.21002	122.25725	422	62.10	17695	6.6
LO07	Lookout Creek	44.20785	122.25995	414	63.35	18022	4.2
MK01	Mack Creek	44.21619	122.16468	798	5.12	3653	13.5
MK02	Mack Creek	44.21768	122.16771	770	5.34	4078	14.4
MK03	Mack Creek	44.22713	122.16817	677	8.64	5167	9.8
MR01	McRae Creek	44.26073	122.1644	883	3.86	3261	13.8
MR02	McRae Creek	44.23409	122.20743	554	15.46	8676	5.5
CC01	Cold Creek	44.2947	122.12386	980	0.64	1313	20.8
NN01	No Name	44.25823	122.18061	810	1.23	1770	13.0

### **3.4 Methods**

#### *3.4.1 Field Methods*

Synoptic field measurements and water samples were collected 12 times over a 13-month study period from July 2013 to July 2014. Sampling occurred at approximately monthly intervals; no samples were collected during April 2014. Low elevation sites were sampled during all 12 sample periods. High elevation sites were sometimes inaccessible due to snowfall and were therefore not sampled during some winter months. Streams that were designed as longitudinal transects were sampled from high elevation to low. Sites were sampled at approximately the same time of day over the study period.

Water samples for the analysis of stream alkalinity were collected in 250 mL HDPE (high-density polyethylene) bottles (Nalgene, Inc., United States). Bottles were acid washed according to the Oregon State University and U.S. Forest Service Cooperative Chemical Analytical Laboratory (CCAL) quality assurance plan [CCAL, 2013]. Prior to collection, bottles were rinsed three times with stream water by filling the sample container 1/4 full, then shaking vigorously with the lid loosely tightened to the bottle, making sure to rinse the inside walls, threads, and cap of the bottle. Samples were collected from the thalweg in locations deep enough to fully submerge the bottle while the sample collector stood downstream of the sampling location. In larger streams, samples were taken as close to the thalweg as possible and always collected from locations with strong downstream transport, thereby avoiding stagnant pools or lateral cavities. Sample bottle caps were secured underwater to minimize air collected with the sample and to minimize the amount of sediment or other particulates collected with the

water sample. Nitrile gloves were worn during sampling to minimize sample contamination. After collection, samples were placed on ice in a dark container until laboratory processing.

Stream pH and temperature were measured at sample sites using a YSI Model 63 handheld pH, conductivity, salinity and temperature system (YSI, Inc., United States). The meter was calibrated for pH at the beginning of each field day with a two point calibration at pH 7.0 and 10.0, bracketing the range of expected field pH values. When making field measurements, the probe was placed in the thalweg of the stream, slightly downstream from the location of water sampling. The meter was given a minimum of 10 minutes to stabilize prior to reading. The probe was positioned so that the pH electrode was suspended in the water column and not resting in mud or sediment.

Direct stream pCO<sub>2</sub> measurements were collected in July 2014 in W1 using a handheld Vaisala Carbocap CO<sub>2</sub> meter (Vaisala, Inc., Finland), calibrated within  $\pm 1.5\%$  of the reading. The probe was modified following the methods in *Johnson et al.* [2010] and was implemented in the field following *Crawford et al.* [2013]. The probe was positioned horizontally just below the water surface and was allowed to equilibrate for a minimum of 10 minutes. Depth from the water surface to the center of the probe was recorded with a measuring tape for water pressure correction. The probe was placed in a protective PVC sleeve during measurements, and while in transport, to protect the PTFE (polytetrafluoroethylene) fabric from scratches or scuffs.

### 3.4.2 *Laboratory Methods*

Analytical lab work was conducted at the Institute for Water and Watersheds Collaboratory at Oregon State University. Carbonate alkalinity was determined using a Radiometer TIM840 AutoTitrator (Radiometer Analytical, SAS, France) according to CCAL procedure 10C.0 by titrating 100 mL of unfiltered sample to a pH of 4.5 with 0.02 N H<sub>2</sub>SO<sub>4</sub> [CCAL, 2013]. Detection limits associated with this method are 0.2 mg CaCO<sub>3</sub> L<sup>-1</sup>. Samples were processed within 7 days of field collection.

### 3.4.3 *pCO<sub>2</sub> Calculation and Data Processing*

Stream pCO<sub>2</sub> was calculated with the CO2SYS program [e.g., *Barnes and Raymond, 2009; Butman and Raymond, 2011; van Heuven et al., 2011*] using field measurements of temperature and pH, and lab measurements of alkalinity. This calculation is based on equilibrium concentrations of the carbonate species in water at a given pressure, temperature, and pH. The dissociation constants of the carbonate species used for this calculation were those from *Millero [1979]* for freshwater systems.

This calculation of pCO<sub>2</sub> is sensitive to uncertainties in field and lab data, with particular sensitivity to pH [*Lauerwald et al., 2013*]. To minimize the effect of individual values overall outcomes while still recognizing the importance of all measurements, we chose to compute study site mean annual pCO<sub>2</sub> for spatial analyses. Measurement averages over the study period provide greater confidence in spatial patterns, minimizing the effect of sample errors that potentially hinder spot measurements [*Roberts et al., 2007*]. Although individual high and low values of pCO<sub>2</sub> are quantitatively important to

overall basin fluxes, mean pCO<sub>2</sub> has been found to be the best estimator for spatial coverage and is used for our analysis of spatial patterns [Striegl *et al.*, 2012].

For inter-site comparison, sites that were missed more than twice have been excluded from the study due to the potential for seasonal bias in mean pCO<sub>2</sub>. The highest elevation sampling location in the lookout transect (LO01) was unreachable between November 2013 and May 2014 due to snow. This site has been excluded from the spatial analysis.

#### 3.4.4 *Calculation of Catchment Properties*

We determined catchment properties and spatial variables within the HJA using a 1 m LIDAR-based digital elevation model, a soils map, a geology map, and a stream network model. This and other spatial data were made available through the H.J. Andrews Long Term Ecological Research Station data catalog (<http://andrewsforest.oregonstate.edu/lter/data.cfm?frameURL=269>). Spatial data analyses were performed in ArcGIS (ESRI, United States). Sample sites were located in the field using a handheld GPS (Garmin, United States). Downstream distance was estimated by summing the length of all stream segments between the sampling location and stream origin point. Drainage area was computed for individual sites using the DEM and a flow accumulation model. Stream slope for each sample site was computed by taking the average slope over the local stream segment, where average stream segment length was 192 m ( $n = 1079$ ).

### 3.4.5 Calculation of Physical Variables

Gauge stations within the HJA were co-located at sample sites W115, W202, W301, W601, W701, W801, W1001, LO06 and MK02. Discharge data were available for all samples collected at gauge stations. Discharge was calculated for sites that were not positioned at gauge stations but were located along streams that contained gauge stations. Measured discharge was scaled linearly with contributing drainage area [Dunne and Leopold, 1979] using the following equation:

$$Q_2 = Q_{GS}(DA_2/DA_{GS}) \quad (1)$$

Where  $Q_{GS}$  is discharge recorded at the gauge station at the time of measurement ( $L s^{-1}$ ),  $Q_2$  is the scaled discharge ( $L s^{-1}$ ),  $DA_{GS}$  is the contributing drainage area above the gauge station ( $m^2$ ) and  $DA_2$  is the drainage area above the sample point ( $m^2$ ). Specific discharge ( $Q_s$ ) was calculated by normalizing each discharge measurement by the contributing drainage area of that location.

The gas transfer velocity, a term that describes gas exchange across the air-water interface of stream, is a function of stream turbulence and can be successfully modeled based on physical characteristics of a site. The gas transfer velocity for carbon dioxide ( $k_{CO_2}$ ) was estimated at each value of discharge. First, stream velocity was calculated for all values of discharge using hydraulic geometry relationships for small streams (median depth 0.28 m) [Leopold and Maddock, 1953; Raymond *et al.*, 2012]. Gas transfer velocity normalized to a fixed temperature with a Schmidt number of 600 ( $k_{600}$ ,  $m day^{-1}$ ) can be calculated following Raymond *et al.* [2012] with the following equation:

$$k_{600} = 1162 \pm 192 \times S^{0.77 \pm 0.028} V^{0.85 \pm 0.045} \quad (2)$$

where  $S$  is reach slope and  $V$  is stream velocity ( $\text{m}^3 \text{s}^{-1}$ ). Values of  $k_{600}$  can be converted to discrete values of the  $\text{CO}_2$  gas transfer velocity ( $k_{\text{CO}_2}$ ) by applying the following equation:

$$k_{\text{CO}_2} = (Sc_{\text{CO}_2}/600)^{-n} * k_{600} \quad (3)$$

where  $Sc_{\text{CO}_2}$  is the Schmidt number for carbon dioxide at a given temperature following *Wanninkhof* [1992], and  $n$  is the Schmidt number exponent which characterizes the stream water and surface conditions. Here, we assigned it a value of 0.5 to represent uncontaminated water with a moderately turbulent surface [*Raymond et al.*, 2012; *Crawford et al.*, 2014].

#### 3.4.6 Statistical Analyses

Linear regressions and one-way analysis of variance (ANOVA) tests were performed to examine the ability of catchment properties and physical variables to explain spatial variability in stream  $\text{pCO}_2$ . These analyses were completed in Matlab (Mathworks, USA). The purpose of these analyses is to identify properties associated with controls of stream  $\text{pCO}_2$ . In identification of these variables we aim to define the processes that drive stream  $\text{pCO}_2$  concentrations. We also calculated the variogram of mean monthly  $\text{pCO}_2$  in the W1 transect to gauge the spatial correlation of this measurement in a longitudinal profile of stream at 50 m intervals. The variogram is defined as the variance between field values at two locations across the field of measurements [*Isaaks and Srivastava*, 1989].

We performed a comparison of mean site  $\text{pCO}_2$  with downstream distance, contributing drainage area, elevation and slope – all physical parameters relating to

drainage network location and relative to stream origin – to interpret the spatial variations of stream pCO<sub>2</sub> within the Lookout creek drainage network [*Leopold and Maddock, 1953*]. We log transformed response and explanatory variables prior to fitting a linear regression.

### **3.5 Results**

Stream pCO<sub>2</sub> within the Lookout Creek drainage network was highly variable both spatially and over the study period. Calculated pCO<sub>2</sub> ranged from atmospheric concentrations (~400 μatm) to approximately 20 times atmospheric concentrations (8150 μatm) (Table 3.3). Individual sites exhibited a range in pCO<sub>2</sub> over the study period. Mean stream pCO<sub>2</sub> for all sites was 945 μatm. The average site pCO<sub>2</sub> range was 1674 μatm, and the average site pCO<sub>2</sub> standard deviation was 464 μatm. We applied several interpretative approaches to identify patterns within the dataset. First, we examined spatial patterns of stream pCO<sub>2</sub> variability within the Lookout Creek drainage network. We compared site average concentrations with local and catchment properties from spatial data, and contrasted patterns between and within longitudinal transects. Second, we examined temporal variations in pCO<sub>2</sub> across the watershed and compared monthly watershed pCO<sub>2</sub> to measured variables. Third, we examined additional measured physical properties and analyze them as physical controls of observed variation in stream pCO<sub>2</sub>.

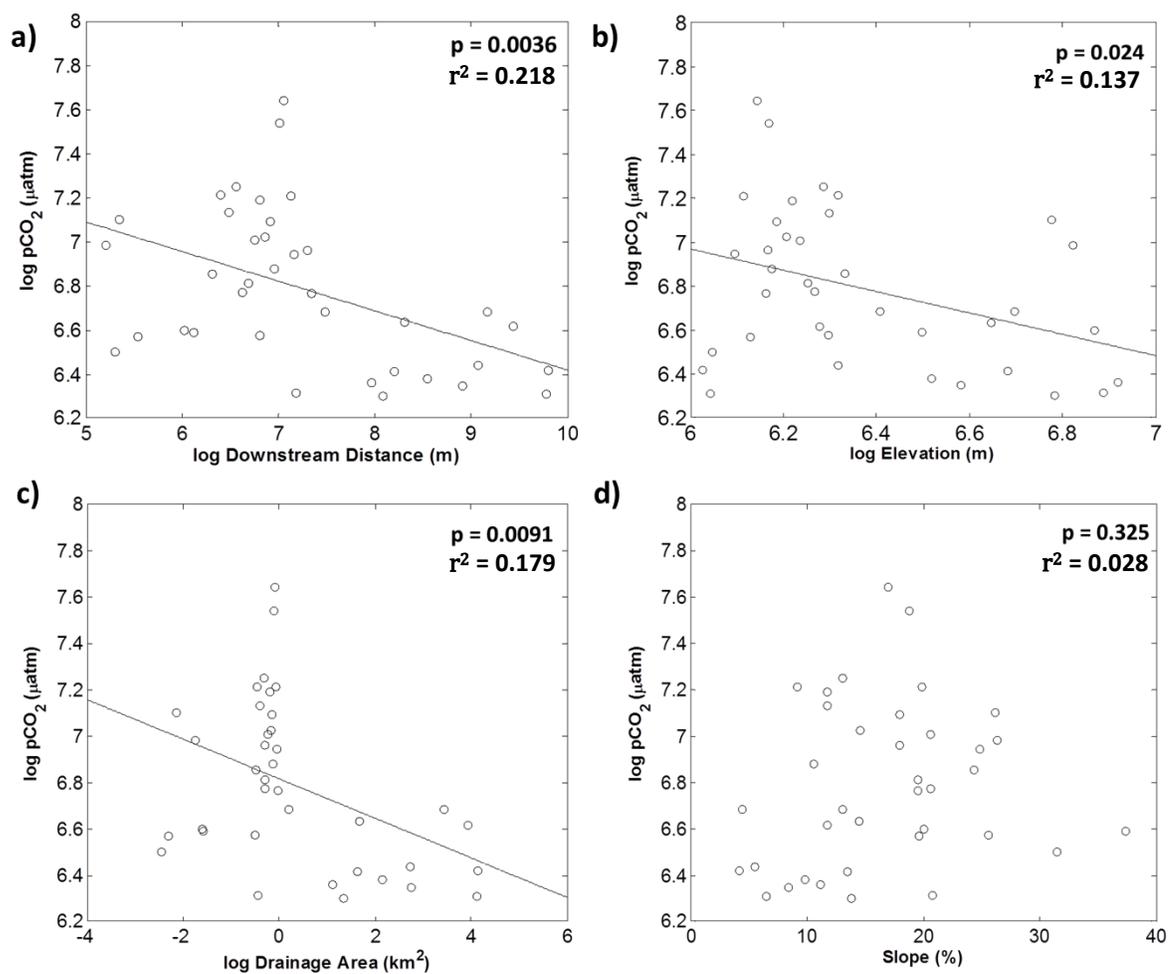
**Table 3.3** – Summary of average pH, temperature, alkalinity, and pCO<sub>2</sub> for each sample site

<b>Site ID</b>	<b>Mean pH</b>	<b>Mean Alkalinity CaCO<sub>3</sub> (mg/L)</b>	<b>Mean Temp °C</b>	<b>Mean pCO<sub>2</sub> µatm</b>	<b>pCO<sub>2</sub> Std Dev. µatm</b>
W101	7.5	23.51	9.71	950	655
W102	7.3	23.39	9.67	1359	705
W103	7.4	23.44	9.77	1254	553
W104	7.3	23.32	9.79	1411	784
W105	7.5	23.25	9.76	874	362
W106	7.5	23.01	9.82	910	385
W107	7.4	22.90	9.83	1106	446
W108	7.3	22.85	9.93	1326	604
W109	7.4	22.76	9.93	1122	426
W110	7.4	22.52	9.91	1204	601
W111	7.4	22.52	10.09	971	472
W112	7.3	22.88	9.94	1887	2179
W113	7.2	22.93	9.92	2091	1448
W114	7.3	22.71	10.01	1354	669
W115	7.4	22.25	10.18	1038	450
W201	7.4	16.17	9.19	728	382
W202	7.5	19.71	10.51	717	390
W203	7.4	20.18	9.14	1057	527
W301	7.4	20.62	10.10	868	294
W601	7.4	20.16	9.50	1212	1022
W701	7.4	24.95	9.34	1080	324
W801	7.5	21.86	9.62	735	269
W901	7.6	24.84	10.58	665	272
W1001	7.6	23.93	11.15	713	324
LO02	7.2	9.15	8.01	578	204
LO03	7.6	20.33	7.10	571	168
LO04	7.4	18.03	8.80	799	210
LO05	7.4	17.14	9.62	747	158
LO06	7.6	17.55	10.87	549	167
LO07	7.5	17.68	10.93	613	193
MK01	7.5	16.37	8.90	610	173
MK02	7.5	15.90	9.23	761	757
MK03	7.5	14.94	8.56	590	169
MR01	7.4	11.62	8.01	545	185
MR02	7.5	15.94	10.00	625	175
CC01	7.7	25.67	6.76	553	215
NN01	7.5	21.19	9.79	800	105

### 3.5.1 *Spatial Patterns*

#### 3.5.1.1 Catchment Patterns

Linear regressions between site mean pCO<sub>2</sub> and downstream distance ( $p = 0.0036$ ), contributing drainage area ( $p = 0.009$ ), and elevation ( $p = 0.024$ ) all exhibit a significant ( $p < 0.05$ ) negative relationship (Figure 3.2 a, b, c). Stream pCO<sub>2</sub> concentration change across the watershed appears to be best characterized by logarithmic transforms. The regression of site mean pCO<sub>2</sub> and slope did not exhibit a significant relationship (Figure 3.2 d). This result contrasts with the other statistical relationships between stream pCO<sub>2</sub> and watershed location. Site slope - like the downstream distance, contributing drainage area and elevation - changes predictably with increasing distance from the stream origin [*Leopold and Maddock, 1953*]. Highest (>25%) and lowest (<15%) site slope exhibited relatively lower associated pCO<sub>2</sub> while moderate slopes (15-25%) showed higher pCO<sub>2</sub>.

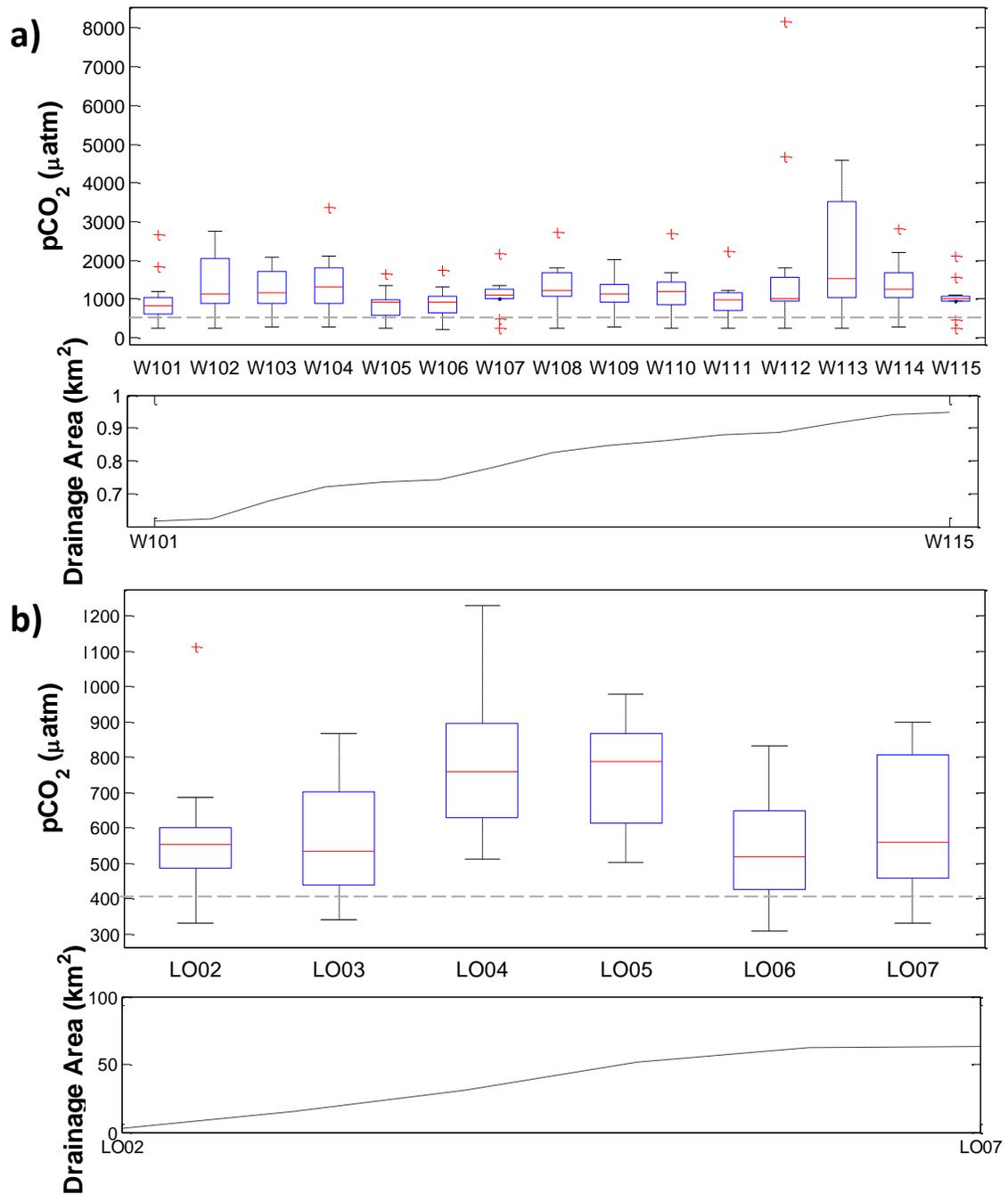


**Figure 3.2** – Log (base  $e$ ) and semi-log transform linear regressions of site average  $p\text{CO}_2$  and (a) site downstream distance (b) site elevation (c) site contributing drainage area (d) reach slope.  $p$ -values from these linear regressions are displayed in the upper right corner of each plot, with significant values  $< 0.05$ .

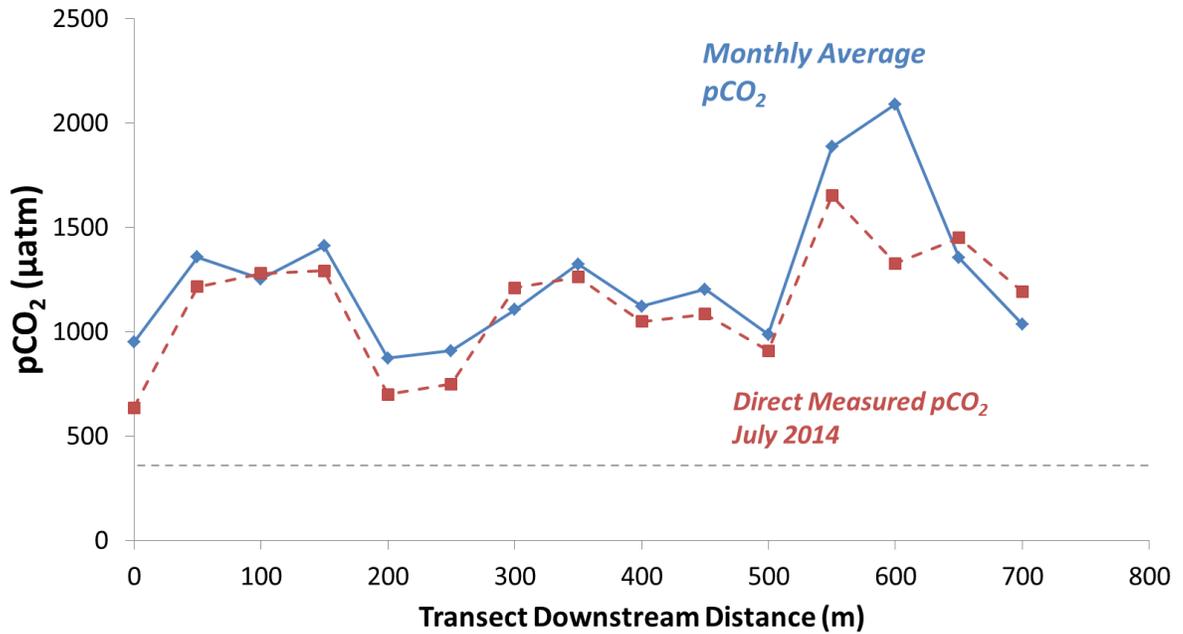
### 3.5.1.2 Transect Patterns

There was considerable variability in observed pCO<sub>2</sub> between and within longitudinal transects studied. There was no consistent downstream trend among the five transects (W1, W2, LO, MK, MR), with W2, and MR displaying increasing trends, while MK, LO and W1 exhibited no directional trend with similar concentrations at upstream and downstream sites. Variation within transects yielded persistent spatial patterns, with transects exhibiting profiles of similar shape over the study period. All profiles contained sites with relatively higher and lower pCO<sub>2</sub> when compared with adjacent transect sampling sites.

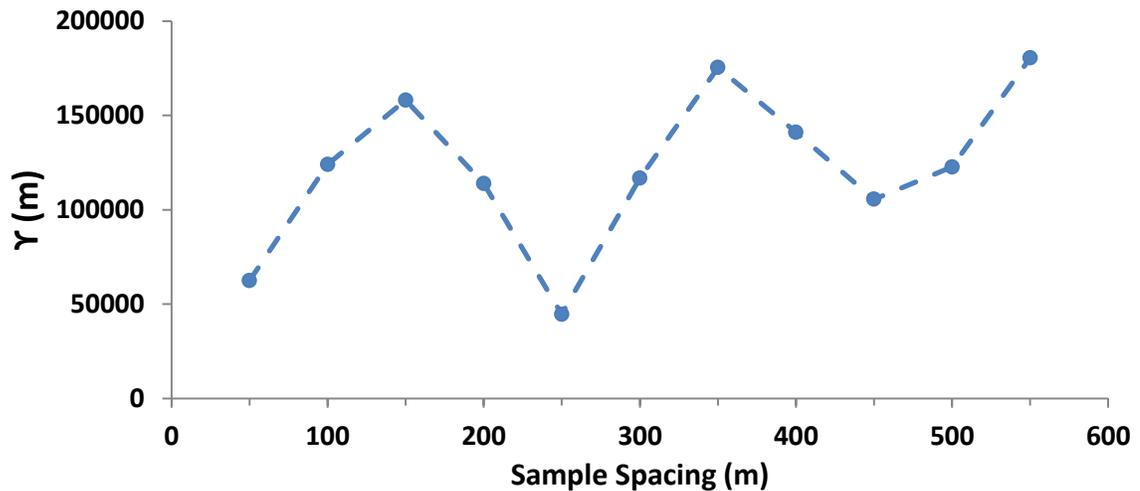
Transect profiles W1 and LO are of particular interest (Figure 3.3), as W1 was the most densely sampled transect (15 sites, sample interval = 50m) and LO was the longest transect sampled (transect length = 17.33 km). The W1 profile displays considerable variation in site pCO<sub>2</sub> and no consistent downstream trends. Two sites near the base of the W1 transect (W112 and W113) that became spatially intermittent during summer low flow had comparatively high mean pCO<sub>2</sub>. Sites W112 and W113 had significantly different pCO<sub>2</sub> concentrations from the other sites along W1 transect (one-way ANOVA test,  $p = 0.040$ ). Similarly, the LO transect does not exhibit a consistent increasing or decreasing trend in the downstream direction. The mean pCO<sub>2</sub> differs among sites along the LO transect (one-way ANOVA test,  $p = 0.0078$ ). The greatest observed pCO<sub>2</sub> in this transect occurred in the middle sites of the LO transect, with lower concentrations at the top and bottom sites.



**Figure 3.3** – Longitudinal  $p\text{CO}_2$  profile variability and contributing transect drainage area. Box plots show medians (red lines), quartiles (boxes), 90 percent confidence intervals (whiskers) and range (red plus symbols) of measured  $p\text{CO}_2$  in (a) Watershed 1 transect (b) Lookout Creek transect. The grey dotted line represents atmospheric concentrations of  $\text{CO}_2$ .



**Figure 3.4** – Persistent spatial trends in longitudinal pCO<sub>2</sub> in W1. Direct measurements of pCO<sub>2</sub> from July 2014 produced a similar longitudinal concentration profile to that from site average pCO<sub>2</sub>. Dotted line represents atmospheric pCO<sub>2</sub>.



**Figure 3.5** – Variogram of mean pCO<sub>2</sub> measurements in Watershed 1, where  $\gamma$  is the variogram strength, a measure of covariance as a function of sample spacing.

There was also variation between transects. W1 and W2 had different pCO<sub>2</sub> than LO, MK and MR (one-way ANOVA,  $p < 0.001$ ). W1 and W2 are considerably smaller streams in the drainage network, MK, and MR are major tributaries, and LO is the largest stream in the catchment.

Direct pCO<sub>2</sub> measurements collected along the W1 transect in July of 2014 were in close agreement to site annual averages. The concentration profile along the longitudinal transect was similar to the profile produced by site average pCO<sub>2</sub>, with strong spatial consistency with relative low and high concentration sites along the profile (Figure 3.4). The variogram for W1 pCO<sub>2</sub> suggests that the correlation scale for pCO<sub>2</sub> is less than 50m (Figure 3.5).

### 3.5.2 *Temporal patterns*

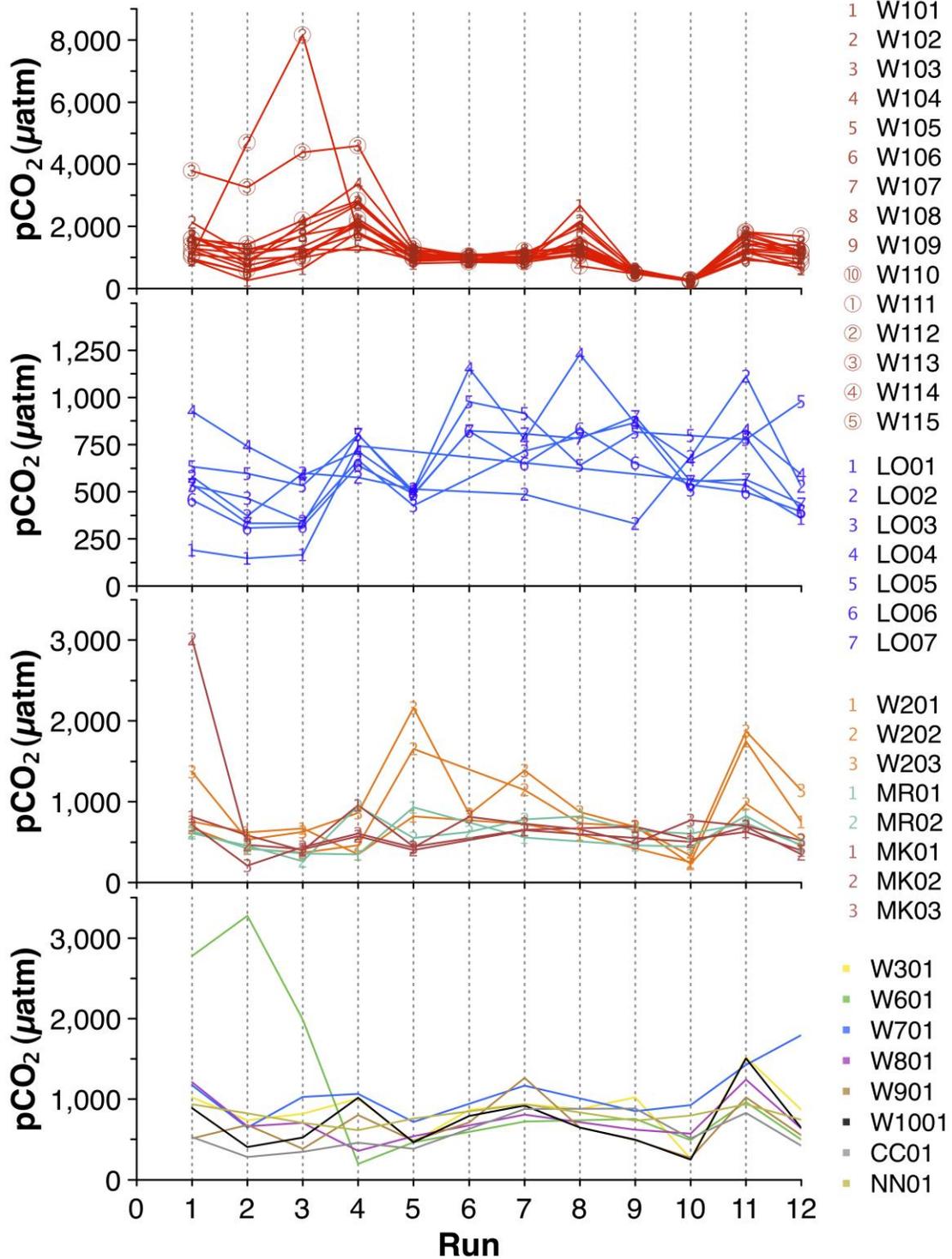
At individual sites, stream pCO<sub>2</sub> was highly variable over the study period (Figure 3.6), with changes in mean concentration and concentration variance on monthly and seasonal time scales (Figure 3.7; Table 3.4). Mean stream pCO<sub>2</sub> concentrations were supersaturated with respect to the atmosphere during all sampling periods. Concentrations showed generally greater mean pCO<sub>2</sub> during warm summer months and lower mean pCO<sub>2</sub> during cool winter months. This is also true of observed pCO<sub>2</sub> variance, with a greater range of observed concentrations in summer months and a smaller range of values observed during the winter. The highest average stream pCO<sub>2</sub> was observed in October, with an average stream concentration of 1356  $\mu\text{atm}$ . The lowest average stream pCO<sub>2</sub> was observed in May, with an average stream concentration of 434  $\mu\text{atm}$ . Stream temperature and alkalinity exhibited much stronger seasonal variation

(Figure D.6). A linear regression of stream temperature and alkalinity produced a positive relationship ( $p < 0.001$ ), with higher stream alkalinity occurring at higher temperatures.

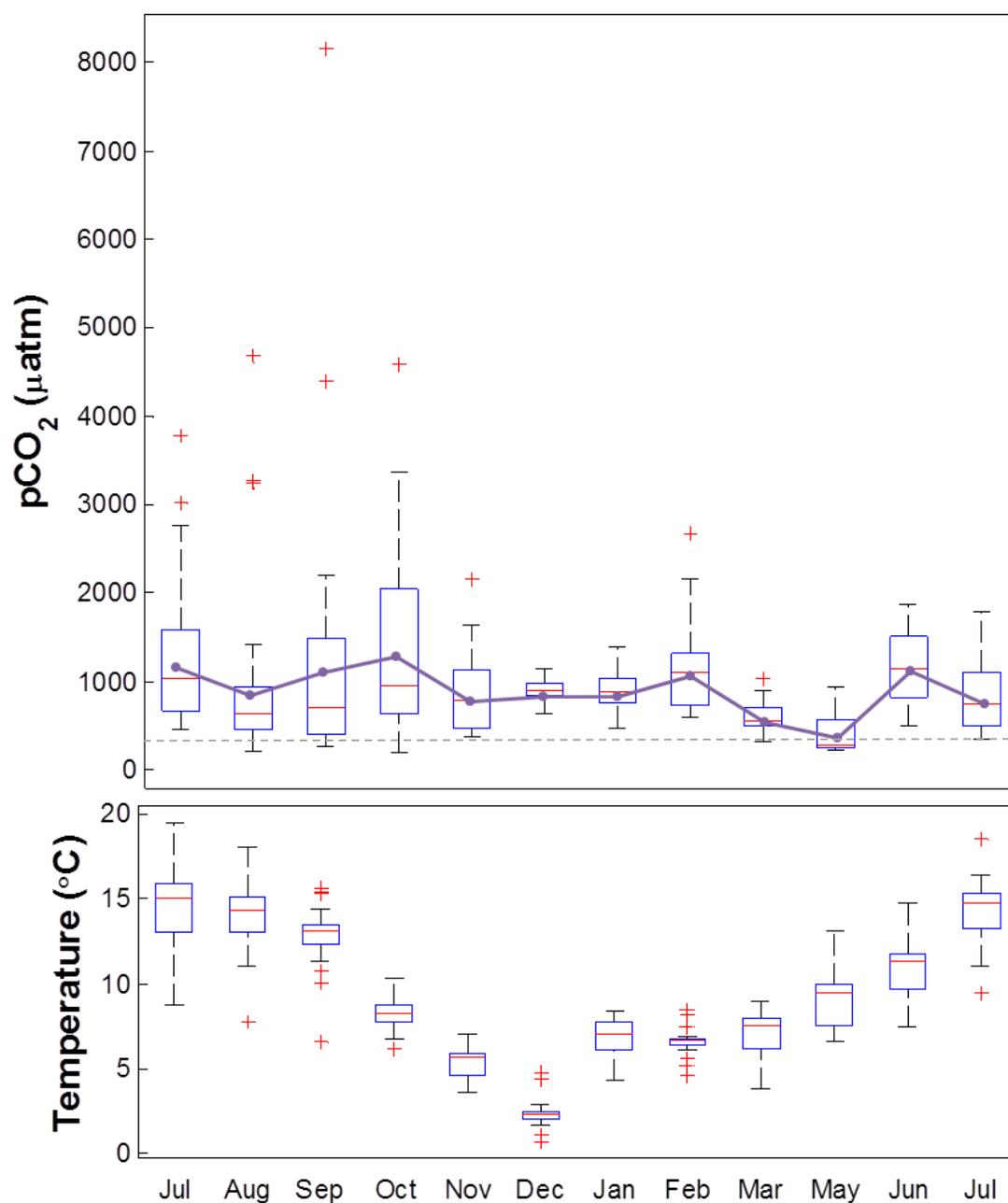
A linear regression of the log transformed excess stream  $p\text{CO}_2$  (concentrations in excess of atmospheric concentrations, i.e.,  $p\text{CO}_{2\text{S}} - p\text{CO}_{2\text{atm}}$ ) and temperature normalized to an arbitrary reference temperature (15 °C) according to the Arrhenius relationship following *Yvon-Droucher et al.*, [2012], produced a weakly significant ( $p = 0.049$ ) negative relationship, indicating some evidence for lower excess stream  $p\text{CO}_2$  with increasing water temperature (Figure 3.8). We applied the Arrhenius relationship to isolate the effect of temperature change and to remove the influence of ecosystem respiration, which does not scale linearly with temperature. This regression using mean site  $p\text{CO}_2$  produces a relationship with greater negative significance ( $p = 0.020$ ), suggesting stronger predictive value at the annual scale (Figure D.5).

**Table 3.4** – Watershed Average  $p\text{CO}_2$  for each sample run and percent change from the previous month

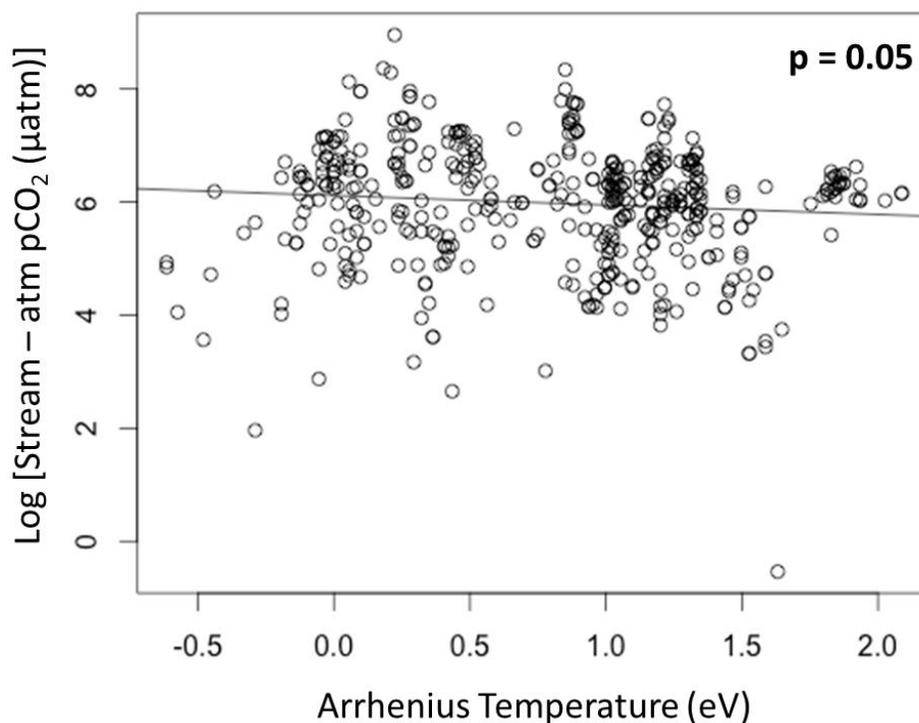
Month	July	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	May	June	July
Run	1	2	3	4	5	6	7	8	9	10	11	12
Average $p\text{CO}_2$ ( $\mu\text{atm}$ )	1233	915	1172	1356	844	905	906	1133	614	434	1185	823
Change From Previous Month (+/- %)		- 26%	+ 28%	+ 16%	- 38%	+ 7%	0%	+ 25%	- 46%	- 29%	+ 173%	- 31%



**Figure 3.6** - Temporal variations in site  $p\text{CO}_2$  over the study period, separated by sample collection run. Each line represents a single sample location. Lines of the same color are sites along a longitudinal transect. Numbers on longitudinal transect lines indicate location along transect.



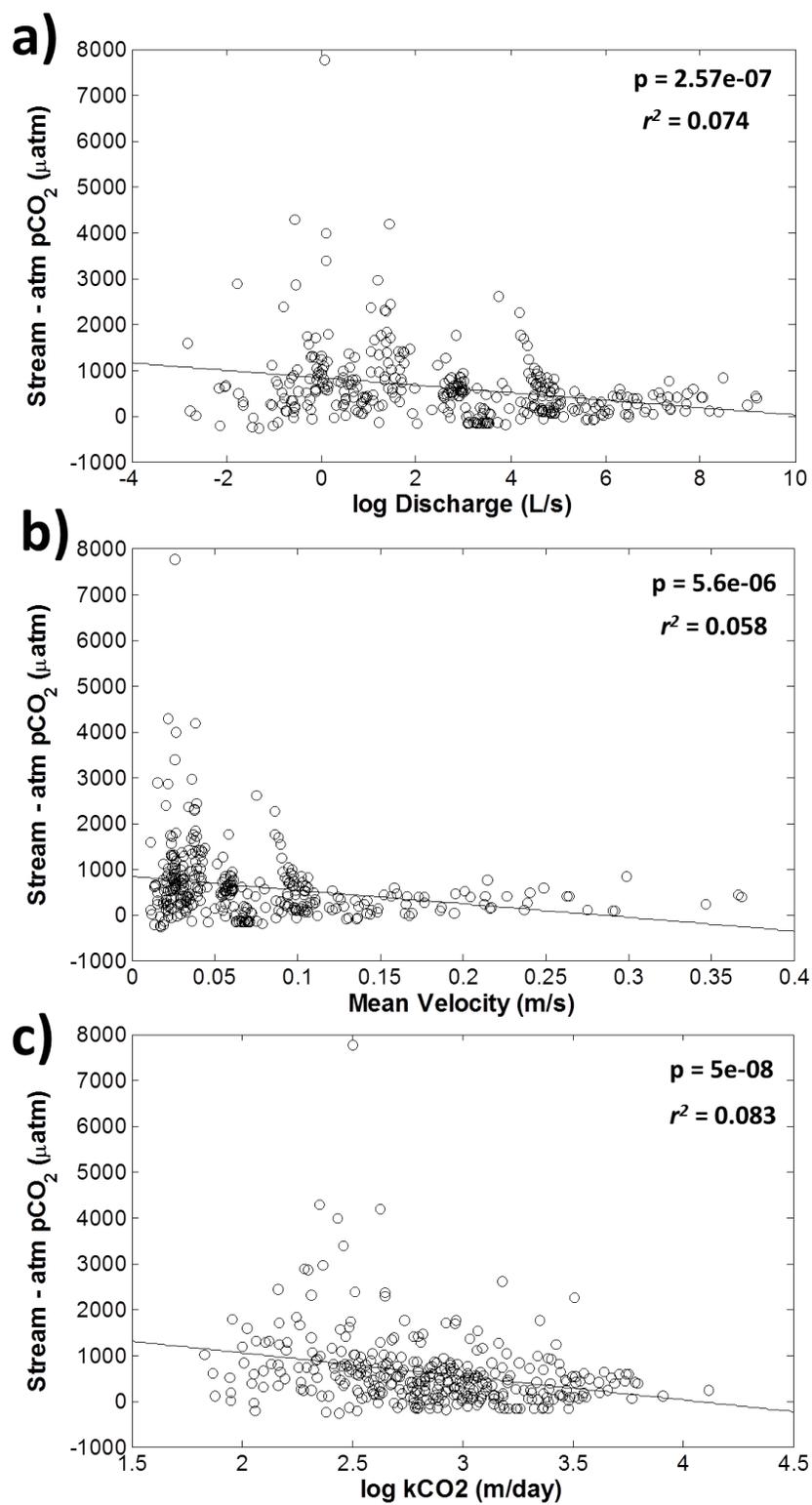
**Figure 3.7** – Annual variation in calculated stream pCO<sub>2</sub> and stream temperature from the Lookout Creek drainage network from July 2013 to July 2014. Box plots show medians (red lines), quartiles (boxes), 90 percent confidence intervals (whiskers) and range (red plus symbols) of measured pCO<sub>2</sub>. Purple dots within box plots represent mean monthly pCO<sub>2</sub>. The dashed line in the top plot represents approximate atmospheric concentration (~400 µatm).



**Figure 3.8** – Linear regression of Arrhenius temperature normalized to a reference temperature (15 °C) and the logarithm of stream minus atmospheric pCO<sub>2</sub>.

### 3.5.3 Hydraulic Patterns

We found negative relationships ( $p < 0.001$ ) between excess stream pCO<sub>2</sub> and stream discharge, stream velocity, and gas transfer velocity (Figure 3.9). Greater discharge, stream velocity and gas exchange led to decreased observed CO<sub>2</sub> supersaturation. We also found a negative relationship between stream excess stream pCO<sub>2</sub> and specific discharge (Figure D.7), though this relationship did not explain any additional variance in that the regression between excess pCO<sub>2</sub> and standard discharge. Log transforms were applied to the explanatory variables discharge and gas transfer velocity to produce a linear relationship. Only measurements of pCO<sub>2</sub> that were



**Figure 3.9** – Linear regressions of excess stream pCO<sub>2</sub> and (a) log discharge (b) mean velocity (c) log carbon dioxide transfer velocity( $k_{CO_2}$ ).

collected with concurrent values of discharge (calculated or measured) were included in this analysis.

### **3.6 Discussion**

#### *3.6.1 Spatial Controls on Stream pCO<sub>2</sub>*

The spatial relationships examined in our analysis suggest decreasing stream pCO<sub>2</sub> with increasing distance from stream origin. This relationship was established with linear regressions between stream pCO<sub>2</sub> and several physical variables associated with relative position in a watershed. Downstream distance, contributing drainage area and elevation all exhibited significant negative relationships. This finding is consistent with other work regarding watershed or regional scale variations of stream pCO<sub>2</sub>. A study of broad-scale stream pCO<sub>2</sub> across the contiguous United States by *Butman and Raymond* [2011] found widespread decrease in stream pCO<sub>2</sub> as a function of Strahler stream order. This pattern has also been observed in studies conducted at the watershed scale. A study conducted by *Jones and Mulholland* [1998a] found a decrease in stream pCO<sub>2</sub> of approximately 50% within two watersheds in the Smoky Mountains, along 46- and 65-km transects. *Crawford et al.* [2013] found a strong decreasing trend in stream pCO<sub>2</sub> with increasing tributary Strahler stream order in the headwater tributaries of the Yukon River in Alaska. Additionally, *Hope et al.* [2001] observed this pattern at the reach scale, reporting high rates of CO<sub>2</sub> removal along a 2.7-km reach of a first-order peatland stream in NE Scotland, with pCO<sub>2</sub> decreasing six-fold from upper to lower study sites.

The finding of decreasing pCO<sub>2</sub> with increasing distance from headwaters is consistent with geomorphic and fluvial changes in a watershed. Headwater streams are

consistently supersaturated with  $p\text{CO}_2$  [e.g., *Jones and Mulholland, 1998b; Cole and Caraco, 2001; Humborg et al., 2010*]. These streams receive high inputs organic matter, are heterotrophic, and receive proportionally large inflows of groundwater considered to be  $\text{CO}_2$ -rich [*Cole and Caraco, 2001; Battin et al, 2008*]. As distance from headwater increases, stream discharge increases, streams become increasingly autotrophic, and terrestrial and groundwater inputs become proportionally less important to overall stream chemistry [*Vanote et al., 1980*]. In this study, decreasing stream  $p\text{CO}_2$  scales with distance from headwater, contributing drainage area, and elevation. These properties applied as explanatory variables of stream  $p\text{CO}_2$  yield significant predictive values in this study. These relationships may be valuable at the watershed scale, but do not fully explain variance observed in  $p\text{CO}_2$ . Stream slope has been shown to scale linearly with watershed position [*Leopold and Maddock, 1953*]. However, slope measurements on the reach scale obtained from spatial data do not appear to scale with  $p\text{CO}_2$ , indicating that these slopes may not accurately represent stream characteristics at the scale of sample collection, or stream  $p\text{CO}_2$  influence.

It is possible that the magnitude of apparent  $\text{CO}_2$  loss could be augmented by a shift in carbonate speciation. A study conducted by *Wallin et al. [2010]* found that, in addition to decreases in stream dissolved inorganic carbon (a summation of dissolved carbon dioxide  $\{\text{CO}_2\}$ , bicarbonate  $\{\text{HCO}_3^-\}$ , and carbonate  $\{\text{CO}_3^{2-}\}$ ) in the downstream direction within a Swedish headwater drainage network, there was a marked increase in the proportion of DIC in the form of bicarbonate due to carbonate weathering. This effect, however, is an unlikely spatial control of  $p\text{CO}_2$  in the Lookout Creek catchment. This watershed has no carbonate bedrock [*Swanson and James, 1975*], thus conversion of

free CO<sub>2</sub> to DIC via carbonate weathering is not likely an important pathway for CO<sub>2</sub> loss in this catchment. We also observe a decrease in alkalinity as a function of downstream distance ( $p < 0.001$ ). Additionally, pH did not show any significant trends with downstream distance, making it difficult to identify consistent patterns of DIC partitioning as a function of position in the Lookout creek drainage network.

Local geomorphic features not characterized by variables associated with watershed position may also be important in controlling gas transfer velocity. Increased stream turbulence, caused by riffle sequences, waterfalls, in-stream woody debris, or boulders can enhance gas exchange between stream and atmosphere, thereby influencing stream pCO<sub>2</sub>. We found a significant negative relationship between  $k_{CO_2}$  and stream excess pCO<sub>2</sub>. We also found a significant relationship between discharge and velocity with stream excess pCO<sub>2</sub> - factors important in scaling site  $k_{CO_2}$  [Billet and Harvey, 2012; Raymond et al., 2012]. These results agree with reported findings that increased gas exchange leads to lower site pCO<sub>2</sub> concentration [Wallin et al., 2011].

The factors that influence gas exchange, however, are difficult to characterize on large scales. A study of watershed-scale patterns in the gas transfer velocity ( $k_{CO_2}$ ) by Wallin et al. [2011] found that this value is highly spatially variable but could be adequately characterized in space by site-specific measurements of slope and hydraulic geometry. A meta-analysis of gas transfer velocity measurements by Raymond et al. [2012] successfully modeled  $k_{CO_2}$  with site characteristics and indicated the importance of local slope, and in small streams, bed roughness. Another study by Hall et al. [2012] investigated variations in pCO<sub>2</sub> along a transect of the Colorado River, and reported variations in the gas transfer velocity spanning two orders of magnitude across rough and

smooth reaches of river. It appears that site gas transfer velocity, though spatially variable, is an important influence on local stream  $p\text{CO}_2$ .

The spatial distribution of groundwater and hyporheic inputs may also be important to longitudinal variation in stream  $p\text{CO}_2$ . Groundwater and hyporheic water can be  $\text{CO}_2$ -rich [e.g., *Schindler and Krabbenhoft*, 1998; *Duarte and Prairie*, 2005; *Öquist et al.*, 2009]. Inputs tend to be focused along preferential flow paths and enter the stream at points of subsurface upwelling [*Findlay et al.*, 1993; *Boulton et al.*, 1998]. Zones of upwelling are associated with marked changes in stream chemistry [e.g., *Boulton et al.*, 1998; *Franken et al.*, 2001]. The distribution of hyporheic and groundwater inputs along a stream may explain variations in longitudinal stream  $p\text{CO}_2$ .

Longitudinal transect concentration profiles from this study appear to support the hypothesis of site-scale controls of stream  $p\text{CO}_2$ . We observed persistent transect  $p\text{CO}_2$  variability inconsistent with watershed scale patterns of  $p\text{CO}_2$  in the downstream direction. Headwater streams in the HJA are characterized by longitudinal changes in stream morphology with alternating sequences of pools, bedrock, steps and riffles [*Kasahara and Wondzell*, 2003]. These changes influence local  $k_{\text{CO}_2}$  and may contribute to persistent site variance in average  $p\text{CO}_2$  along longitudinal transects in this study (Figure 3.3, Figure 3.4). However, we also observe local increases in stream  $p\text{CO}_2$  along transects in addition to observed decreases. This indicates that there must also be continual sources of  $\text{CO}_2$  to the stream along these transects. Sections of stream that have relatively low turbulence, and therefore low  $k_{\text{CO}_2}$ , may allow for local recovery of  $p\text{CO}_2$  and account for local increases in  $p\text{CO}_2$  along a transect. Diffuse inputs of  $\text{CO}_2$ -rich

groundwater or hyporheic exchange flows may control stream pCO<sub>2</sub> in these locations [Dawson *et al.*, 2001; Crawford *et al.*, 2014; Peter *et al.*, 2014].

Studies that have observed longitudinal pCO<sub>2</sub> changes at the reach-scale have found similar results. Crawford *et al.* [2014] measured stream pCO<sub>2</sub> along six, 2000-m transects and found spatially variable pCO<sub>2</sub> with persistent profile shape. Dawson *et al.* [2001] observed persistent peaks and troughs in a pCO<sub>2</sub> profile over a year along a headwater reach of stream. Longitudinal transect pCO<sub>2</sub> profiles at the reach-scale suggest that in-stream processes, groundwater inputs, and local morphology control stream pCO<sub>2</sub> at this scale, and longitudinal changes in stream pCO<sub>2</sub> cannot be accurately characterized by unidirectional downstream trends [Lauerwald *et al.*, 2013; Crawford *et al.*, 2014].

### 3.6.2 Spatial Considerations

The scale of stream pCO<sub>2</sub> variability is important for scaling point measurements of pCO<sub>2</sub> to the reach or watershed scale. Results from the variogram analysis in W1 (Figure 3.5) illustrate the importance of site-scale controls on pCO<sub>2</sub>, with no identifiable covariance at sample intervals of 50 m. Stream pCO<sub>2</sub> increment tolerance in W1 appears to be smaller than this interval, indicating that finer resolution sampling may be required to capture longitudinal stream pCO<sub>2</sub> gradients. Field duplicates collected in this study showed very good agreement ( $\pm 0.03\%$ ) with original aliquots, indicating negligible kernel effect (variance with a sample spacing of 0 m) [Isaaks and Srivastava, 1989]. These findings suggest that the appropriate scale for identifying pCO<sub>2</sub> gradients in W1 is at some interval between 0 and 50 m. It is difficult to predict how fine of sample spacing is required as it will likely depend on site specific geomorphic or environmental factors.

Extreme examples of spatial  $p\text{CO}_2$  variation were reported by *Fiedler et al.* [2006] and *Johnson et al.* [2008]. *Fiedler et al.* sampled spring water at its source and then again 17 m downstream and found a 93% decrease in dissolved  $\text{CO}_2$  on average over this distance. *Johnson et al.* also monitored a site of groundwater emergence in an Amazonian headwater stream and found changes in  $p\text{CO}_2$  greater than 500% within 50 m downstream of the spring due to rapid outgassing. It appears that stream  $p\text{CO}_2$  can vary greatly over short distances. We observed similar phenomena at sites W112 and W113 during August and September sample runs. The W1 stream became spatially intermittent at these locations as a result of low discharge, with the stream entering subsurface flowpath and reemerging downstream. At W112 and W113 in August and September, water samples were collected where stream water emerged from the subsurface. Measured  $p\text{CO}_2$  at these instances were between  $\sim 4500\text{--}8000 \mu\text{atm}$ , considerably higher than all other measurements collected across the Lookout Creek drainage network during the entire study period (Figure 3.6; Figure 3.7). Concentrations at the W114 and W115 – sites 50 m and 100 m below the stream discontinuity – had much lower  $p\text{CO}_2$ . The magnitude and spatial controls of stream  $p\text{CO}_2$  variability may have important implications for representative scaling across drainage networks and estimations of carbon fluxes.

### 3.6.3 Temporal Controls on $p\text{CO}_2$

We observed monthly variability in the mean and variance of measured stream  $p\text{CO}_2$  and found weak evidence of seasonal patterns. The magnitude of seasonal variation was smaller than we expected. A different study that performed high resolution

monitoring of pCO<sub>2</sub> over 11 months in W1 found strong seasonal variations, with concentrations on average 2.5 times larger during summer months than winter months [Dosch, 2014]. Other studies have also observed strong annual variability with a seasonal pattern in stream pCO<sub>2</sub> [e.g., Raymond *et al.*, 1997; Jones and Mulholland, 1998b; Parasad *et al.*, 2013]. In this study, temporal variations across the entire Lookout Creek drainage network were variable from month to month (Table 3.4) and lacked a coherent seasonal pattern (Figure 3.7). However, most studies that report seasonal variations in pCO<sub>2</sub> do so from a single location. It is possible that aggregating watershed data to produce basin-wide monthly averages masks seasonal trends. However, we found that individual sites did not exhibit discernable seasonal patterns (Figure 3.6). We did not find spatially uniform seasonal variation in stream pCO<sub>2</sub> at the basin-scale. It is likely that temporal changes in small streams are different from those large streams within this network. This hypothesis is supported by results from the ANOVA test that indicate annual distributions of pCO<sub>2</sub> in the small tributaries W1 and W2 are significantly different than those in larger streams LO, MR, MK.

Stream temperature had strong monthly variability with a distinct seasonal trend, but was a weak predictive variable of stream pCO<sub>2</sub> in this study. Stream temperature did not scale with stream pCO<sub>2</sub> as well as we expected. A study that collected stream pCO<sub>2</sub> measurements at 30-minute intervals in W1 found that stream temperature explained 53 percent of the variance in observed pCO<sub>2</sub> [Dosch, 2014]. In this study, however, stream temperature was only able to explain 5 percent of the variance. We did find a significant negative relationship between standardized temperature (Arrhenius temperature) and stream pCO<sub>2</sub> excess. It is possible that this inverse relationship is due to changing

solubility of CO<sub>2</sub> in water as a function of temperature, with CO<sub>2</sub> being more soluble at cool temperatures [Stumm and Morgan, 1996]. However, it is difficult to isolate the effect of a single process in the Lookout Creek drainage network. Temperature has been shown to influence the gas transfer velocity, enhancing gas fluxes at warmer temperatures [Demars and Manson, 2013]. Stream temperature also has a strong positive influence on ecosystem metabolism, with warmer temperatures leading to increased respiration and thereby local CO<sub>2</sub> production [Bott et al., 1984; Roberts et al., 2007; Yvon-Durocher, 2012]. Stream temperature was also indirectly associated with seasonal and hydrologic changes, with the warmest waters observed in late summer when discharge is also lowest. When discharge is low, surface turbulence and  $k_{CO_2}$  are decreased [Billet and Harvey, 2012; Raymond et al., 2012] and stream travel time is increased. These conditions increase the probability that an individual parcel of water will enter the subsurface via hyporheic exchange, encounter subsurface microbial communities, and become enriched in CO<sub>2</sub> while also decreasing the probability of CO<sub>2</sub> loss through evasion [Crawford et al., 2014].

The scale of temporal sampling may also have an influence on the temporal results in this study. Synoptic sampling offers only a snapshot of stream chemistry and does not yield insight toward event- or finer-scale dynamics. Several studies that have applied continuous or high resolution sampling reveal diurnal and event-scale patterns of variability that were indiscernible by discrete sampling alone [Dinnsmore et al., 2013; Crawford et al., 2013; Peter et al., 2014; Dosch, 2014]. It is possible that the measurements presented in this study are representative of basin temporal variations in pCO<sub>2</sub> at a fixed time. However, it appears that the discrete nature of point sampling

misses the context of these changes. We conclude that the samples collected at monthly intervals can provide coarse temporal patterns, but do not offer sufficient resolution to identify processes that drive stream pCO<sub>2</sub> on a seasonal scale.

#### 3.6.4 Assessment of Parameter Uncertainty

Calculations of pCO<sub>2</sub> are sensitive to error in field measurements of pH. Variations in the accuracy of measured pH are probable, but there is no evidence to indicate directionality of these errors [Jones *et al.*, 2003]. It is also possible that there were sources of noncarbonate alkalinity that could contribute to an over estimation of pCO<sub>2</sub>, specifically organic acids or mineral rich groundwater. However, neither of these appear to be major sources of error, as a regression between direct pCO<sub>2</sub> measurements agreed well (Figure D.10) with a series of pCO<sub>2</sub> calculations made with the methods described in this study. Additionally, direct measurements are in close agreement with monthly averaged calculated pCO<sub>2</sub> along the W1 transect (Figure 3.4). This result gives us confidence in our calculated values and the use of mean site averages as predictors of transect profile variability. Other work that has calculated values of pCO<sub>2</sub> report method accuracy of 10% of the true value [Raymond *et al.*, 1997], which is a safe confidence interval for the values reported here.

We also sought to test the temporal stability of the alkalinity in HJA water samples over time, to assess directional error introduced by variable sample-processing intervals, eight random samples were processed within the initial 7 day window, then again 31 days later (Figure D.9). Results show no evident change in alkalinity ( $r^2=0.997$ ; slope = 1.0098), with differences within the detection limit of the autotitrator. This result

suggests that alkalinity in surface water samples collected from the HJA are stable over this time period.

### **3.7 Conclusions**

Stream  $p\text{CO}_2$  across the HJA was consistently supersaturated with respect to atmospheric concentrations and exhibited strong spatial and temporal variability. Declines in  $p\text{CO}_2$  were observed at the watershed scale with increasing distance from headwaters, but results at the reach-scale did not exhibit clear patterns in the downstream direction. We find strong negative relationships between stream  $p\text{CO}_2$  and stream discharge, calculated mean velocity and calculated carbon dioxide gas transfer velocity. The correlation scale for  $p\text{CO}_2$  appears to be less than 50 m in second-order Watershed 1, indicating that some of the processes that control  $\text{CO}_2$  are highly variable at scales less than 50 m. This longitudinal variability underscores the importance of in-stream drivers of  $p\text{CO}_2$  at reach and subreach scales. Stream  $p\text{CO}_2$  shows generally higher concentrations during the summer and lower concentrations in the winter, with considerable intrannual variability. The distribution of  $\text{CO}_2$  concentrations was larger in small streams than in large streams within the drainage network. Monthly sampling may provide approximate annual patterns in watershed  $p\text{CO}_2$ , but higher resolution sampling is needed to capture event-scale dynamics and to give context to discrete measurements. This work indicates the importance of measurement scale, and we find that use of coarse resolution  $p\text{CO}_2$  data for flux estimates or spatial coverage may bias results to reflect local or transient conditions.

### 3.8 Acknowledgements

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<http://andrewsforest.oregonstate.edu/lter/data.cfm?frameURL=173>

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## 4 Conclusion

We examined the dynamics of stream and hyporheic  $p\text{CO}_2$  in headwater stream ecosystems located in H.J. Andrews Experimental Forest in the Western Cascades of Oregon. We conducted our data collection and analysis in two parts. The first part focused on temporal variability in and drivers of stream and hyporheic  $p\text{CO}_2$  in Watershed 1, a small 95.5-ha catchment. We utilized high resolution  $p\text{CO}_2$  measurements to observe seasonal and storm-driven patterns in hyporheic and stream  $p\text{CO}_2$  and to evaluate the potential for hyporheic exchange flow to influence stream water  $p\text{CO}_2$ . The second part focused on spatial variability in stream  $p\text{CO}_2$  within the 6400-ha Lookout Creek drainage network. We investigated physical and hydraulic drivers of spatial variation at the watershed scale and along longitudinal transects.

In Watershed 1, stream and hyporheic  $p\text{CO}_2$  showed strong seasonal and event-scale variability with distinct stream and hyporheic dynamics during storm discharge events. By measuring and modeling hyporheic DIC, we estimate  $37.5 \text{ kg-C yr}^{-1}$  per watershed hectare (confidence interval  $4.0\text{--}122.3 \text{ kg-C ha}^{-1} \text{ yr}^{-1}$ ) is exported to the stream via hyporheic exchange flow. This result indicates that approximately one third of stream inorganic carbon export from the sum of  $\text{CO}_2$  evasion and downstream advection originated in the hyporheic zone. Hyporheic exchange flow had greatest influence over stream  $p\text{CO}_2$  during low and high baseflow, while  $\text{CO}_2$  evasion had greatest influence during storm discharge events. These findings suggest that the hyporheic zone actively participates in carbon cycling in this headwater stream and continuously replenishes stream  $\text{CO}_2$ .

In the Lookout Creek drainage network, we calculated  $p\text{CO}_2$  at 38 sites at monthly intervals over one year. We selected the sites to capture a range of spatial resolutions and to represent the physical variability of the catchment. Stream  $p\text{CO}_2$  was consistently supersaturated with respect to atmospheric concentrations at all 38 locations. Stream  $p\text{CO}_2$  ranged from atmospheric ( $\sim 400 \mu\text{atm}$ ) to 20 times atmospheric concentrations ( $8150 \mu\text{atm}$ ) and exhibited strong spatial and temporal variability. The distribution of  $p\text{CO}_2$  over the study period was different in small and large streams within the drainage network. At the watershed scale,  $p\text{CO}_2$  decreased with distance downstream. At the reach scale, we did not detect clear patterns in the downstream direction. However, individual transects displayed persistent profile shape, with consistent high and low  $p\text{CO}_2$  locations. We found negative relationships between stream  $p\text{CO}_2$  and stream discharge, mean velocity and the carbon dioxide gas transfer velocity. Stream  $p\text{CO}_2$  exhibited changes over short distances, with large changes in  $p\text{CO}_2$  over less than 50 m. Longitudinal variability indicates spatial non-uniformity of in-stream controls on  $p\text{CO}_2$  at this scale.

Our analysis of temporal dynamics in stream and hyporheic  $p\text{CO}_2$  in Watershed 1 illustrates that high resolution temporal sampling captures event-scale dynamics and could provide context to discrete measurements. Larger-scale efforts in the Lookout Creek drainage network in turn indicate that the spatial scale at which stream  $p\text{CO}_2$  is measured is important. The use of coarse resolution  $p\text{CO}_2$  data for flux estimates or spatial coverage may bias results to reflect local or transient conditions. Future work will focus on combining these techniques to scale high-temporal resolution  $p\text{CO}_2$  data longitudinally and across drainage networks.

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**APPENDICES**

## Appendix A Monte Carlo Simulation Supporting Information

We performed a Monte Carlo simulation to constrain the total uncertainty of modeled hyporheic DIC export. We randomly selected values within the confidence bounds of parameters listed in Table A.1 and completed 10000 iterative calculations of DIC export according to (1), (2) and (3) from the text. Confidence intervals (CI) for model inputs that were time varying (i.e. stream discharge  $\{Q_s\}$ , and stream temperature  $\{T_s\}$ ) were obtained from H.J. Andrews experimental Forest gauge station metadata. The confidence interval for apparent ecosystem activation energy ( $E_o$ ) was obtained from *Yvon-Durocher et al.* [2012]. CIs for nonlinear parameters  $DIC_{max}$  and  $\lambda_o$  were calculated according to (A.1) [e.g., *Bard*, 1974; *Draper and Smith*, 1981; *Haggerty et al.*, 2001].  $J$  is the Jacobian, which is the matrix of sensitivities to model output to the parameter estimates  $DIC_{max}$  and  $\lambda_o$ .  $\sigma$  is the common variance of the terms (assumed here to be RMSE according to *Haggerty et al.*, [2001]) and  $V_p$  is the first-order approximation to the parameter covariance matrix. Confidence intervals for  $Q_{hef}$  were calculated from the standard errors of the coefficients (Table A.1;  $a$  and  $b$ ) of the regression model between  $Q_s$  and  $Q_{hef}$  according to (A.2). The mean of these 10000 models was used as a statistically representative value of hyporheic DIC export. We calculate 95 percent confidence intervals for total estimate uncertainty (Figure A.1, Table A.2). The percentage of stream inorganic carbon export originating in the hyporheic was calculated according to (A.3). To constrain the total error of this estimate, we performed a Monte Carlo simulation to calculate 1000 values of hyporheic DIC export (from this study) and

1000 values of total DIC export (the sum of stream DIC export and CO<sub>2</sub> evasion) with data from *Argerich et al.* [manuscript in preparation, 2014]. The percentage of hyporheic contribution to total inorganic carbon export was calculated 1000 times for each iterative calculation. The mean value was used as a representative percentage of hyporheic contribution, and the 95 percent confidence intervals were calculated for total uncertainty.

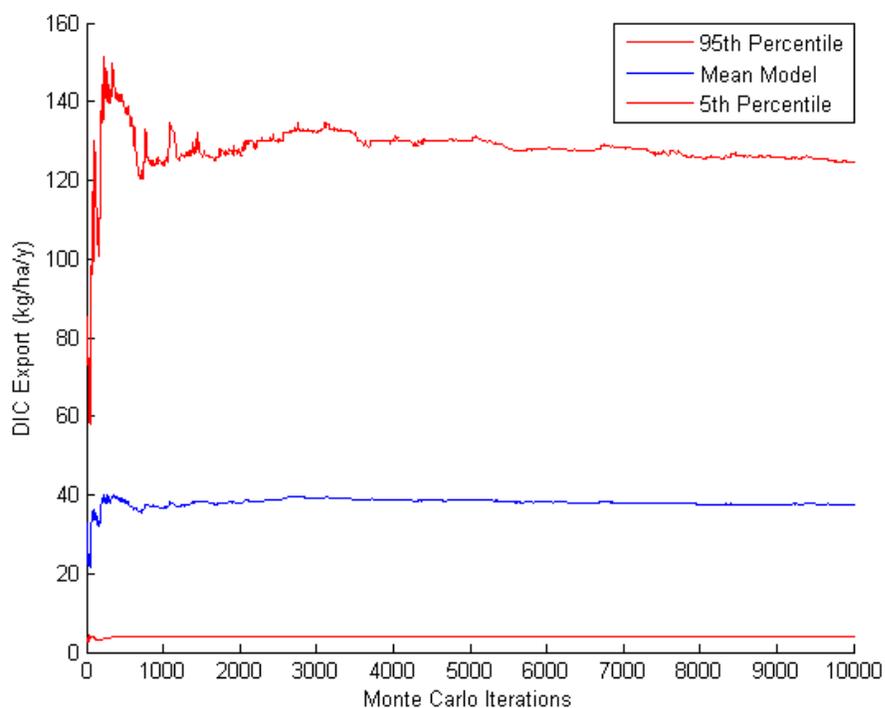
**Table A.1** – Hyporheic DIC model parameter confidence intervals (CI)

Entity	Variable	Value	CI (±)	Units
<i>Inputs - Time Varying</i>				
	Q <sub>s</sub>	-	0.10%	L s <sup>-1</sup>
	T <sub>s</sub>	-	1.0	°C
<i>Derived Constants</i>				
	E <sub>o</sub>	0.58	0.14	eV
	λ <sub>o</sub>	1.01E-02	3.96E-03	hr <sup>-1</sup>
	DIC <sub>max</sub>	5.04E-04	1.37E-04	mol L <sup>-1</sup>
	a	-0.3279	0.63796	-
	b	-0.83	0.35304	-

$$V_p = \sigma^2(J^T J)^{-1} \quad (\text{A.1})$$

$$\%HZ = 0.47Q_s^{-0.83} = 10^a Q_s^b \quad (\text{A.2})$$

$$\% \text{ Export Hyporheic} = \frac{\text{Hyporheic DIC Export}}{\text{Stream DIC Export} + \text{CO}_2 \text{ Evasion}} \times 100 \quad (\text{A.3})$$



**Figure A.1** - Monte Carlo simulation results for 10,000 iterations. Upper red line is the 95 percent confidence interval, the blue line is the mean model, and the lower red line is the 5 percent confidence interval. This figure shows these values as a function of iterations. Mean and 5% confidence interval show convergence after 1,000 -2,000 iterations, while 95% confidence interval reaches convergence near 10,000 iterations.

**Table A.2** - Monte Carlo simulation results of hyporheic DIC export, 10,000 iterations

Mean Hyporheic Export ( $\text{kg-C ha}^{-1} \text{yr}^{-1}$ )	37.5383
95 Percent Confidence interval ( $\text{kg-C ha}^{-1} \text{yr}^{-1}$ )	122.3278
5 Percent confidence interval ( $\text{kg-C ha}^{-1} \text{yr}^{-1}$ )	4.0314

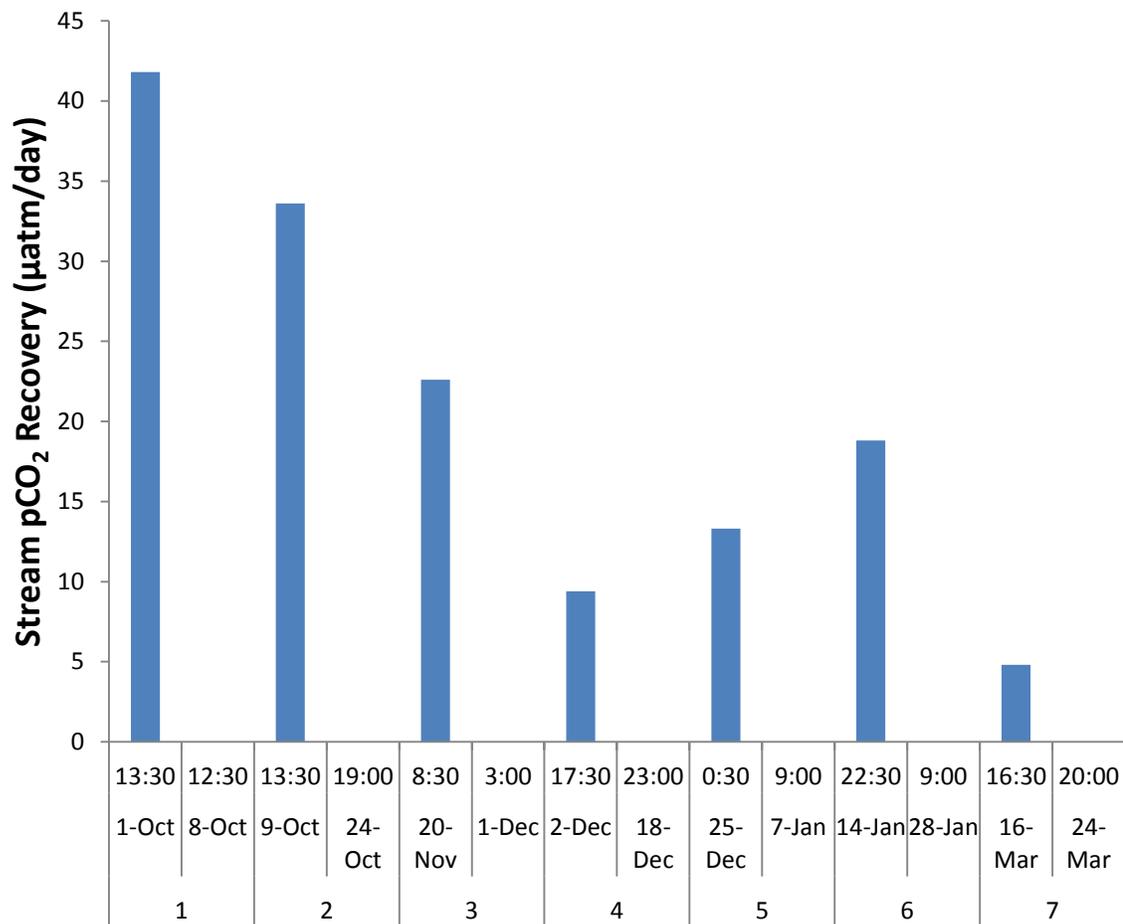
**Table A.3** - Monte Carlo simulation results of the percentage of total Watershed 1 DIC export originating from the hyporheic zone, 1000 iterations

Mean Hyporheic Contribution (%)	34.6
95 Percent Confidence Interval (%)	3.6
5 Percent Confidence Interval (%)	100.0

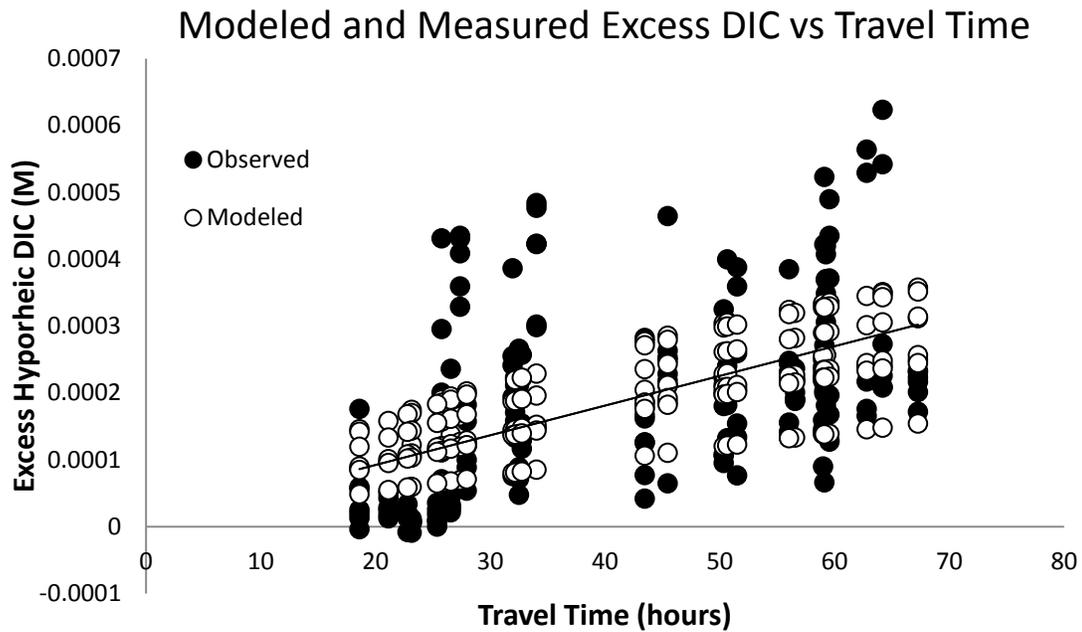
## Appendix B Additional Figures and Tables Chapter 1

**Table B.1** - Recovery in stream pCO<sub>2</sub> following fall/winter storms

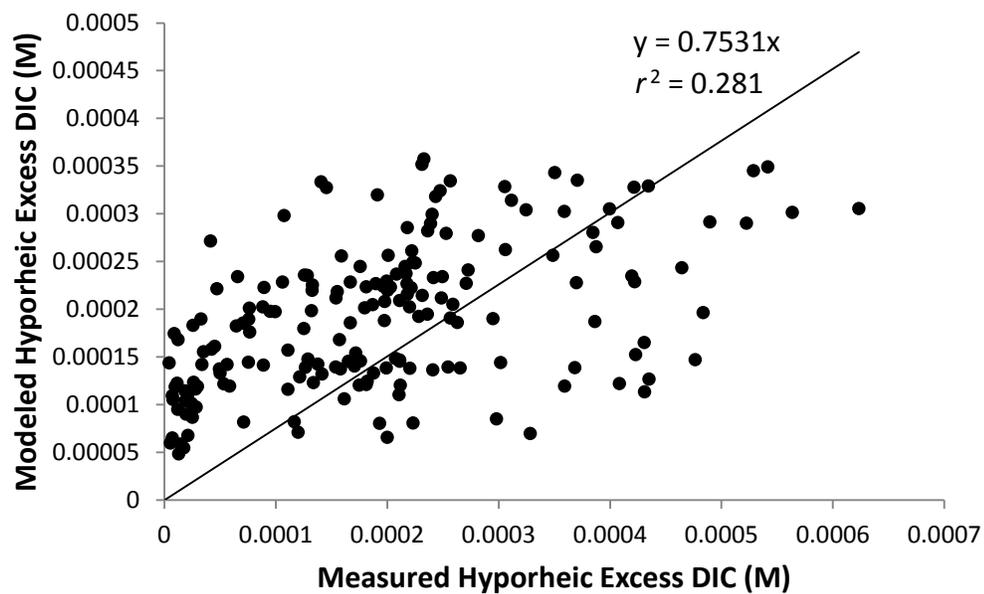
Storm Event	Recovery Period		Stream pCO <sub>2</sub> μatm	Recovery		
	Date	time		magnitude μatm	% Increase %	Rate of Recovery μatm /day
1	1-Oct	13:30	607	333	55	41.8
	8-Oct	12:30	940			
2	9-Oct	13:30	853	512	60	33.6
	24-Oct	19:00	1365			
3	20-Nov	8:30	574	244	43	22.6
	1-Dec	3:00	818			
4	2-Dec	17:30	540	152	22	9.4
	18-Dec	23:00	692			
5	25-Dec	0:30	573	178	31	13.3
	7-Jan	9:00	751			
6	14-Jan	22:30	519	253	49	18.8
	28-Jan	9:00	772			
7	16-Mar	16:30	517	39	7.5	4.8
	24-Mar	20:00	556			



**Figure B.1** – Rate of recovery in stream pCO<sub>2</sub> following fall/winter storms



**Figure B.2** - Modeled and Measured Excess hyporheic DIC with respect to travel time. Results of model calibration to lowest RMSE.



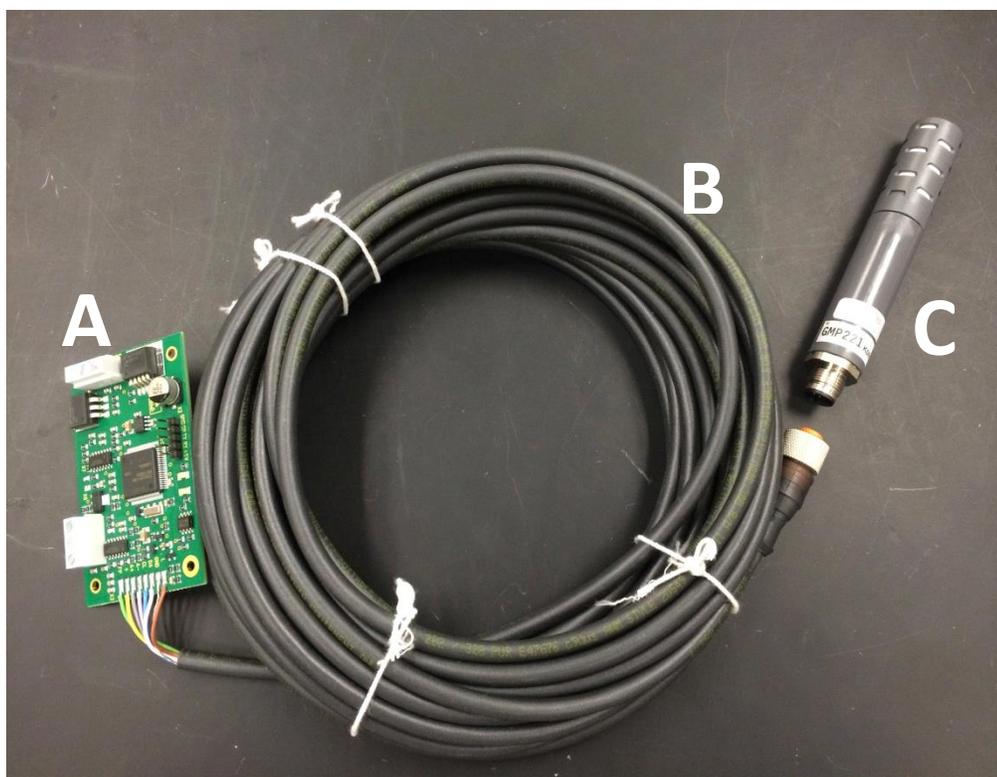
**Figure B.3** – Model calibration results, modeled as a function of measured excess hyporheic DIC.

## Appendix C Vaisala GMM220 CO<sub>2</sub> Module Modification/Implementation Instructions

The purpose of this appendix is to provide instructions for the modification of Vaisala CARBOCAP GMM220 CO<sub>2</sub> modules for aquatic deployment for continuous aquatic measurements of pCO<sub>2</sub>. This method was adapted following :

Johnson, M., M. Billett, and K. Dinsmore (2010), Direct and continuous measurement of dissolved carbon dioxide in freshwater aquatic systems—method and applications, *Ecohydrology*, 3, 68–78, doi:10.1002/eco.95.

Please refer to this publication for additional details on deployment and correction of sensor output.



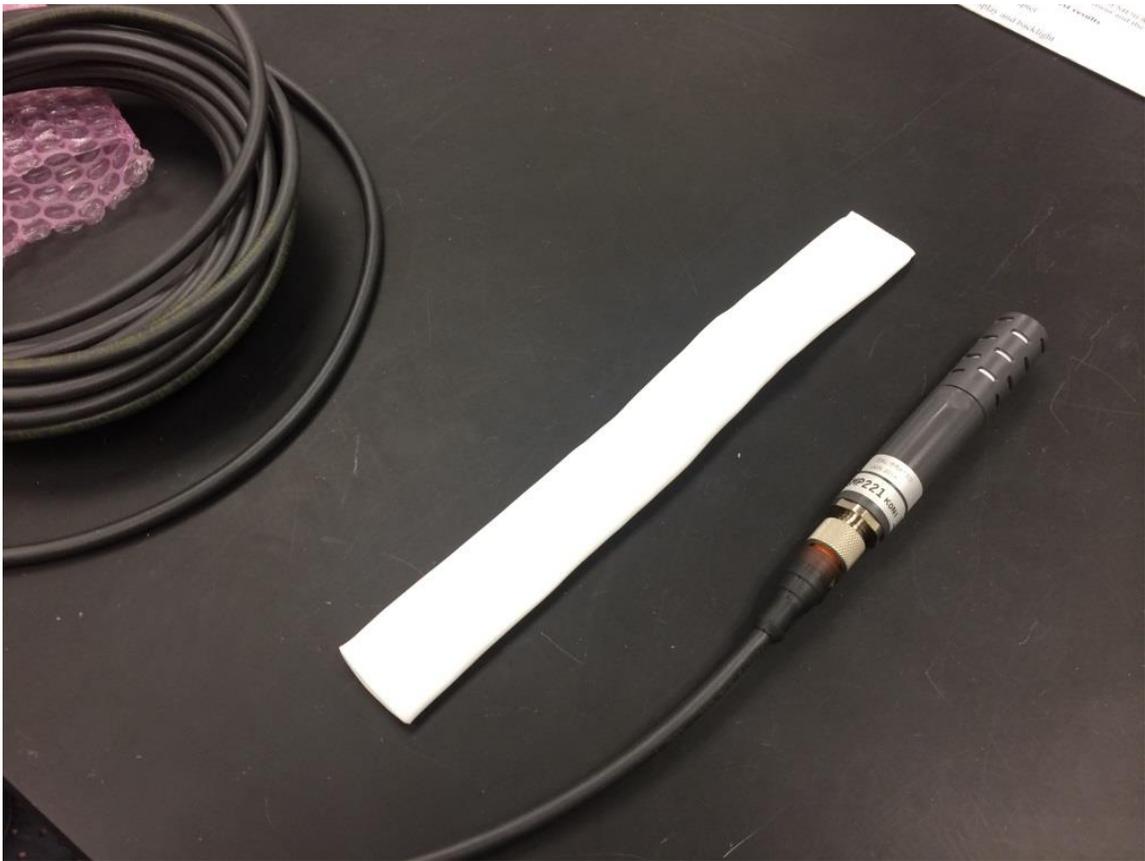
**Figure C.1** - Overview of the Vaisala GMM 220 CO<sub>2</sub> probe pre-modification. Three main components (A) Component board (B) cable (C) CO<sub>2</sub> probe



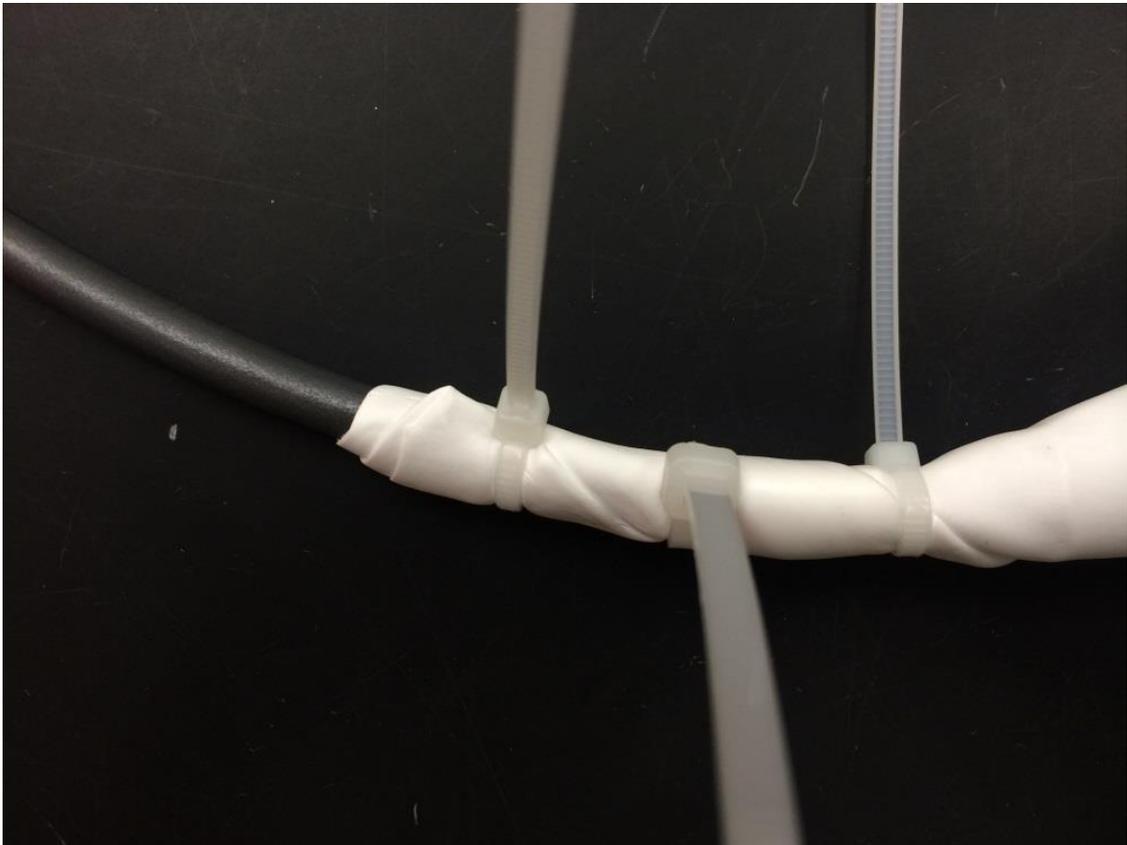
**Figure C.2** - Close-up view of the CO<sub>2</sub> probe. The infrared sensor is housed within the vented section. This will be sealed by the PTFE fabric.



**Figure C.3** - PTFE fabric used for the modification from International Polymer Engineering, Inc. This model is 200-07-S-2 and was sealed at one end like a sock.



**Figure C.4** - PTFE sleeve adjacent to Vaisala pCO<sub>2</sub> probe, here attached to the cable. The First step of modification is to place the probe inside the PTFE sleeve



**Figure C.5** - Once the probe is inside the PTFE sleeve, secure the open end around the cable by wrapping the loose sleeve tightly and securing with zip ties. We have used 3 zip ties in alternating orientations.



**Figure C.6** - Trim the excess plastic from the zip ties. Make sure to be gentle with the PTFE tubing during this step – any abrasions or holes created may allow water to penetrate the sleeve and damage the sensor. If any holes in the PTFE fabric are identified, they must be patched during the next step of the modification process



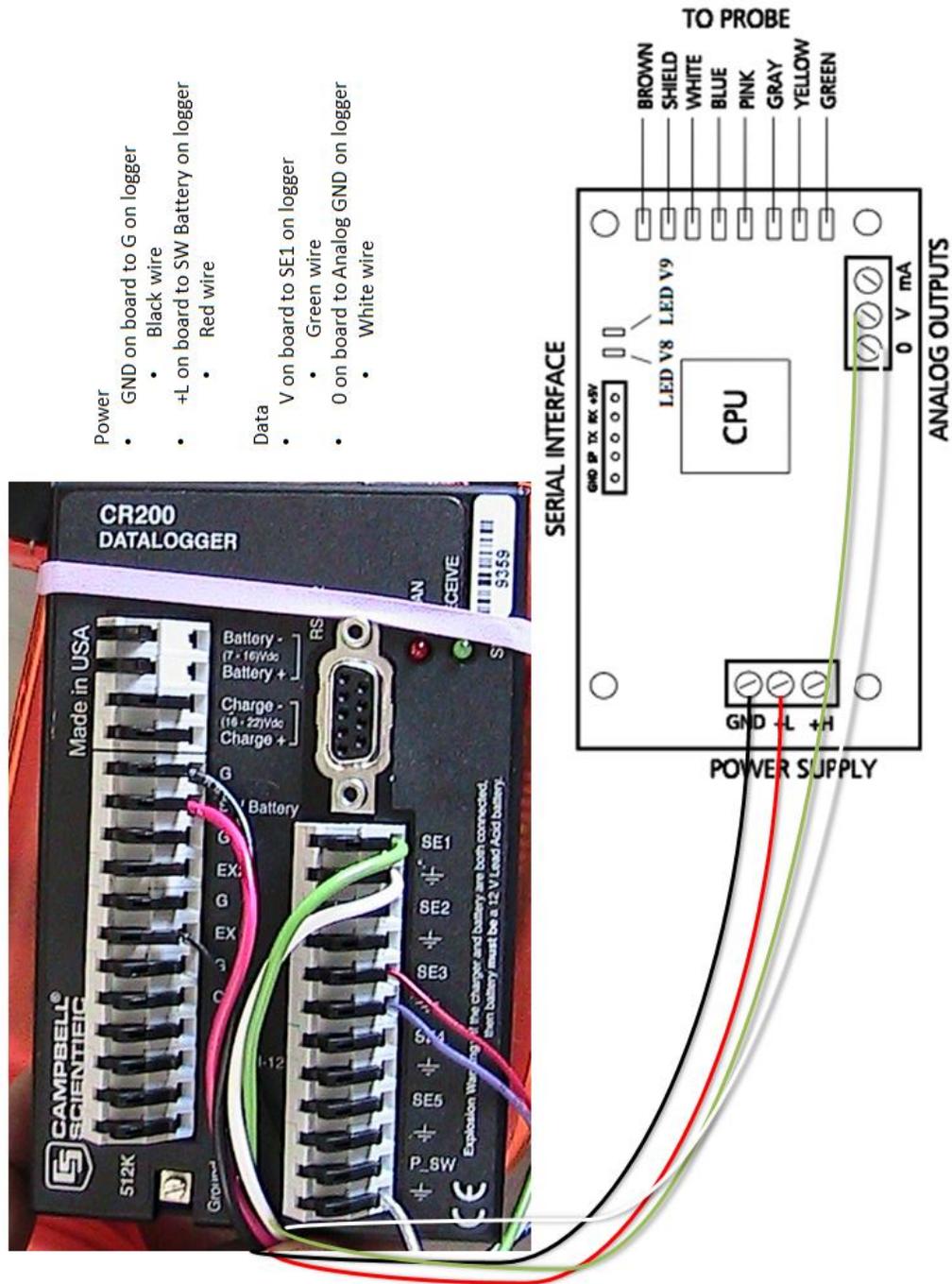
**Figure C.7** - Apply a thick but even layer of Liquid Tape (Plasti Dip International, USA) with the brush applicator around the edge of the PTFE fabric and cable and the zip ties. Make sure to cover all places where water could enter the sleeve.



**Figure C.8** - Apply the liquid tape above the zip ties and below the bottom of the PTFE. Look for any abrasions or rips in the fabric that require spot applications of liquid tape for waterproofing.



**Figure C.9** - After the first layer is applied, allow the probe to dry in a well-ventilated area (i.e., fume hood) for 4-5 hours. Reapply an additional 3 to 4 layers of liquid tape in the same location. Make sure to look for bubbles or holes in the dry liquid tape. It is critical that there is a complete seal over the end of the probe. Once the 4<sup>th</sup> or 5<sup>th</sup> layer of liquid tape has been applied and given sufficient time to dry, the probe is ready for field deployment.



**Figure C.10** - Schematic wiring diagram to connect a Vaisala GMM 220 pCO<sub>2</sub> probe to a Campbell C200 series data logger. The diagram on the upper right is the GMM 200 component board. Red and black wires are power supply and green and white are sensor output. The data logger needs to be attached to an external power source. We used a 12-V deep cycle car battery. Image courtesy of Dr. Mark Johnson.



**Figure C.11** - Data logger and GMM 220 deployed in the field. This box contains the data logger. Cables leaving the box lead to the probe and external power supply.



**Figure C.12** - GMM deployed in the field. Probe is attached to Styrofoam float below the surface of the stream. The cable leads to the data logger in the logger box in Figure C.11

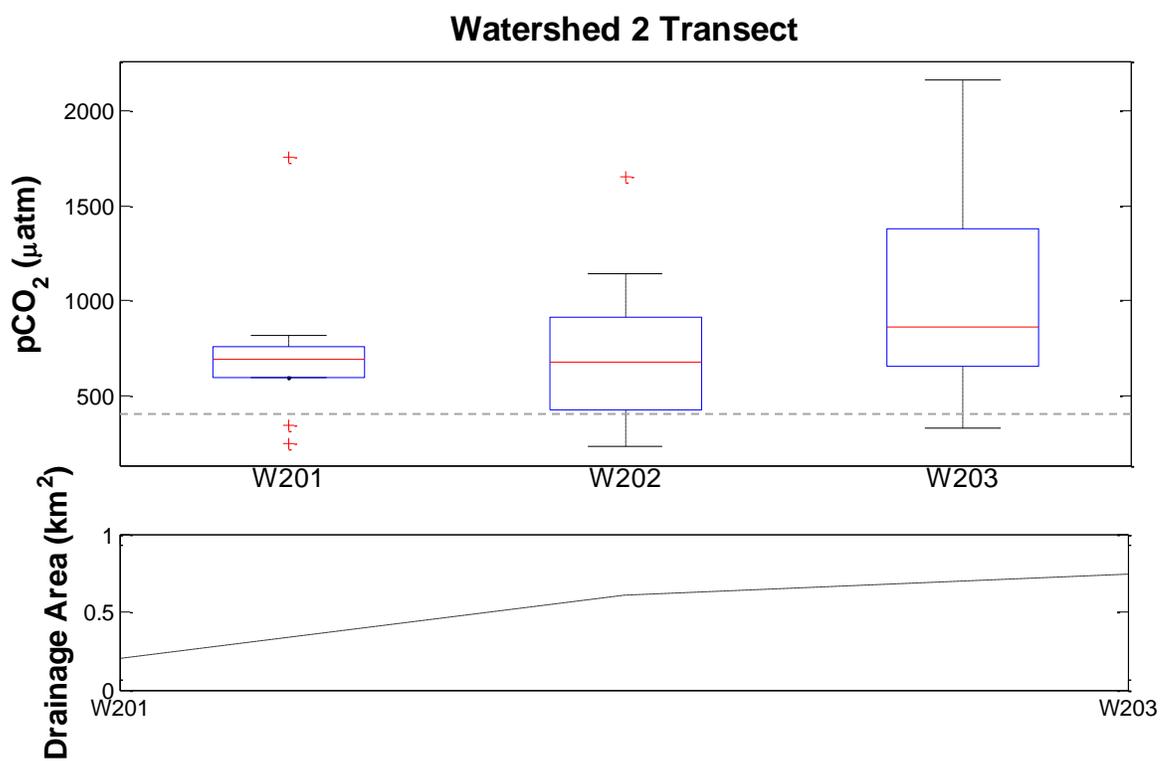
**Table C.1 - Material list for modified stream pCO<sub>2</sub> probe**

<b>Stream/hyporheic pCO<sub>2</sub> measurement shopping list - Materials for one modified probe</b>							
Roy Haggerty and Nick Dosch, May 2014							
	<b>Item</b>	<b>Code</b>	<b>link to item</b>	<b>Company</b>	<b>Description</b>	<b>Number</b>	<b>Aproximate unit cost</b>
1	NDIR Probe	GMM 220	<a href="http://www.vaisala.com/en/products/carbondioxide/Pages/GMM220.aspx">http://www.vaisala.com/en/products/carbondioxide/Pages/GMM220.aspx</a>	Vaisalla	This is the nondispersive infrared CO2 sensor	1	\$870
2	PTFE sleeve	200-07-S-2 F1	<a href="http://www.ipeweb.com/joomla/index.php/products/ptfe-tubes">http://www.ipeweb.com/joomla/index.php/products/ptfe-tubes</a>	International Polymer Engineering	This is the gas permeable but water impermeable sleeve to be fit to the outside of the probe before it can be submerged in water.	1	\$39
3	Campbell datalogger	CR200X	<a href="http://www.campbellsci.com/cr200x">http://www.campbellsci.com/cr200x</a>	Campbell Scientific	CO2 and Temperature datalogger	1	\$223
4	Temperature sensor	109-L	<a href="https://www.campbellsci.com/109-temperature">https://www.campbellsci.com/109-temperature</a>	Campbell Scientific	Temperature probe	1	\$108
5	Campbell Datalogger case	ENC 10/12R	<a href="https://www.campbellsci.com/enc10-12r-ordering">https://www.campbellsci.com/enc10-12r-ordering</a>	Campbell Scientific	Weatherproof Datalogger enclosure	1	\$120
6	plasti dip liquid tape	Liquid Tape 4 oz	<a href="http://www.plastidip.com/home_solutions/Liquid_Tape">http://www.plastidip.com/home_solutions/Liquid_Tape</a>	Plasti Dip International, Inc	Waterproof sealant to prevent water from entering the PTFE sleeve.	1	\$10

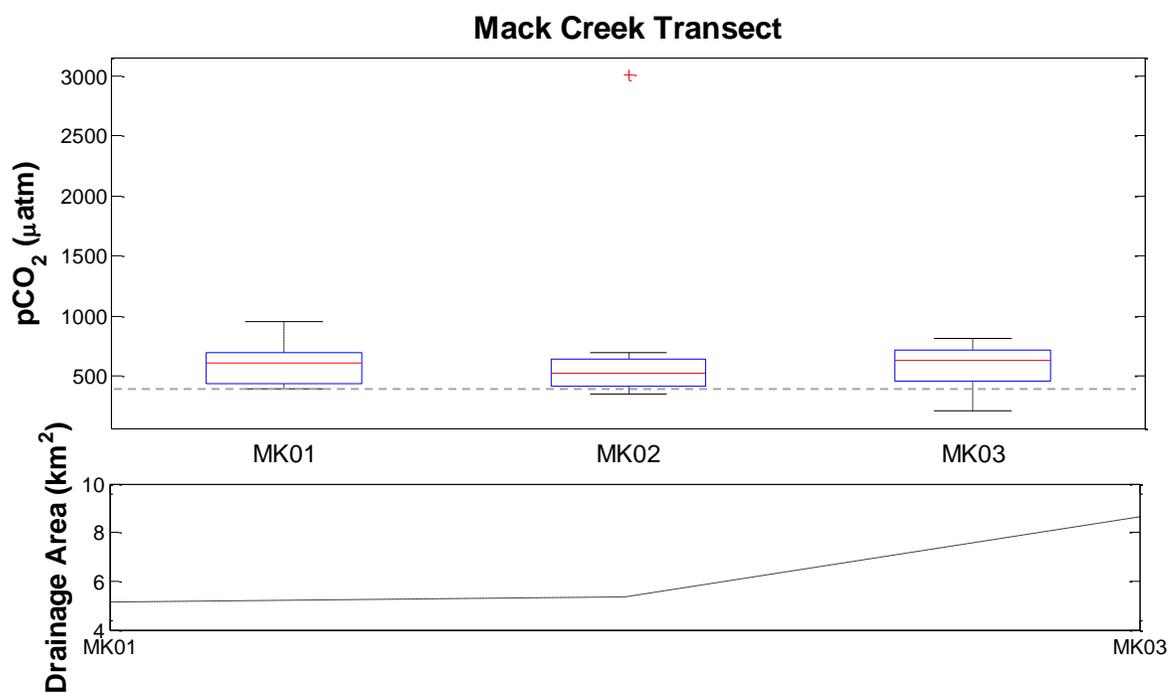
**Table C.2 - Additional items for probe modification**

<b>Additional items for construction/operation</b>		
	<b>Item</b>	<b>Purpose</b>
7	zip ties	To secure the the PTFE sleeve to the cable and get a partial seal between the two. Plasti-dip liquid tape is required to achieve a full seal
8	electrical wire	Connect the logger to the power supply and the logger to the component board of the GMM 220
9	2" pvc	To be zip-tied around the modified probe with holes drilled for probe protection if deployed in stream
10	Deep cycle 12 volt battery	To power the system
11	Battery maintainer	If there is AC power nearby, this has been a useful item for us to keep a constant charge in the batteries

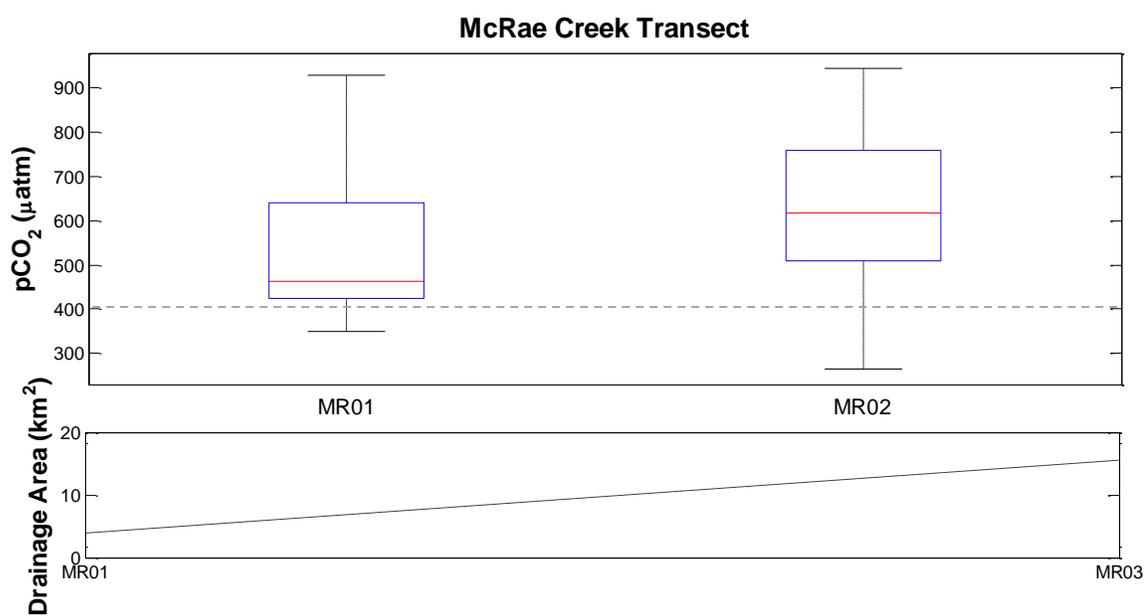
## Appendix D Additional Figures and Tables Chapter 2



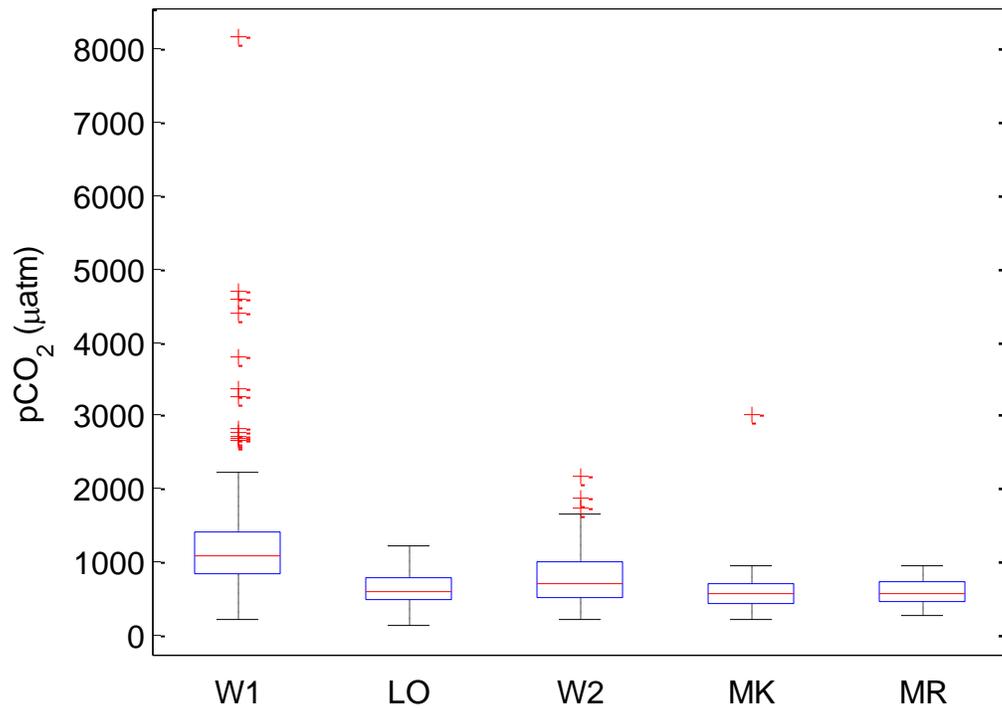
**Figure D.1** - Longitudinal pCO<sub>2</sub> profile variability and contributing transect drainage area. Box plots show medians (red lines), quartiles (boxes), 90 percent confidence intervals (whiskers) and range (red plus symbols) of measured pCO<sub>2</sub> in Watershed 2 transect. The grey dotted line represents atmospheric concentrations of CO<sub>2</sub>.



**Figure D.2** - Longitudinal  $p\text{CO}_2$  profile variability and contributing transect drainage area. Box plots show medians (red lines), quartiles (boxes), 90 percent confidence intervals (whiskers) and range (red plus symbols) of measured  $p\text{CO}_2$  in Mack Creek transect. The grey dotted line represents atmospheric concentrations of  $\text{CO}_2$ .

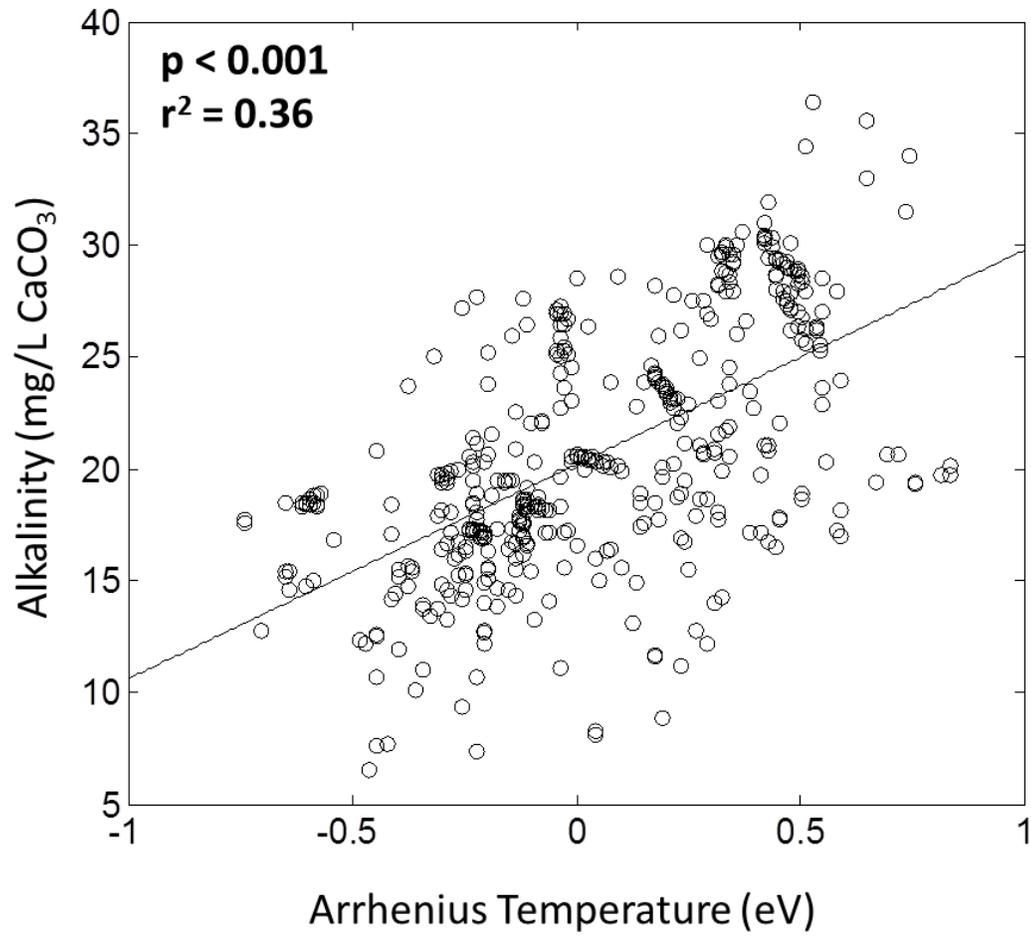


**Figure D.3** - Longitudinal  $p\text{CO}_2$  profile variability and contributing transect drainage area. Box plots show medians (red lines), quartiles (boxes), 90 percent confidence intervals (whiskers) and range (red plus symbols) of measured  $p\text{CO}_2$  in McRae Creek transect. The grey dotted line represents atmospheric concentrations of  $\text{CO}_2$ .



**Figure D.4** - Box plots show medians (red lines), quartiles (boxes), 90 percent confidence intervals (whiskers) and range (red plus symbols) of measured pCO<sub>2</sub> in the 5 longitudinal transects. W1 and W2 are significantly different than the other transects (One-way ANOVA test,  $p < 0.001$ )





**Figure D.6** - Linear regression of Arrhenius temperature normalized to a reference temperature (15 °C) and carbonate alkalinity.

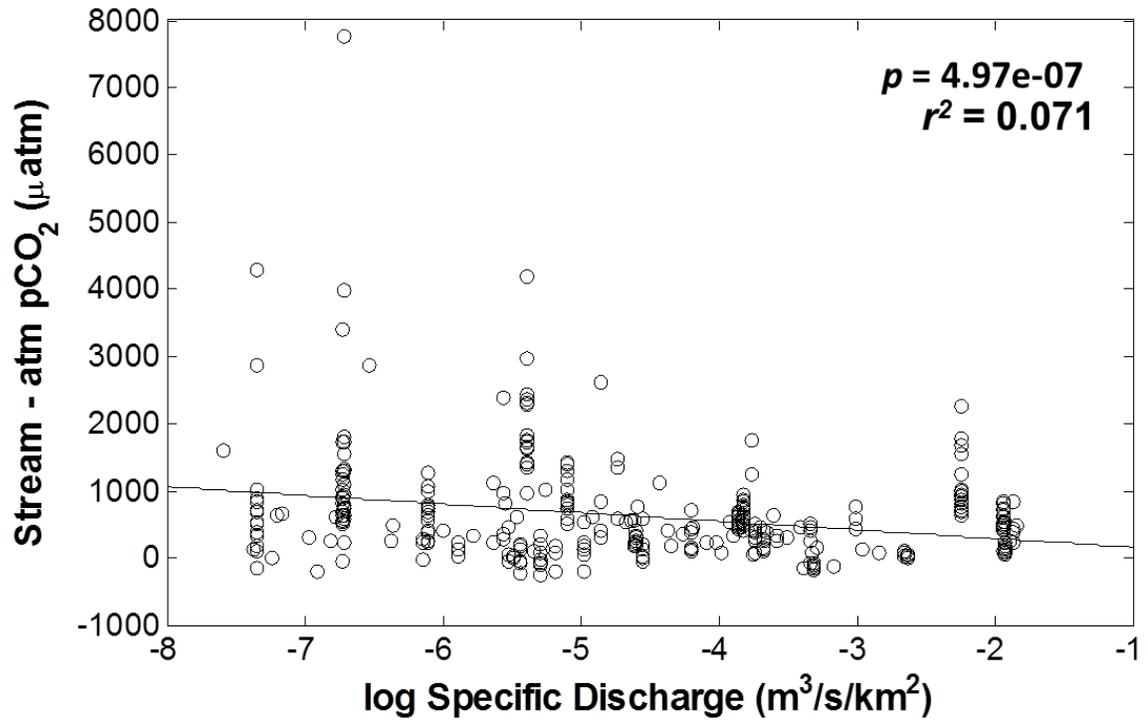
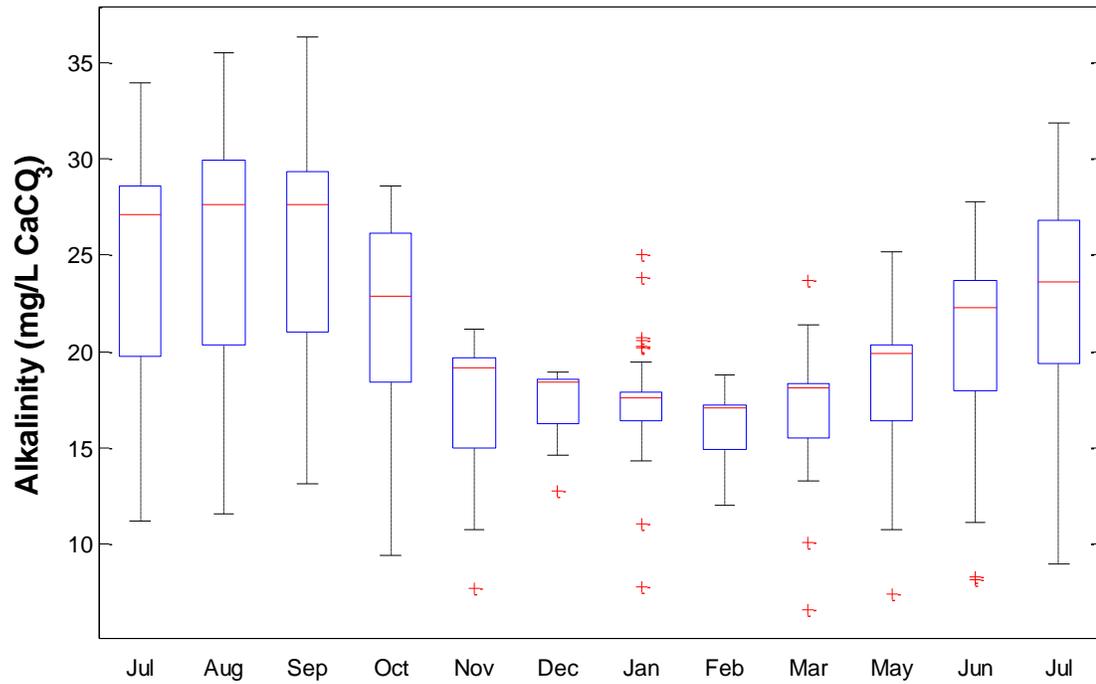
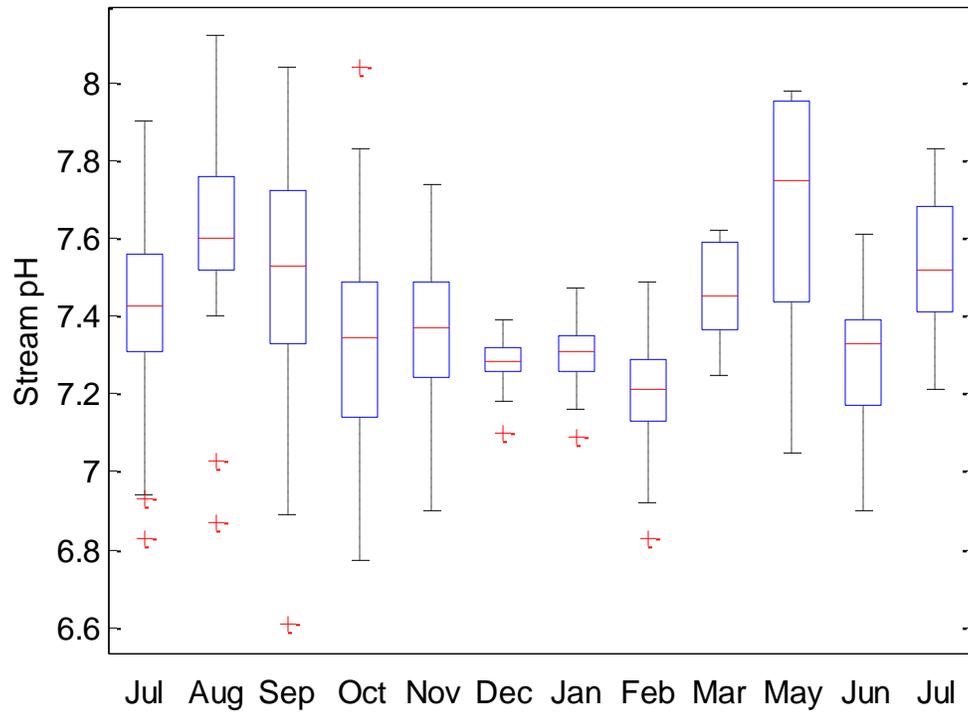


Figure D.7 – Regression between the log of specific discharge and excess stream pCO<sub>2</sub>



**Figure D.8** - Annual variation in stream carbonate alkalinity from the Lookout Creek drainage network from July 2013 to July 2014. Box plots show medians (red lines), quartiles (boxes), 90 percent confidence intervals (whiskers) and range (red plus symbols) of measured alkalinity.

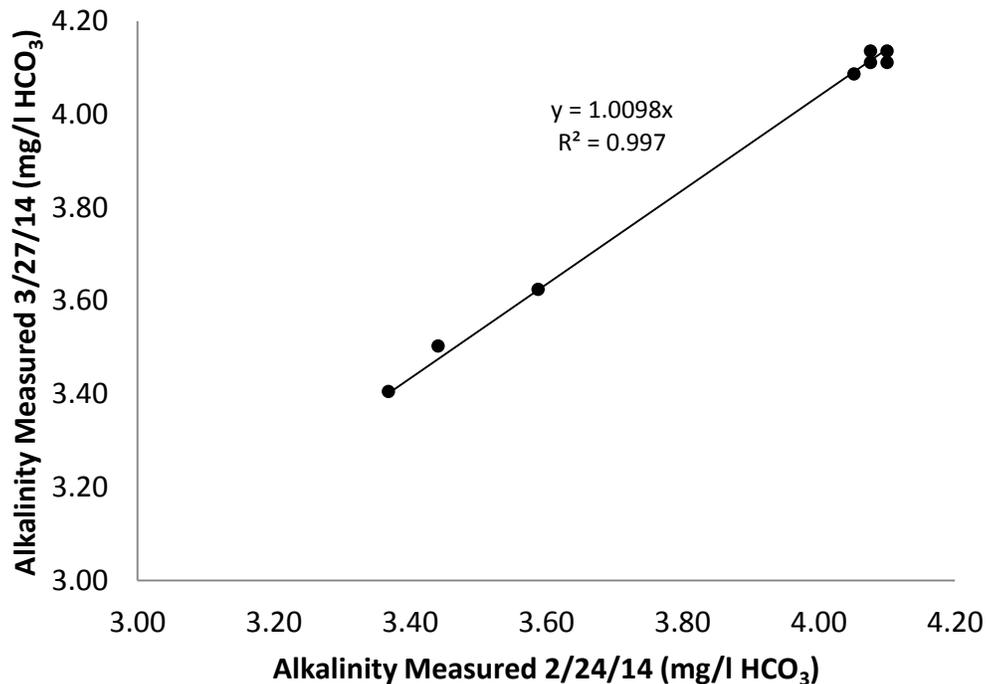


**Figure D.9** - Annual variation in stream pH and from the Lookout Creek drainage network from July 2013 to July 2014. Box plots show medians (red lines), quartiles (boxes), 90 percent confidence intervals (whiskers) and range (red plus symbols) of measured pH.

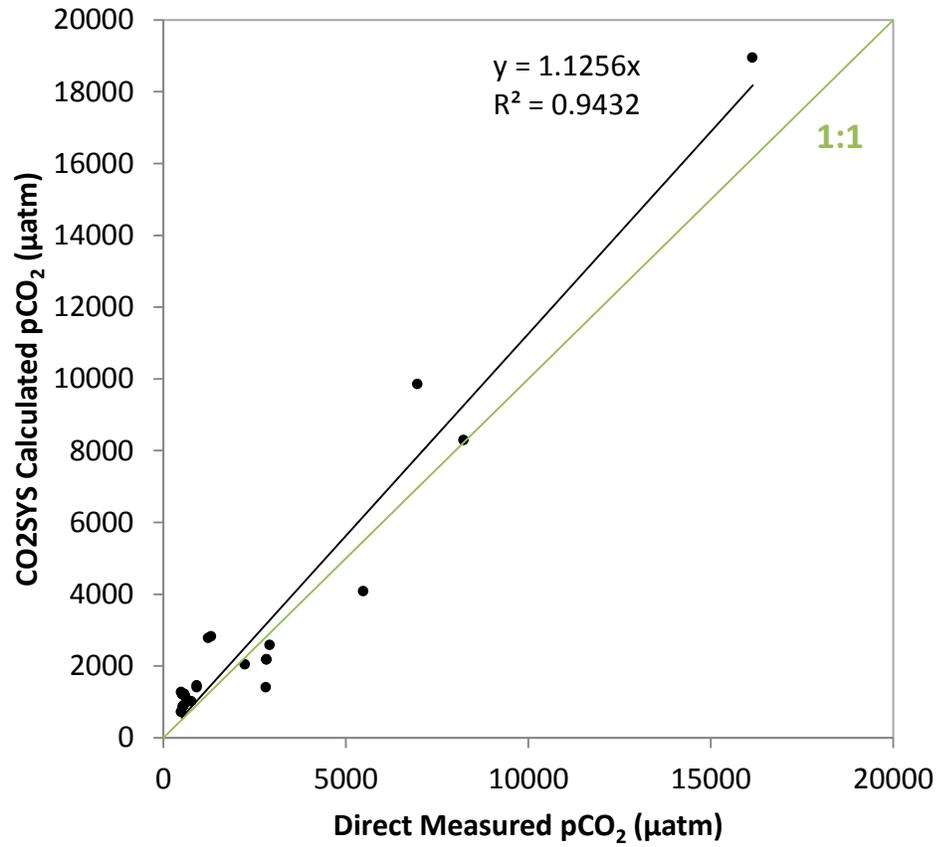
**Table D.1** - Time sensitivity error analysis in laboratory determination of carbonate alkalinity. 8 random samples from the February sampling round were selected and processed again 31 days later.

Sample Location	$\text{HCO}_3\text{-C}$ (mg/L)	
	2/24/2014	3/27/2014
W203	3.62	3.59
W109	4.11	4.10
W1001	4.11	4.08
W110	4.09	4.05
W112	4.14	4.08
LO07	3.50	3.44
LO06	3.41	3.37
W108	4.14	4.10

### Measured Alkalinity 2/23/14 vs. 3/27/14



**Figure D.10** - Alkalinity time sensitivity regression. Samples processed 31 days later show good agreement with samples processed according to standard procedure.



**Figure D.11** - Directly measured pCO<sub>2</sub> and pCO<sub>2</sub> calculated with CO2SYS regression. The green line is the 1:1 line, simulating a perfect relationship. The regression indicates that calculated pCO<sub>2</sub> slightly over predicts direct measurements of pCO<sub>2</sub>.