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CONTROLS ON VARIABILITY OF DISSOLVED GREENHOUSE GAS CONCENTRATION AND EMISSIONS FROM SMALL STREAMS IN SOUTHEASTERN NEW HAMPSHIRE

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BY

JASON BAILLIO

B.A., College of the Holy Cross, 2010

THESIS

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Submitted to the University of New Hampshire in partial fulfillment of the requirements for the degree of

Master of Science

In

Natural Resources: Water Resources

December, 2012

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Abstract

Controls on Variability of Dissolved Greenhouse Gas Concentration and Emissions from Small Streams in Southeastern New Hampshire

by

Jason Philip Baillio

University of New Hampshire, December, 2012

Thesis Advisor: William H. McDowell

Small streams often present the first opportunity for dissolved greenhouse gases to exchange with the atmosphere and can be potential hot spots for evasion. In this study three streams in southeastern New Hampshire representing differing landuse were monitored for emissions of nitrous oxide, methane, and carbon dioxide. Average emission rates of N₂O varied from -84 µg N m⁻² day⁻¹ to 2,561 µg N m⁻² day⁻¹ and correlated strongly with NO₃⁻ concentration. One stream, Rum Brook, was found to be a net sink for N₂O from the atmosphere. Methane emissions varied from 1.1 mg C m⁻² day⁻¹ to 21 mg C m⁻² day⁻¹ and were highest at Rum Brook. Controls on CO₂ evasion varied between sites with rates ranging from 569 to 1637 mg C m⁻² day⁻¹. Results indicate greenhouse gas evasion from small streams respond to a variety of biogeochemical drivers, resulting in broad temporal and spatial variation.

Chapter 1

Introduction

Atmospheric concentrations of nitrous oxide (N_2O) , methane (CH_4) , and carbon dioxide (CO₂), continue to rise and feed the greenhouse effect contributing to global warming. Primarily due to an increase in these greenhouse gases in the atmosphere, average global temperatures have risen 0.74 °C over the last 100 years (IPCC, 2007). Anthropogenic activities are largely responsible for the increase in these gases as production rates have escalated from preindustrial time to the present. Direct production of carbon dioxide through burning of fossil fuels and industrial processes comprise the majority of emissions; in the United States 94.5 % of carbon dioxide emissions were from burning fossil fuels in 2010 (EPA, 2012). In addition, humans have also indirectly affected production of these gases in significant ways. The rapidly increasing population has led to intensification in agriculture, deforestation, energy demand, and waste production. Globally, non-fossil fuel sources of carbon dioxide to the atmosphere contribute 20% to the greenhouse effect, nitrous oxide contributes 8%, and methane contributes 14%, all of which are heavily influenced by human activities indirectly (IPCC, 2007).

Nitrous Oxide

Humans have altered the nitrogen cycle by adding large quantities of nitrogen fertilizer and producing human waste. These additions have led to an increase in reactive

nitrogen of 120% since 1970, largely due to an increase in agriculture to feed the growing population (Galloway et al., 2008). This increased load of nitrogen has resulted in greater production of nitrous oxide (N₂O) through both denitrification and nitrification and greater evasion rates to the atmosphere (Seitzinger, 1998). Denitrification is an anaerobic process carried out by denitrifying bacteria which reduces nitrate NO_3^- to atmospheric nitrogen and releases a small fraction as N₂O. Nitrous oxide is also created during nitrification, or the process of oxidizing ammonium to nitrate by nitrifying bacteria (Cole and Caraco, 2001; Seitzinger, 1998).

Nitrous oxide, which has a greenhouse potential 310 times that of CO_2 , has increased from a preindustrial concentration of 270 ppbv in 1750 to 314 ppbv in 2000 (IPCC, 2007). Nitrous oxide is also harmful because it reacts with and depletes stratospheric ozone in the atmosphere which protects against UV radiation (Vitousek et al., 1997). Denitrification of NO₃⁻ by denitrifying bacteria in soils produces N₂O which can be carried away by runoff and groundwater into surface streams. Runoff of excess NO₃⁻ and waste from agricultural fields, lawns, septic systems and other sources is also carried directly to streams. This nitrate can be denitrified under anoxic conditions in the riparian zone and within stream bed sediments. Nitrification of ammonium (NH₄⁺) in organic rich stream sediments can also supply NO₃⁻ for denitrification (Seitzinger, 1998).

Studies attempting to estimate denitrification rates in small streams have produced varying results. An experimental approach conducted on stream sediment from headwater streams in the Appalachian mountain region did not show significant removal of nitrogen via denitrification (Martin et al., 2001). However, contradictory results were found by

both Steinhart et al. (2001) and Bernhardt and Likens (2002). Their results showed a large portion of nitrogen input to streams can be permanently removed through denitrification, largely from areas with sediments that are rich in organic matter, such as debris dams where organic matter accumulates. Denitrification within the floodplain and stream sediment has been shown to remove significant quantities of nitrate from groundwater flow to rivers as well. A study in Greeley, Colorado found that denitrification can remove a significant amount of nitrogen from groundwater with a high concentration of NO_3^- due to fertilizer application and irrigation for agriculture (McMahon and Bohlke, 1996).

A positive relationship has been found between NO_3^- concentration and dissolved N_2O in small streams (Difranco, 2009; Martin et al., 2001; Beaulieu et al., 2010). A carbon source is also necessary for denitrification to occur but there has been conflicting results on the effects of increased dissolved organic carbon (DOC) concentrations on denitrification rates in streams. No significant increase in denitrification rates was found after addition of DOC in a forested headwater stream at Hubbard Brook in central New Hampshire (Bernhardt and Likens, 2002). Similarly, two streams in the Appalachian Mountains, Walker Branch and Noland Creek, showed no increase in denitrification with DOC enrichment (Martin et al., 2001). Interestingly, tributaries along the Lamprey River in southeastern New Hampshire did show a strong negative relationship between in stream DOC concentration and N₂O (Difranco, 2009). Pfenning and McMahon (1996), on the other hand, demonstrated strong experimental evidence that denitrification in river sediments with high nitrate levels can be limited by available organic carbon.

Nitrous oxide production is also influenced by seasonal and chemical changes in the stream. Increased temperature may allow for greater microbial activity and thus greater denitrification rates as long as nitrate is available (Seitzinger, 1998; McMahon and Pfenning, 1996). Increased nitrate loading carried with spring snowmelt has been shown to result in greater denitrification rates (Beaulieu et al., 2009). Changes in the pH of a stream may also play a role in how much N₂O is produced. Lowering of pH has been shown to influence the ratio of N₂O:N₂, with more acidic conditions allowing for greater production of N₂O; although it still remains a very small fraction compared to N₂ (Seitzinger, 1998).

A wide range of emission rates for N₂O from small streams has been reported in the literature (Beaulieu et al., 2010) and so more information could prove helpful in identifying broad control factors. With their shallow water small streams may contain higher concentrations of N₂O due to increased contact of water with bottom sediment. Also, small headwater streams often receive runoff linked to terrestrial nutrient sources and shallow groundwater first, which may contain very high concentrations of both NO₃⁻ and N₂O. Emissions of N₂O could be higher in small streams due to more interaction of water with the atmosphere as well, especially in fast moving turbulent streams. Streams have been shown to be typically supersaturated with N₂O and therefore are most often a source to the atmosphere (Cole and Caraco, 2001; Baulch et al., 2011a)

Figure 1: Basic diagram of stream nitrogen cycling



<u>Methane</u>

Methane has increased in the atmosphere from 715 ppb at preindustrial levels to a concentration of 1,774 ppb in 2005 (IPCC, 2007). As a greenhouse gas it is 21 times more potent than carbon dioxide (IPCC, 2007). It is produced naturally in the environment by methanogenesis, an anaerobic process carried out by archaea under reduced anoxic conditions (Jones and Mulholland, 1998a; De Angelis and Lilley, 1987). A significant amount of dissolved CH₄ can also be removed from streams and rivers through oxidation by methanotrophic bacteria; Jones and Mulholland (1998a) reported that between 2.2 and 21.1% of dissolved CH₄ in streams could be removed due to this process.

Wetlands and estuaries are a well-studied source of CH₄ to the atmosphere (EPA, 2010; Abril and Borges, 2004). Decomposition of organic rich sediment and the anoxic

conditions favor methanogenesis in these environments. However, there has been little research on CH₄ emissions from small streams and rivers, which could potentially be a significant source as they have frequently been shown to be supersaturated with CH₄ with respect to the atmosphere (Billet and Moore, 2007; Hope et al., 2004; de Angelis and Lilley, 1987). Recent research conducted by Bastviken et al. (2011) has shown total emissions of CH₄ from freshwater systems may exceed 103 Tg per year with rivers contributing 1.5 Tg of CH_4 per year. This report is likely an underestimate as emissions from small streams were not included. It is important for estimates of CH₄ emissions from freshwater to take streams into account because they often receive input from supersaturated sources first and may provide the first opportunity for CH₄ to degas. Emissions of CH₄ to the atmosphere from streams may also be underestimated due to episodic release of CH₄ through ebullition which is difficult to monitor. It has been estimated that 20-67% of CH₄ emissions from streams may occur through ebullition (Baulch et al., 2011c) yet few studies have attempted to monitor this in calculating flux from streams.

A study conducted at Walker Branch in Tennessee found the largest contributor of CH₄ to streams was from subsurface flow draining forested or agricultural soils (Jones and Mulholland, 1998a). Deep groundwater and production in stream bed sediments were found to be an insignificant source of CH₄ to streams dominated by shallow groundwater flow (Hope et al., 2004; Jones and Mulholland, 1998a). It has been shown that very little CH₄ is typically produced in the hyporheic zone because the sediment is more oxygenated due to contact with surface water (Jones and Mulholland, 1998a, Jones et al., 1995). Also, deep groundwater will have less contact with organic rich shallow soil

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where decomposition occurs and so it typically carries a much lower concentration of dissolved CH₄. The few existing studies on small streams show terrestrial sources of CH₄ and production in anoxic riparian soils produce the majority of CH₄ which is transported to streams via shallow groundwater (Hope et al., 2001; Jones and Mulholland, 1998a,b; Jones et al., 1995). Supersaturation of dissolved CH₄ in large rivers has also been attributed to lateral flow from forest and agricultural soils and not due to production in river bottom sediment (De Angelis and Lilley, 1987).

During summer months when temperatures increase biological decomposition also increases and more CH₄ may be produced in soils and transported to streams (Billet and Moore, 2007; Jones et al., 1995). An increase in stream flow during spring snowmelt could potentially dilute CH₄ from soil runoff and reduce methane concentrations in streams (Hope et al., 2004). Beaver dams have also been linked to increased dissolved CH₄ production. Decomposition of the organic rich sediments at the bottom of beaver ponds as well as reduced turbulence likely can increase the concentration of dissolved CH₄ and CO₂ in streams (Billet and Moore, 2007).





Carbon Dioxide

The global average concentration of atmospheric CO_2 has increased by over 100 ppm from pre-industrial levels and continues to increase at an even faster pace (IPCC, 2007). In 2005 CO_2 levels were recorded at 379 ppm, an increase of 19 ppm over 10 years from 1995 levels (IPCC, 2007). Carbon dioxide is produced through respiration from bacteria, roots, and other organisms in both terrestrial and aquatic environments. Other potential sources of CO_2 to surface waters include exchange with the atmosphere and dissolution of carbonate minerals from underlying bedrock in groundwater (Hope et al., 2004; Worral et al., 2005). Dissolved CO_2 in streams can be supplied both from runoff of soil respiration as well as from instream production (Kling et al., 1991). However, groundwater is regularly supersaturated with CO_2 and is often the most important contributor to small streams (Jones and Mulholland, 1998b; Kling et al., 1991).

Research has shown that streams are normally supersaturated with CO₂ with respect to the atmosphere (Billet and Moore, 2007; Hope et al., 2004). As such, degassing of CO₂ from turbulent streams could represent a substantial fraction of the total carbon released (Butman and Raymond, 2011; Hope et al., 2004; Worral and Burt 2005). The amount of carbon dioxide dissolved in streams is influenced largely by temperature, flow, and to a lesser extent pH. Production of CO₂ through soil respiration is strongly correlated with change in temperature. Increased temperatures result in more active bacteria and could result in higher respiration rates during summer months. The water table is also lower during summer which allows for a greater aerobic zone in the soil for respiration to occur (Worral and Burt, 2005). This, combined with longer residence time of water during low flow in the summer can lead to higher evasion rates of CO₂ to the atmosphere. However, during severe drought conditions there may be less runoff and shallow groundwater flow to carry dissolved CO₂ to streams (Worral and Burt, 2005). For the majority of the year, streams often receive a large percentage of flow directly from groundwater. Groundwater is typically supersaturated with CO₂, and this potentially makes turbulent small streams important hot-spots for degassing to the atmosphere as it is the first opportunity for evasion after emerging from the ground (Hope et al., 2001).

Flux and Reaeration

In order to calculate flux (F) of a dissolved gas to the atmosphere it is necessary to calculate a gas transfer velocity (k) which is then multiplied by the difference between

the water concentration (*Cw*) and the concentration of the gas at equilibrium with atmospheric air (*Ceq*) (Clark et al., 1994; Wanninkhof and Knox, 1996; Beaulieu et al., 2010; Raymond and Cole, 2001). The gas transfer velocity in units of length per time is calculated by the product of the reaeration coefficient (K or k_2) and stream depth (Raymond et al., in press; Baulch et al., 2011).

Estimating a reaeration coefficient for small streams has been attempted using a number of different methods. Using the direct gas tracer method, frequently with either propane or sulfur hexafluoride (SF_6) , is considered the most accurate of these as it directly measures loss of the gas over time. The evasion rate of the tracer gas is easily corrected to evasion rates for other gases in question based on a ratio of their Schmidt numbers which is calculated based on the diffusion coefficient of each respective gas and the kinematic viscosity of water (Mulholland et al., 2004; Wanninkhof, 1992). Other studies have relied on floating chambers to estimate K but this method blocks wind disturbance from the surface which is potentially an important process for influencing stream to atmosphere exchange (Billet and Moore 2007; Clark et al., 1994). Previous research has shown that turbulence is the dominant factor in determining evasion rates from streams; therefore mathematical approaches to estimating reaeration have been developed based on slope, velocity, average depth, and width of streams (Raymond et al., in press). However, in small streams there is often large variability in stream geometry and these parameters can be difficult to accurately define.

Study Goals

Measurements reporting total greenhouse gas emissions from small streams which compare combined emissions of N_2O , CH_4 , and CO_2 from streams is lacking in the literature. Small streams are often the first opportunity for dissolved gases in groundwater to be exposed to the atmosphere, therefore small streams have the potential to significantly contribute to greenhouse gas emissions, either as a conduit of terrestrially produced gases or through in stream production. The purpose of this study is to try and measure greenhouse gas concentration and evasion from small streams in New Hampshire representing a variety of landuse patterns. Both spatial and temporal variability of dissolved greenhouse gas concentrations within stream transects were also investigated. Specifically my objectives are as follows:

Objective 1:

Measure the concentrations of dissolved CO_2 , N_2O , and CH_4 across landuse patterns in three streams within the Lamprey River Watershed and compare these concentrations to stream water chemistry. Investigate spatial variation within each stream along a transect reach.

Hypothesis:

Sampling locations containing elevated NO₃⁻ concentrations will have increased denitrification and thus higher concentrations of dissolved N₂O. Higher DOC concentrations may also lead to higher rates of respiration and thus higher concentrations of CO₂.

<u>Objective 2:</u>

Calculate and quantify the emissions of the greenhouse gases CO_2 , N_2O , and CH_4 from three streams in the Lamprey River watershed and observe temporal patterns related to changes in stream discharge, temperature, and chemistry.

Hypothesis:

Streams will emit the highest concentrations of dissolved CO_2 , and CH_4 to the atmosphere during summer months when temperature is highest. Increases in N₂O will likely depend on changes in NO₃⁻ concentration. An increase in stream turbulence will also lead to an increase in emission due to more interaction with the atmosphere.

Chapter 2

Materials and Methods

Study Area

Three streams representing a variety of landuse and water chemistry characteristics were chosen from within the Lamprey River watershed area in southeastern New Hampshire. Wednesday Hill Brook (WHB) is a first order stream located in the town of Lee in a suburban setting with a population density of 157 people per km^2 . The stream drains a basin surrounded by homes on septic systems and has been shown to have an elevated concentration of NO₃. A transect including a range of geomorphic features with a length of 220 m was established beginning 50m downstream of a culvert where the stream crosses Wednesday Hill Road. The stream bed sediment was made up mostly of cobble and boulders at the upstream sampling location. Approximately 110 m further downstream was the middle sampling station characterized as having large gravel with some coarse sand and fine gravel. The downstream sampling station was approximately another 110 m further downstream and stream bed sediments at this location were mostly fine gravel and coarse sand (Truslow, 2009). The first half of the transect alternated between riffles, chutes and runs with a number of log dams creating cascades entering pools. The second half of the transect had a lower gradient (Truslow, 2009) and was characterized mostly by chutes and runs with a few debris dams resulting in cascades.

Rum Brook (RMB) is a tributary to the Lamprey River located in Epping, New Hampshire. A stream transect of 150 m was used to include a range of geomorphology influence. Rum Brook is also downstream of a number of wetlands. Stream bed sediment at Rum Brook was composed of boulders and cobble throughout the study transect. Only one large cascade located between the upstream and middle sampling locations was present in the Rum Brook transect. There was much less variability in geomorphology at Rum Brook compared with Wednesday Hill Brook but it roughly followed a riffle-run pattern. A beaver dam was created in July of 2011 upstream of the sampling transect and was removed sometime between November and December 2011.

Burley Demeritt Creek is a first order stream which drains part of the University of New Hampshire Organic Dairy Farm in Lee. It drains pastureland on the farm and has a forested riparian buffer zone that is approximately 50 m next to the pasture and increases to 1000 m downstream (Dunlap, 2010). The stream at Burley Demeritt is also directly downstream of a wetland located next to the farm. A 150 m transect was established at Burley Demeritt beginning approximately 300 m upstream of where the stream meets the Lamprey River. The beginning of the transect was also located about 100 m downstream of an intermittent tributary draining the pasture. Burley Demeritt Creek is a slow moving stream for most of the year at normal flow conditions and was composed mainly of runs with a riffle present before the middle sampling station. Stream bed sediment at the upstream sampling location at Burley Demeritt was mostly made up of sand. The middle sampling station was made up of clay with cobble, and the downstream sampling station was mostly sand (Dunlap, 2010). The soil surrounding and underneath Burley Demeritt is clay (Dunlap, 2010). The downstream sampling station is also located in a floodplain (Galvin, 2010).

The entire Lamprey River watershed encompasses 479 km² and is located within the towns of Barrington, Brentwood, Candia, Deerfield, Durham, Epping, Exeter, Fremont, Lee, Newfields, Newmarket, Nottingham, and Raymond. The main stem of the river averages a population density of about 53 people per km² and although the majority of the watershed is forested (68.3%), the area is developing at a fast pace and is becoming more populated.

Figure 3: Location of the monthly study streams located within the Lamprey River watershed in Southeastern New Hampshire.



Sample Collection

Three streams representing different landuse patterns were sampled approximately monthly for concentrations of dissolved greenhouse gases and stream chemistry from May 2011 until April 2012. During March and April when high flows were anticipated streams were sampled bi-weekly in order to look at changes in chemistry more frequently. Reaeration measurements at each of these streams were also performed seasonally. Triplicate water samples taken at each station for both monthly and weekly samples were averaged and one value for each station was then reported.

Stream Dissolved Chemistry

Measurements of dissolved oxygen (DO), water temperature, specific conductivity, and pH were recorded at each sampling date using a YSI meter. Stream chemistry was assessed with water samples collected for nitrate (NO₃⁻), ammonium (NH₄⁺), chloride (CI⁻), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC). Water samples to be analyzed for nutrient concentrations were collected in previously acid washed 60 mL syringes and then stored in 60 mL bottles. Syringes were washed three times with stream water before filling. Water samples were passed through a 0.7 μ m Whatman glass fiber filter and then frozen in the lab before being analyzed. All samples were analyzed for NH₄⁺ using automated colorimetry with a WestCo Scientific SmartChem 200 discrete analyzer in the Water Quality Research Laboratory at the University of New Hampshire. Both Cl⁻ and NO₃⁻ were analyzed using ion chromatography (Anions/Cations Dionex ICS-1000). Samples for TDN and DOC were analyzed using high temperature catalytic oxidation (Shimadzu TOC-V with a TNM-1 nitrogen analyzer).

Gas Collection and Analysis

Water samples to be analyzed for dissolved gases were collected in triplicates at each sampling station using previously acid washed 60 mL syringes that were rinsed three times with stream water prior to use. In order to eliminate air bubbles the syringes were filled to 30 mL with water, cleared of air bubbles and then emptied under water before being refilled to 30 mL and closed off while still underwater. Before analysis each syringe containing the 30 mL water sample was injected in the lab with 30 mL of Helium following the methods used by Difranco (2009). Syringes were then shaken for 5 minutes to equilibrate the water and headspace. The 30 mL equilibrated head space was then injected into 20 mL pre-evacuated vials to be analyzed by gas chromatography. Samples were stored under refrigeration and were analyzed within 1 month of collection. Dissolved gas concentrations were measured using a Shimadzu GC-2014 gas chromatograph equipped with a flame ion detector (FID) to detect CH₄, an electron capture detector (ECD) used to detect N₂O and SF₆, and a thermal conductivity detector(TCD) used to detect CO₂. For N₂O analysis standards of 0.1, 1, and 10 ppm were used. Standards of 255 ppm, 1000 ppm, and 1990 ppm were run for CO₂, and standard concentrations of 10 ppm and 101 ppm were used for CH₄ analysis. Pure Helium was also run and included as blanks for each analysis.

Gas Evasion

Reaeration was measured seasonally in the summer, fall, and spring using the direct gas tracer method with SF_6 as a conservative gas tracer. An SF_6 injection site was established approximately 50 m upstream of the beginning of the established transect to allow time for the gas to completely mix. SF_6 was pumped from a tedlar bag using a peristaltic pump. It was distributed through plastic tubing and released through an air stone located in a deep location such as a pool to allow more time for the SF_6 to dissolve. Rhodamine dye was also added as a hydrologic conservative tracer along with the gas

tracer in order to make sure that the dissolved SF₆ had traveled the length of the reach before samples were taken. The rhodamine solution was pumped at a rate of approximately 100 ml/minute into the stream where it was allowed to completely mix with SF₆ in the water before reaching the beginning of the transect. Hydrolab probes put in place at the upstream and downstream stations were used to detect the peak in rhodamine tracer between the upstream and downstream locations which was used to calculate travel time and dilution across the transect. Once rhodamine had reached peak levels across the transect, triplicate water samples for dissolved SF₆ and greenhouse gas concentrations were collected at the upstream, middle, and downstream stations. Measurements of stream width were taken every 10m along the transect to estimate average width of the stream channel. Average depth of the stream was then calculated by dividing discharge by width and average velocity over the transect based on travel time of rhodamine.

In order to calculate a reaeration coefficient (K_{SF6}), the difference in the natural log concentration of SF₆ at the upstream and downstream station after being corrected for dilution was divided by the travel time (t) across the transect. This equation was modified from the equation used by Jones and Mullholland (1998a) where they were using propane as the gas tracer and specific conductance rather than rhodamine as the conservative tracer to account for dilution.

$$K_{SF6} = t^{1} x Ln \frac{[SF6up][rhodamine down]}{[SF6down][rhodamine up]}$$

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The reaeration coefficient K_{SF6} was then converted to a reaeration coefficient for the gas in question based on the ratio of their Schmidt numbers determined at stream temperature (Wanninkhof, 1992). The reaeration coefficient K was then converted to a gas transfer velocity k by multiplying by average stream depth. An average K value was determined for each stream and used to calculate flux (see calculations). No K value was determined at Wednesday Hill Brook in the spring and so an average of summer and fall was used.

It is difficult to obtain a K value and there can be a large amount of error associated with estimates. Therefore, calculations based on stream characteristics were also utilized to define K with mathematical equations. Raymond et al. (In Prep) found that equations that included average stream velocity (V), depth (D) and slope (S), were the best models for predicting reaeration in small first order streams. Therefore, the following equations from Raymond et al. (In Prep) were used to compare between modeled and measured K values in order to try and estimate the possible range of fluxes from each stream.

Equation 1: $k600 = (VS)^{0.89} * D^{0.54} * 5037$ Equation 2: $k600 = 5937 * (1-2.40F^2) * (VS)^{0.89} * D^{0.58}$

The F term represents the Froude number $(F=V/(gD)^{0.5}$ where g is the acceleration due to gravity (Raymond et al., In Prep). Slope was determined using 30 m digital elevation maps based on elevation loss between the upstream and downstream stations.

The mathematical formulas report gas piston velocities normalized to k600 values specific to oxygen (O₂) at a temperature of 17.5 degrees C (Raymond et al., In Prep). It

was therefore necessary to back calculate to gas piston velocities for each respective gas at the measured stream temperatures from when the data was collected. In order to estimate flux, an average of the three modeled gas piston velocities at each stream was used following the same procedures for results from the measured gas tracer experiments above.

Discharge

Discharge measurements were recorded for each monthly sampling date. At Wednesday Hill Brook, Rum Brook, and Burley Demeritt Creek, width and depth measurements were taken to calculate the area of a section of the stream. Velocity readings were then taken using a Marsh-McBirney flowmeter and were used to calculate discharge with the product of area and velocity. At Burley Demeritt Creek, flow was often too low to measure using the Marsh-McBirney flowmeter and this resulted in missing values for a number of study dates.

Calculations

Reported values from the GC of the headspace gas concentration from sample vials were converted to a gas concentration at equilibrium in parts per million by volume (ppmv) using a standard curve line calculated from standards run along with the samples in question. Gas concentration in ppmv for the headspace was then converted to μ mol/L of dissolved gas present in the water sample and values were finally reported as units of mass in μ g/L. Water concentration in the field was calculated based on the Bunsen Solubility Coefficient of the gas in question, the volume of water and helium headspace,

barometric pressure, and both stream and lab temperature. Calculations were made following the methods of Mulholland et al. (2004) and the LINX II project (S.K. Hamilton, professor, Michigan State University, unpublished) as used by Difranco (2009). The following is an example of the equations used to calculate N₂O; the Bunsen Solubility Coefficient differed for each gas and all other equations can be found in Appendix F.

Equation 1: Bsc (N₂O) = $2.7182818^{(-165.8806 + (222.8743*(100/(temperature)))) + (92.0792*LN((temperature)/100)) + (-1.48425*((temperature)/100)^2))*0.0821*273.15$

Equation 2: $C_1 = [N_2O_{(in ppmv)}] / (0.0821 \times 273.15)$

Equation 3: $C_2 = [N_2O_{(in ppmv)}] * BP * Bsc_L^* (Bsc_F/Bsc_L) * 1/(0.0821*293.15)$.

Equation 4: $G = (C_1 * V_1) + (C_2 * V_2)$

Equation 5: $C^* = G/V_2$

The Bunsen solubility coefficient Bsc was calculated both for stream temperature (K°) in the field (Bsc_F) and for lab conditions (Bsc_L) based on the lab temperature (K°) with which the water samples were equilibrated. C₁ is the final headspace mixing ratio and C₂ is the liquid concentration (μ mol/L). The equation for C₂ included "1/(0.0821*293.15)" in order to account for room temperature in the lab (Difranco, 2009). The total dissolved gas in the water sample is calculated as "G" (μ mol). The terms "V₁"and "V₂" used to calculate total dissolved gas in the water (G) are the volume of the headspace and the liquid respectively. The final concentration in the water is denoted C* (μ mol/L). All gas concentrations were then multiplied by their respective molecular weights in order to report them as $\mu g/L$.

An average atmospheric concentration of N₂O, CO₂, and CH₄ was determined from air samples taken at each site during monthly sampling. Atmospheric equilibrium concentrations were then determined using the average air concentration from the specific site and the Bunsen Solubility Coefficient calculated at stream temperature from the monthly sampling dates. Flux was then calculated using the product of the average gas transfer velocity k and the difference between the water concentration (*Cw*) and the concentration of the gas at equilibrium with atmospheric air (*Ceq*) (Clark et al, 1994; Wanninkhof and Knox, 1996; Beaulieu et al, 2010; Raymond and Cole 2001). The mean evasion flux at each site was then reported based on the mean evasion from their respective monthly samples.

$$F = k(Cw-Ceq)$$

Monthly gas concentrations at each stream were averaged from all three sampling sites on their respective transects in order to be able to relate average monthly concentrations of the three streams to one another. All statistical analysis was done using SPSS 18.0. Linear regression was used to compare the relationships between gas concentration and water chemistry or stream characteristics. Values were log transformed (log₁₀) where necessary when they did not follow a normal distribution. One way ANOVA with post-hoc Tukey test were used to compare sampling stations to one another across transects within each site.

Chapter 3

Results

Stream Chemistry

Burley Demeritt Creek contained the highest average concentration of $NO_3^$ during the sampling year. Wednesday Hill Brook also contained elevated concentrations of NO_3^- (Table 1). Both Burley Demeritt Creek and Rum Brook contained much higher concentrations of DOC and NH_4^+ than Wednesday Hill Brook (Table 1).

Site	Cl ⁻ (mg/L)	NO3 ⁻ (mg N/L)	NPOC (mg C/L)	NH 4 ⁺ (μg N/L)	Q (L/s)
BDC	20.05	1.37	7.65	32.77	not enough data
WHB	51.44	1.02	2.50	9.01	10.43
RMB	28.54	0.15	6.00	36.07	58.79

Table 1: Mean stream chemistry parameters by site.

Instream Variation of N2O

N₂O was always higher at the upstream location throughout the study year at Burley Demeritt Creek (Figure 4, Appendix B). The concentration of N₂O at the middle and downstream sampling locations were always higher than the upstream station at Wednesday Hill Brook. (Figure 5, Appendix B). At Rum Brook there was very little variation between sampling locations (Figure 6, Appendix B).

Figure 4: Mean monthly concentration of nitrous oxide at each sampling station at BDC. N_20 concentrations at the upstream location were significantly higher than both the downstream and middle locations (p<0.001).



Figure 5: Mean monthly concentration of nitrous oxide at each sampling station at WHB. Both the downstream and middle sampling locations had significantly higher concentrations of N₂O compared with the upstream sampling location (p<0.001 and p=0.001 respectively). The downstream and middle sampling locations also had significantly greater NO₃⁻ concentrations than the upstream station (p=0.001, and p=0.003 respectively).


Figure 6: Mean monthly concentration of nitrous oxide at each sampling station at RMB. No significant difference was found in the concentration of N_2O across sampling locations at Rum Brook (p=0.958).



Instream Variation of CH4

The downstream sampling location at Burley Demeritt Creek showed a strong seasonal trend in CH₄ with highest values in the summer and lowest values in the fall and winter. During summer the concentration of CH₄ at the downstream station was much higher than at the upstream and middle sampling stations. The upstream sampling station was also slightly higher than the middle sampling station throughout the study year at Burley Demeritt Creek (Figure 7). At Wednesday Hill Brook CH₄ concentration reached a maximum of 10.95 μ g C/L on April 6, 2012 at the downstream sampling location. When not including this data from April 6, Wednesday Hill Brook did not show any significant differences in CH₄ concentration along it's transect. Methane concentration was highest at the upstream sampling location at Rum Brook. The middle sampling location was also slightly higher than the downstream sampling station for the majority of

the study year (Figure 9, Appendix B).

Figure 7: Mean monthly concentration of methane showing in-stream variability at BDC. The downstream sampling location had a significantly higher CH_4 concentration than both the middle and upstream sampling locations (p=0.001, and p=0.026 respectively).



Figure 8: Mean monthly concentration of methane showing in-stream variability at WHB. After removing the downstream sample from April 6 as an outlier, no significant difference was found across sites at L1 (p=0.233).



Figure 9: Mean monthly concentration of methane showing in-stream variability at RMB. The concentration of methane at the upstream station was significantly higher than at the downstream station (p=0.044).



Instream Variation of CO2

The concentration of CO_2 at Burley Demeritt Creek was larger at the upstream sampling location for most of the study year with the highest peak occurring in January (Figure 10, Appendix B).

The downstream sampling location at Wednesday Hill Brook had slightly higher CO_2 concentrations than the upstream station for the majority of the year. On April 6, 2012 at the downstream sampling location a large peak in CO_2 with a concentration of 2,898.06 µg C/L was recorded. This value was more than double the next highest CO_2 concentration recorded at the stream, which occurred in August (Figure 11, Appendix B).

At Rum Brook the highest CO₂ concentrations were typically found at the upstream sampling location (Figure 12, Appendix B).

Figure 10: Mean monthly concentration of CO_2 showing in-stream variability at BDC. The upstream sampling location had significantly higher CO_2 concentration in comparison with the downstream location (p=0.020).



Figure 11: Mean monthly concentration of CO_2 showing in-stream variability at WHB. A significant difference in CO_2 concentration between the downstream and upstream sampling locations was found after removing the downstream sample from early April as an outlier (p=0.013).



Figure 12: Mean monthly concentration of CO_2 showing in-stream variability at RMB. The upstream sampling location had a higher concentration of CO_2 than the downstream station (p=0.033).



Nitrate

Average concentration of NO_3^- was highest at Burley Demerit Creek (Table 1) and ranged from 0.55 to 3.33 mg N/L (Appendix C). Using data from all sites there was a strong positive relationship between N_2O and NO_3^- (Figure 11). However, there was no relationship found between N_2O and NO_3^- at Burley Demeritt Creek (Figure 15).

At Wednesday Hill Brook the range of NO_3^- concentration was from 0.54 to 1.36 mg N/L with the lowest values occurring in autumn (Figure 13, Appendix C). A strong positive relationship between N₂O and NO₃⁻ was found at Wednesday Hill Brook (Figure 16).

The concentration of NO_3^- at Rum Brook increased in November and remained higher for the rest of the study year (Figure 13, Appendix C). A mean concentration of only 0.15 mg N/L was observed (Table 1). There was also a strong positive relationship between N_2O and NO_3^- observed at Rum Brook (Figure 17).



Figure 13: Scatter plot showing average monthly NO_3^- (mg N/L) concentrations at all three sites

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Figure 14: Linear regression showing the relationship between dissolved N₂O μ g N/L (log10) and NO₃⁻ mg N/L (log10) using data from all sites. A significant relationship between N₂O and NO₃⁻ was found using all monthly data (p<.001).



Figure 15: Linear regression showing the relationship between dissolved N₂O μ g N/L (log10) and NO₃⁻ mg N/L (log10) at BDC. No significant relationship was found between N₂O and NO₃⁻ at BDC (p=0.352).



Figure 16: Linear regression showing the relationship between dissolved N₂O μ g N/L (log10) and NO₃⁻ mg N/L (log10) at WHB. A strong positive relationship between N₂O and NO₃⁻ was found (P<0.001).



Figure 17: Linear regression showing the relationship between dissolved N₂O μ g N/L (log10) and NO₃⁻ mg N/L(log10) at RMB. A strong significant relationship was found (p<0.001).



DOC

The concentration of DOC was highest at Burley Demerit Creek which had a range of 2.53 to 15.35 mg C/L, but was above 6 mg C/L for most of the year (Appendix C). Peaks in DOC at Burley Demerit occurred in May and June as well as in September and October. Lowest values of DOC occurred in July and August (Figure 18). Mean concentration for the stream was 7.65 mg C/L (Table 1).

At Rum Brook the concentration of DOC ranged between 2.85 and 11.51 mg C/L, with the highest peak also occurring in May and September, similar to Burley Demerit Creek. Lowest values occurred in the winter with a large dip in February (Figure 18, Appendix C). A strong negative relationship between N_2O and DOC was found (Figure 21). There was also a positive relationship between CO_2 and DOC at Rum Brook (Figure 25).

Wednesday Hill Brook had a much lower concentration of DOC for most of the year compared to the other two streams with an average of only 2.5 mg C/L (Table 1). Peaks in DOC occurred on September 9, 2011 and March 8, 2012. DOC was lowest at Wednesday Hill Brook during the winter (Figure 18, Appendix C). A negative relationship was found between N₂O and DOC while a positive relationship was found between CH₄ and DOC (Figure 20, 23).



Figure 18: Scatter plot showing average monthly dissolved DOC concentrations at all three sites.

Figure 19: Linear regression showing the relationship between dissolved $N_2O \ \mu g \ N/L$ (log10) and DOC mg N/L (log10) using data from all sites. No significant relationship was found between N_2O and DOC using all monthly data (p=0.384).



Figure 20: Linear regression showing the relationship between dissolved N₂O μ g N/L (log10) and DOC mg N/L (log10) at WHB. A significant negative relationship between N₂O and DOC was found at WHB (p<0.001).



Figure 21: Linear regression showing the relationship between dissolved N₂O μ g N/L (log10) and DOC mg N/L (log10) at RMB. A significant negative relationship between N₂O and DOC was also found at RMB(p<0.001).



Figure 22: Linear regression showing the relationship between dissolved CH₄ μ g C/L (log10) and DOC mg N/L (log10) using data from all sites. A significant positive relationship between CH₄ and DOC was found when using data across all three sites (p<0.001).



Figure 23: Linear regression showing the relationship between dissolved CH₄ μ g C/L (log10) and DOC mg N/L (log10) at WHB. A significant positive relationship between CH₄ and DOC was found at WHB (p=0.01). However, no relationship was found at either of the other two streams.



Figure 24: Linear regression showing the relationship between dissolved CO₂ μ g C/L (log10) and DOC mg N/L (log10) using data from all sites. A significant relationship was found between CO₂ and DOC with all combined data (p<0.001).



Figure 25: Linear regression showing the significant relationship between dissolved CO₂ μ g C/L (log10) and DOC mg N/L (log10) at RMB. A significant positive relationship between CO₂ and DOC was found (p<0.001)



Stream Temperature

A weak positive relationship was found between CH_4 and temperature at Burley Demeritt Creek when using average values for the entire stream (Figure 26). A much strong positive relationship was found between stream temperature and CH_4 (R²=0.609) at the downstream sampling station at Burley Demeritt Creek (Figure 27). There was also a positive relationship between CH_4 and temperature found at Wednesday Hill Brook (Figure 28) No significant relationship between CH_4 and temperature was found at Rum Brook but there was a significant positive relationship between CO_2 and temperature found at Rum Brook.

Figure 26: Linear regression showing the relationship between dissolved CH₄ μ g C/L and stream temperature at BDC. A significant relationship was found between dissolved CH₄ and stream temperature at BDC (p=0.045).



Figure 27: Linear regression showing the relationship between dissolved CH₄ μ g C/L and stream temperature at the downstream sampling station at BDCdn0.45. The downstream sampling station at Burley Demerit showed a strong (R²=0.609) positive relationship between CH₄ and stream temperature (p=0.001).



Figure 28: Linear regression showing the relationship between dissolved CH₄ μ g C/L and stream temperature at WHB. A significant positive relationship was found between CH₄ and stream temperature (p=0.001).



Figure 29: Linear regression showing the relationship between dissolved CO₂ μ g C/L and stream temperature at RMB. A significant relationship was found between dissolved CO₂ and stream temperature at Rum Brook (p=0.022).



<u>рH</u>

No significant relationship was found between Dissolved N₂O and pH when comparing all monthly data. The only significant negative relationship between the two variables was found at Rum Brook with a weak R^2 value(0.1073). No significant relationship was also found between CO₂ and pH using both all the monthly data combined or using data from each individual site.

Figure 30: Linear regression showing the relationship between dissolved N₂O μ g N/L and pH. A significant negative relationship was found between N₂O and pH at RMB (p=0.042).



Discharge

There was not enough data to make comparisons between dissolved gas concentrations and discharge at BDC. No relationship was found between dissolved CH_4 and discharge at either WHB or RMB. There was also no relationship between dissolved CO_2 and discharge at WHB and RMB. A significant positive relationship between N₂O and discharge at Rum Brook was the only relationship that was found.

Figure 31: Linear regression showing the relationship between dissolved N₂O μ g N/L (log10) and discharge l/s (log10) at RMB. A significant relationship was found between N₂O and discharge at RMB (P=0.005).



Average Gas Concentrations at Monthly Sites

Burley Demeritt Creek was found to have the highest average concentration of dissolved N₂O out of all three monthly sites with an average concentration of 3.86 μ g N/L (Table 2). Rum Brook had the lowest concentration of N₂O and averaged only 0.39 μ g N/L over the study year (Table 2). Average Dissolved CO₂ at both Burley Demeritt and Rum Brook were very similar at 1027.0 and 941.56 μ g C/L respectively, whereas Wednesday Hill brook had a much lower average concentration of 676.66 μ g C/L (Table 2). Average dissolved methane was highest at Rum Brook (10.37 μ g C/L) and lowest at Wednesday Hill Brook (2.06 μ g C/L) (Table 2).

Site	Dissolved N ₂ O (µg N/L)		Dissolv (µg (red CO ₂ C/L)	Dissolved CH ₄ (µg C/L)		
	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev	
BDC	3.86	1.80	1027.85	401.81	4.75	2.38	
WHB	1.07	0.32	676.66	198.96	2.06	1.47	
RMB	0.39	0.17	941.56	338.72	10.37	6.51	

Table 2: Mean dissolved gas concentrations and standard deviation at each site

$\underline{N_2O}$

The highest average monthly concentration of N_2O was found at Burley Demerit Creek in June where it reached 9.11 µg N/L (Appendix C). However, No clear seasonal trend in N₂O was seen at Burley Demeritt Creek, and the lowest concentration (1.26 µg N/L) was found in July (Figure 32, Appendix C).

At Wednesday Hill Brook the highest monthly average N_2O concentration was in January (1.95 µg N/L) (Appendix C). For the rest of the year the concentration of N_2O was right around 1 µg N/L at Wednesday Hill Brook, with slightly lower values occurring in spring and autumn (Figure 32).

 N_2O concentration at Rum Brook peaked in December where it reached 0.79 µg N/L. Values were lowest in May-October 2011 (Appendix C, Figure 32). The concentration of dissolved N_2O at Rum Brook often remained at more than double what it was before November 2011 (Figure 32).



Figure 32: Average monthly dissolved N₂O concentrations at all three sites.

<u>CO</u>₂

The highest CO₂ concentration (2122.03 μ g C/L) was found at Burley Demeritt Creek in January 2012. The lowest value at Burley Demeritt Creek (531.23 μ g C/L) was found in March 2012 and no seasonal trend was found (Figure 33, Appendix C).

 CO_2 at Rum Brook was highest in June (1644.94 µg C/L) and showed a decrease in concentration after October 2011 (Figure 33, Appendix C).

Wednesday Hill Brook had a large peak in CO_2 at the downstream sampling station on April 6, 2012 which influenced the average monthly concentration on that date. Not including that sampling date, concentrations of CO_2 at Wednesday Hill Brook were highest during the summer up through October and started to increase again in April (Figure 33, Appendix C).



Figure 33: Average monthly dissolved CO₂ concentrations at all three sites.

<u>CH4</u>

Rum Brook had a consistently higher CH₄ concentration than both Burley Demerrit and Wednesday Hill Brook for most of the year. The highest stream average methane concentration (31.69 μ g C/L) was found at Rum Brook in November 2011 (Figure 34, Appendix C). This point may have been influenced by the beaver dam created upstream of the transect. Without including this large spike in CH₄ at Rum Brook in November, the average dissolved concentration of CH₄ was reduced to 8.72 μ g C/L.

Burley Demeritt Creek was consistently higher in methane concentration than Wednesday Hill Brook and followed a seasonal pattern with highest concentration during the summer and the lowest values in late March and early April 2012 (Figure 34). Methane also followed a seasonal pattern at Wednesday Hill Brook with highest values occurring between May and September 2011 with the exception of a peak on April 6, 2012 which was again influenced by a large peak at the downstream sampling station on that day (Appendix C, Figure 34).



Figure 34: Average monthly dissolved CH₄ concentrations at all three sites.

Gas Evasion

Results from the 8 measured gas tracer experiments exhibited strong correlations with both of the mathematical equations used to estimate gas piston velocities (Table 3). Equation 2 was found to have a slightly stronger correlation than Equation 1 (R^2 =0.843, and R^2 =0.825 respectively).

Table 3: k600 values derived from both gas tracer experiments and two mathematical models based on stream depth, slope, and velocity.

Site	Dete	Measured k600	Equation 1:	Equation 2:	
	Date	(m/day)	k600 (m/day)	k600 (m/day)	
RMB	7/27/2011	0.55	1.53	1.60	
RMB	11/6/2011	6.03	5.96	6.45	
RMB	3/31/2012	3.20	5.36	5.54	
WHB	7/7/2011	2.04	2.40	2.54	
WHB	11/2/2011	2.03	2.68	2.86	
WHB	5/11/2012	No Data	3.81	4.10	
BDC	6/9/2011	0.73	0.23	0.24	
BDC	11/19/2011	0.85	0.50	0.52	
BDC	4/2/2012	1.10	0.34	0.35	

Estimates of evasion to the atmosphere at Burley Demeritt Creek using average k values determined with the mathematical equations were much lower than estimates relying on measured k values from the gas tracer experiments. Estimated evasion based on modeled k values for all three gases at Burley Demeritt Creek were less than half of the evasion estimates using the measured k values (Table 4). The opposite trend was seen at both Wednesday Hill Brook and Rum Brook. Estimates of evasion based on the mathematically derived k values were higher than those based on measured k values at these two streams (Table 4).

Table 4: Estimates of the mean flux of N_2O , CO_2 , and CH_4 from the three monthly sites using gas piston velocities from both measured gas tracer experiments and mathematical models.

Site	$N_2O \text{ mg N m}^{-2} \text{ day}^{-1}$			$CO_2 \text{ mg C m}^{-2} \text{ day}^{-1}$			CH ₄ mg C m ⁻² day ⁻¹		
	Gas	Model	Model	Gas	Model	Model	Gas	Model	Model
	Tracer	Eq. 1)	Eq. 2)	Tracer	Eq. 1)	Eq. 2)	Tracer	Eq. 1)	Eq. 2)
BDC	2.6	1.0	1.0	569	208	214	2.3	0.9	0.9
WHB	1.1	1.6	1.8	722	1040	1110	1.1	1.5	1.6
RMB	-0.1	-0.1	-0.1	1640	2260	2380	20.9	28.9	30.5

Based on estimates using reaeration rates derived from the gas tracer experiments the average evasion of N₂O to the atmosphere was highest at Burley Demeritt Creek and ranged between 0.7 and 6.5 mg N m⁻² day⁻¹(Table 4, Appendix D). At Wednesday Hill Brook N₂O evasion had a range of 0.5-2.5 mg N m⁻² day⁻¹(Appendix D). Rum Brook was a sink for N₂O from the atmosphere for most of the year except during December and April. Gas exchange with the atmosphere at Rum Brook varied between -0.4 and 0.5 mg N m⁻² day⁻¹ (Appendix D).

 CO_2 emissions were highest on average from Rum Brook with a range between 435 and 3,390 mg C m⁻² day⁻¹ (Appendix D). Emissions were highest during the summer and fall and lowest in the spring. The average emissions of CO_2 from Rum Brook were more than double that of the other two streams (Table 4).

At Burley Demeritt Creek the range of CO_2 emissions was between 205 and 1300 mg C m⁻² day⁻¹. Emissions were highest in January and lowest in late March and April (Appendix D). Burley Demeritt Creek had the lowest yearly average emission of CO_2 out of all three streams (Table 4).

Wednesday Hill Brook had an average CO_2 emission of 722 mg C m⁻² day⁻¹ (Table 4). Emissions were consistently high in summer with a peak of 1620 mg C m⁻² day⁻¹ in early April 2012. CO_2 emissions were lowest during the winter months with the lowest estimated value of 300 mg C m⁻² day⁻¹ occurring in early March 2012 (Appendix D).

Methane evasion was highest on average at Rum Brook by a huge margin (Table 4). The lowest emission estimated from monthly sampling was 9.5 mg C m⁻² day⁻¹ in March, which was still higher than any CH₄ emissions estimated at the other streams. The highest estimated evasion of CH₄ from Rum brook was 69.9 mg C m⁻² day⁻¹ in November 2011, but this was likely influenced by a beaver dam upstream of the transect(Appendix D). After removing the peak in November, the average flux of CH₄ from Rum Brook for the year was found to be reduced to 17.2 mg C m⁻² day⁻¹.

At Burley Demeritt Creek CH_4 emissions were highest in the summer and lowest in the spring with an average emission of 2.3 mg C m⁻² day⁻¹. Although much lower than emissions from Rum Brook, average CH_4 emission from Burley Demeritt were still more than double the average CH_4 emissions from Wednesday Hill Brook (Table 4).

Wednesday Hill Brook had an average evasion of only 1.1 mg C m⁻² day⁻¹ but had a large range between -3.1 and 6.2 mg C m⁻² day⁻¹. It was actually a sink for methane from the atmosphere between November 2011 and February 2012, and again in late March late April 2012. Emissions were highest during the summer with a peak in early April (Appendix D).

Chapter 4

Discussion

Temporal Variability

<u>N₂O</u>

Seasonal variability in dissolved N₂O concentrations at Rum Brook and Wednesday Hill Brook may be driven in part by fluctuations in the availability of NO₃⁻ as a result of both changes in discharge and biological activity. A very strong relationship was found between NO₃⁻ and N₂O at Rum Brook (R²=0.6835) indicating that it is likely denitrification occurring in the riparian zone and within the stream bed which drives the concentration of N₂O. A peak in NO₃⁻ occurred in December at Rum Brook and NO₃⁻ remained higher throughout the winter and spring. This increase in NO₃⁻ available for denitrification corresponded with a rise in N₂O. The increased NO₃⁻ may have been caused by higher flows in winter and spring and a reduction in biological activity as a result of colder temperatures (Beaulieu et al., 2008). The significant positive relationship found between N₂O and discharge at Rum Brook (p=0.005, R²=0.191) supports the theory that increased runoff is transmitting more NO₃⁻ to the stream (Figure 31). The source of the increased N₂O and NO₃⁻ may alternatively have been due to nitrification of NH₄⁺ in riparian soils which would produce NO₃⁻ and release N₂O in the process.

The concentration of N_2O was lowest in autumn at Wednesday Hill Brook. This coincided with a drop in NO₃⁻ over the same period. NO₃⁻ was possibly being taken up by heterotrophs during autumn when DOC concentration was high because of leaf drop and so NO₃⁻ was less available for denitrification. This is supported by Figure 20 showing the significant negative relationship between N₂O and DOC at Wednesday Hill Brook $(p<0.001, R^2=0.3145)$. Strong experimental evidence for increased microbial uptake of NO3⁻ with increased DOC concentrations from leaf leachate in fall has been demonstrated (Sobczak et al., 2003). Alternatively, other mechanisms related to the availability of DOC in the stream may also be responsible. A recent study conducted by Beaulieu et al. (2010) found that the percent yield of N₂O from denitrification was reduced when there was more available organic carbon. An increase in DOC concentration may have resulted in a lower nitrous oxide yield from denitrification which contributed to the decreased concentration of N₂O in the stream. Another possibility is that there is an increase in dissimilatory reduction of NO_3^- to NH^4 with more available DOC in autumn which may have led to lower denitrification rates (Martin et al., 2001).

No clear seasonal fluctuation in dissolved N_2O was apparent at Burley Demeritt Creek. There was also no relationship found between N_2O and NO_3^- which indicates that NO_3^- is not limiting denitrification (Figure 15). Burley Demeritt Creek was found to have both the highest average concentration of N_2O and NO_3^- out of the three study streams. It receives inputs of groundwater draining a dairy farm pasture and a pig waste lagoon and so it is plausible that there is never a shortage of NO_3^- . <u>CO</u>₂

 CO_2 concentration was much higher during summer and early autumn at Rum Brook when temperatures were warmer and soil and root respiration were likely more active (Figure 12). This is supported by the significant positive relationship between CO_2 and temperature (p=0.022, R²=0.135) as seen in Figure 29. Other studies have also confirmed this seasonal pattern in CO_2 . Jones and Mulholland (1998c) found that highest soil evasion of CO_2 occurred in summer, and an increase in groundwater dissolved CO_2 derived from soil was clear at Walker Branch. Another study conducted by Jones and Mulholland on streams in Tennessee and North Carolina also found that dissolved CO_2 concentration in streams was much higher during summer months due to increased soil respiration carried with shallow groundwater (Jones and Mulholland b).

Peaks in dissolved CO_2 occurred in January and March at Burley Demeritt Creek and were associated with snow melt events (Appendix C). Flushing of CO_2 from soil and groundwater from the pasture may have been responsible. It was a warmer winter than usual during the study and year and snowfall was less than what is typical for northern New England. Therefore, there was no normal large spring snow melt event and further studies during a typical year would likely find increased CO_2 peaks later in the spring. The theory that increased flows could lead to flushing of CO_2 from soil to streams is supported by work conducted by Butman and Raymond (2011) who found a strong correlation between precipitation and dissolved CO_2 in streams across the United States. <u>CH4</u>

Temperature was found to be an important driver of dissolved CH₄ in streams. An increase in CH₄ was seen during the summer months (Figure 34) and there was a significant positive correlation between dissolved CH₄ and temperature at Burley Demeritt Creek (Figure 27). Increased activity of methanogen bacteria during summer due to warmer temperatures could be responsible for the increase as this has been well documented in other studies (Billet and Moore, 2007; Jones et al., 1995).

An increase in dissolved CH₄ at Wednesday Hill Brook during the summer was also found. Shallow groundwater input with a higher concentration of methane picked up from active forest and riparian soils is a probable source. It is unlikely that significant production is occurring in the stream according to previous studies which found stream bed sediments to be oxygenated by surface water (Jones and Mulholland, 1998a,b; Jones et al., 1995). The concentration of CH₄ at Wednesday Hill Brook was lowest in the winter months when riparian soils were inactive and decomposition of organic matter had decreased. A significant relationship between dissolved CH₄ and temperature at Wednesday Hill Brook provides strong supporting evidence (p=0.001, $R^2=0.2589$). No relationship was found between dissolved CH₄ concentration and discharge at Wednesday Hill Brook. It is also unlikely that increased oxidation of CH₄ in the water column was responsible for the drop in concentration because oxidation by methanotrophic bacteria has been shown to be highest in summer when water temperature is above 15 degrees C (Pulliam, 1993). At Rum Brook the concentration of CH₄ began to increase in July and then peaked in November before dropping again and remaining lower throughout the winter and spring. This trend may have been confounded by a beaver dam which was created in July and was then removed sometime between November and December (Figure 9). Billet and Moore have shown increased concentrations of dissolved methane downstream of beaver dams due to decomposition of accumulated organic matter (2007). It is difficult to distinguish between the influence of the beaver dam and the natural occurrence of high levels of CH₄ at Rum Brook. However, a decrease in biological production would be expected with lower temperatures in November and the other two study streams did not show an increase in CH₄ during this period. The large peak in dissolved CH₄ in November at Rum Brook may have been due to a buildup of CH₄ produced in flooded forest soils and decomposition of organic matter contained by the dam.

Spatial Variability

Burley Demeritt Creek

Significant variability in dissolved gas concentrations between sampling locations within all three streams were found. At Burley Demeritt Creek the upstream sampling location was found to contain a significantly higher concentration of dissolved N₂O than the middle and downstream stations. The upstream sampling station was located about 100m downstream of an intermittent tributary which drains the dairy farm pasture. The tributary is likely a large source of N₂O and NO₃⁻ to the stream as shallow groundwater wells located in the pasture have been shown to contain very high concentrations. Nitrous oxide produced in the pasture and riparian soil can begin to degas as it enters the stream through the tributary, but likely has not completely degassed as it travels downstream. This explains why it still remains considerably higher at the upstream location. On the one occasion in August when dissolved N₂O was measured near the tributary a concentration of between 21.91 and 29.41 μ g N/L was found which was much higher than any other measured gas sample from the study (Appendix A). Baulch et al. (2011b) also reported significant spatial variability among its study locations and found that areas receiving direct inputs form tile drainage had elevated concentrations.

The concentration of dissolved CO_2 at Burley Demeritt Creek was also higher at the upstream sampling location (Figure 10). The upstream sampling location is closest to the wetland as well as where the pasture drains into the stream. Both of these two sources may contribute to the larger input of CO_2 which is then likely degassed to the atmosphere as it travels downstream.

Methane was much higher at the downstream sampling location at Burley Demeritt Creek during the summer months (Figure 7). The downstream sampling station is located in an area with the lowest gradient where water velocity is slower which allows for increased contact time with bottom sediment. Stagnant water overlying streambed sediments at the downstream sampling location could drive anoxic conditions to allow for production of CH₄. However, most research has shown instream production to be insignificant (Jones and Mulholland, 1998a; Jones et al., 1995, de Angelis and Lilley, 1987). Alternatively, the downstream sampling location was located in a floodplain where there is an accumulation of organic matter due to flooding from the Lamprey River (Galvin 2010). Shallow groundwater input to the stream from the floodplain is a more likely source of the increased methane in summer when decomposition of organic matter is greatest.

The upstream sampling location at Burley Demeritt was consistently higher than the middle sampling location throughout the study year. Loss of CH₄ due to degassing and oxidation by methanotrophic bacteria both may have contributed to the difference between stations. The middle sampling location was also located within a riffle and stream bed sediment was mostly exposed clay and cobble. A lack of organic matter and reduced contact time with bottom sediment at this sampling location could be responsible for the slightly lower CH₄ concentration in the middle of the transect.

Rum Brook

There was a significantly higher concentration of dissolved CO_2 at the upstream sampling location at Rum Brook (p=0.033). This higher CO_2 concentration may be a result of the upstream sampling stations closer proximity to wetlands upstream of the transect. Dissolved CO_2 at the middle sampling location was also higher in turn than the downstream sampling station for most of the year which supports the explanation that CO_2 produced in the wetland is degassing as it travels downstream (Figure 12). Koprivnjak et al. (2010) also found CO_2 concentration decreased downstream due to degassing.

The upstream sampling station at Rum Brook contained a significantly greater concentration of CH₄ than the downstream station as well (p=0.044). Again, the upstream station was closest to wetlands upstream of the transect that could provide a substantial

source of CH_4 . The beaver dam upstream of the transect may also have contributed to higher CH_4 at the upstream station. Like CO_2 , CH_4 will degas it travels downstream and it can also be consumed by oxidation. These processes both may have resulted in the lower concentrations at the subsequent sampling stations.

Very little variability in dissolved N_2O was found within Rum Brook. This was expected as there were no large anthropogenic sources of NO_3^- to the stream and concentrations of NO_3^- were uniform across the sampling transect. Without an anthropogenic source of nitrogen there were no hot spots of denitrification or other large sources of N_2O entering Rum Brook.

Wednesday Hill Brook

The downstream sampling station at Wednesday Hill Brook contained significantly higher levels of CO₂ than the upstream station (Figure 11). Input of shallow groundwater with a high concentration of dissolved CO₂ entering after the upstream station is likely responsible for the increase. There was always a substantial dilution of rhodamine from the upstream to the downstream sampling stations and visible seeps of groundwater could be seen entering the transect after the upstream station. This strongly supports the likelihood of groundwater being responsible for the increase in dissolved gases along the transect. The large peak in CO₂ that occurred at the downstream sampling station on April 6, 2012 may have been caused by an input of groundwater or an upwelling from stream bed sediment at that exact location where water samples were taken. No significant difference in CH_4 concentration between sampling stations was found at Wednesday Hill Brook. However, the middle and downstream sampling stations were higher during summer months than the upstream station. Shallow groundwater input with a higher concentration of CH_4 picked up from forest and riparian soils is the likely source.

A significantly greater concentration of both N₂O and NO₃⁻ was also detected at the middle and downstream sampling stations at Wednesday Hill Brook. Leaching of NO₃⁻ into groundwater from septic systems in the surrounding area is believed to be responsible. Shallow groundwater wells located downstream of the upstream station have been shown to contain very high concentrations of NO₃⁻. Nitrate in groundwater entering the stream after the upstream station can be denitrified both in the riparian zone and stream bed sediment. This is most likely driving the much higher concentrations of N₂O at the middle and downstream stations since N₂O and NO₃⁻ were closely linked at Wednesday Hill Brook (p<0.001, R²=0.4555).

Dissolved Greenhouse Gas Concentration and Evasion to the Atmosphere

Rum Brook was found to be the largest contributor to global warming from gas emissions out of all three study streams. The combination of having the highest gas piston velocity and high dissolved CH_4 and CO_2 concentrations offset the fact that it was a sink for N₂O. The average evasion rate of CH_4 from Rum Brook (20.9 mg C m⁻² day⁻¹) was considerably larger than at both Burley Demeritt Creek (2.3 mg C m⁻² day⁻¹) and Wednesday Hill Brook (1.1 mg C m⁻² day⁻¹). This suggests that forested streams with little anthropogenic influence can naturally contain high concentrations of dissolved CH_4 . Average CO₂ emissions were also highest from Rum Brook (1640 mg C m⁻² day⁻¹). Natural decomposition and respiration in wetlands and from forest soils provided Rum Brook with dissolved CH₄ and CO₂ concentrations that were respectively about 16 and 4 times higher than atmospheric equilibrium. Therefore, streams will likely continue to act as sources of CH₄ and CO₂ to the atmosphere regardless of human attempts to moderate their contribution. However, without an anthropogenic source of nitrogen Rum Brook was found to be a net sink for N₂O from the atmosphere with an average exchange rate of -0.1 mg N m² day⁻¹.

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Both Burley Demeritt Creek and Wednesday Hill Brook were found to be sources of N₂O to the atmosphere with average evasion rates of 2.6 mg N m⁻² day⁻¹ and 1.1 mg N m⁻² day⁻¹ respectively. Although the mass flux of N₂O from these streams was much lower than emissions of CO₂, implications for global warming are still high because N₂O is many times more potent as a greenhouse gas and it has a long life span of 120 years in the atmosphere (EPA, 2012). Average dissolved N₂O concentration at Burley Demeritt Creek was found to be almost an order of magnitude higher than what naturally occurred at Rum Brook (Table 2). Drainage from the Organic Dairy farm pasture and pig waste lagoon was responsible for the elevated concentrations of N₂O which were almost 10 times higher than atmospheric equilibrium on average for the study year. At Wednesday Hill Brook the nitrogen input from septic systems in the surrounding area caused dissolved N₂O concentrations to be more than double atmospheric equilibrium. Although more than 60% of all N₂O emissions in the United States are said to come from natural sources (EPA, 2012), anthropogenic inputs of increased nitrogen are accelerating natural processing and production. Butman and Raymond (2011) estimated that streams and rivers cover an area of approximately 40,600 km² in the United States alone, and as nitrogen inputs continue to increase with the growing human population the contribution of N₂O emitted from these freshwater systems will also continue to escalate.

On the other hand, dissolved CO_2 and CH_4 concentrations were found to be lowest at Wednesday Hill Brook, the stream in the study which had the greatest percentage of urban landuse in its watershed area. Groundwater and runoff may be transported to the stream much faster at Wednesday Hill Brook and have less contact time to pick up dissolved gases from forest and riparian soils. Alternatively, the concentration of DOC at Wednesday Hill Brook was much lower than at Rum Brook and Burley Demeritt Creek (Table 1). Less organic matter in the more urbanized watershed could have led to reduced decomposition and respiration rates which may be responsible for the much lower concentrations of CH_4 and CO_2 in the stream.

Comparisons with the Literature

Evasion rates of N₂O from the three study streams varied considerably but fell within the range of reported values in the literature for small streams. Average emissions of N₂O to the atmosphere at Wednesday Hill brook (1139.9 mg N m⁻² day⁻¹) and Burley Demeritt (2560.7 μ g N m⁻² day⁻¹) were much higher than measured results on the Hudson River of only 153 .42 μ g N m⁻² day⁻¹ (Cole and Caraco 2001), but this was expected due to the high concentrations of nitrogen from anthropogenic sources in these streams. Results from this study were well within the range reported for the South Platte River (<90 to 32,600 μ g N m⁻² day⁻¹) with a median emission rate of 1490 μ g N m⁻² day⁻¹ (McMahon
and Dennehy, 1999) as well as within the range reported by Beaulieu et al. (2008) for midwestern headwater streams draining an agricultural basin (-213.6 and 6403.2 µg N m⁻ 2 day⁻¹). The comprehensive LINX 2 study which explored N₂O emissions from streams across the United States reported a wide range of N₂O emissions from -600 to 12984 µg $N m^{-2} day^{-1}$. The northern deciduous forest region represented by streams in Massachusetts was located in close proximity to streams from this study. In Massachusetts N₂O emissions ranged between 24 μ g N m⁻² day⁻¹ in a forested reference stream and 8359 µg N m⁻² day⁻¹ in a stream draining an urban watershed (Beaulieu et al., 2010). Rum Brook, the reference stream in this study, was below this range found in Massachusetts (-84.3 µg N m⁻² day⁻¹) but both Burley Demeritt Creek and Wednesday Hill Brook were comparable. Burley Demeritt Creek was found to have an evasion rate more than three times greater than any of the three agricultural streams reported in Massachusetts, but was still much lower than 2 of the urban streams (Beaulieu et al., 2010). No fully urban site was included in this study for comparison with results in Massachusetts.

In this study the average CO_2 emissions from Burley Demeritt (569 mg C m⁻² day⁻¹), Wednesday Hill Brook (722 mg C m⁻² day⁻¹), and Rum Brook (1637 mg C m⁻² day⁻¹) all fall within the lower range of reported values for Brocky Burn, a peatland headwater stream located in Scotland (Hope et al., 2001). Values from this study were slightly lower than the range of 1884-4476 mg C m⁻² day⁻¹ reported by Jones and Mulholland at Walker Branch (1998c) but were very similar to results from Koprivnjak et al (2010) for small boreal streams. Measured reaeration coefficients at Walker Branch and Brocky Burn were much higher than those measured on streams in this study (Appendix F), and this is

the main driver behind why evasion was lower (Hope et al, 2001; Genereux and Hammond, 1992). Average concentrations of dissolved CO_2 from this study were comparable to the range of 288 to1862.4 µg C/L described at Brocky Burn (Hope et al., 2001, Table 2). It is important to consider that the reaeration coefficient or gas transfer velocity can make a large difference when comparing fluxes from different streams. Even within this study Burley Demeritt Creek was much shallower than the other two study streams and this resulted in a lower gas transfer velocity. The concentration of dissolved CO_2 at Burley Demeritt Creek was actually slightly higher than those found at Rum Brook but the larger gas transfer velocity at Rum Brook because it is much deeper resulted in a greater flux.

The average CH₄ evasion from Burley Demeritt (2.3 mg C m⁻² day⁻¹), Wednesday Hill Brook (1.1 mg C m⁻² day⁻¹) and Rum Brook (20.9 mg C m⁻² day⁻¹) are low compared with values reported at Brocky Burn which had a range of 52 to 311 mg C m⁻² day⁻¹. The study catchment at Brock Burn was draining a peatland with waterlogged soils that transported high concentrations of CH₄ to the stream. However, the upper range of dissolved CH₄ concentration at Brocky Burn was only slightly higher than those found in this study at Rum Brook. Average dissolved CH₄ concentrations in all three streams from this study were also higher than dissolved CH₄ reported at Walker Branch. As discussed earlier, the much lower reaeration coefficients from this study resulted in lower evasion rates in comparison with Brocky Burn and Walker Branch (Jones and Mulholland, 1998a; Genereux and Hammond, 1992). Modeled reaeration coefficients at both Wednesday Hill Brook and Rum Brook, but were still much lower than was found at Brocky Burn and Walker Branch. It is also probable that both this study and previous studies in the literature considerably underestimated CH_4 emissions from their study streams by not including loss of CH_4 through ebullition. Ebullition may account for significant losses from streams according to Baulch et al. (2011c).

Chapter 5

Conclusion

Two of the three streams from this study were shown to be net sources of N_2O to the atmosphere. These two streams were heavily influenced by an input of anthropogenic derived nitrogen whereas the undisturbed stream was found to be a net sink for N_2O . Robust evidence was found supporting instream production of N_2O through denitrification given that dissolved N_2O was strongly correlated with stream dissolved NO_3^- concentration.

 CO_2 emissions indicate that a substantial amount of carbon is released from streams in the form of CO_2 . However, sources of dissolved CO_2 to stream water are likely terrestrially derived from forest or agricultural soils. Dissolved CH_4 in streams was also likely produced from terrestrial sources and transported via groundwater to the study streams. Further studies are needed to monitor shallow groundwater input at all three locations. Assessing soil water concentrations of dissolved gases in riparian soils would provide the evidence necessary to determine where exactly the gas is being produced.

All three study streams showed significant spatial variability in dissolved gas concentrations along the length of their respective transects. This indicates that hot spots linked to sources of groundwater input can exist within small streams and it is probable that sampling in only one location will result in overestimating or underestimating gas flux from the stream of interest. Instead, I recommend that samples be taken frequently at shorter intervals along the length of streams in question. This method will allow scientists to more accurately predict gaseous evasion as well as help pinpoint large inputs to the stream.

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Appendix A

All Samples

UNH ID	Sample	Collection	N20-N	CO2-C	CH4-C
#	Name	Date	µg/L	µg/L	μg/L
99758	WHB	17-May-11	0.54	6.86	3.51
99759	WHB	17-May-11	0.50	422.78	3.21
99760	WHB	17-May-11	0.64	982.39	3.87
99761	Lamprey	17-May-11	0.18	367.02	3.42
99762	Lamprey	17-May-11	0.28	651.25	4.04
99763	Lamprey	17-May-11	0.19	390.38	3.53
99764	WHBdn1.3	20-May-11	0.97	745.81	1.88
99765	WHBdn1.3	20-May-11	1.11	799.98	2.15
99766	WHBdn1.3	20-May-11	0.69	543.42	. 1.80
9 9767	WHBmid1.2	20-May-11	0.87	608.70	2.11
99768	WHBmid1.2	20-May-11	0.80	609.78	2.16
99769	WHBmid1.2	20-May-11	0.99	669.48	2.11
99770	WHBup1.1	20-May-11	0.53	566.77	2.75
99771	WHBup1.1	20-May-11	0.60	509.98	2.48
99772	WHBup1.1	20-May-11	0.43	337.65	2.19
99 79 0	WHB	24-May-11	0.47	394.32	2.53
99791	WHB	24-May-11	0.51	669.34	2.52
99792	WHB	24-May-11	0.62	669.53	2.55
99793	Lamprey	24-May-11	0.26	685.85	4.07
99794	Lamprey	24-May-11	0.27	575.28	5.46
99795	Lamprey	24-May-11	0.20	567.80	3.59
99817	RMBup0.41	26-May-11	0.28	1689.02	10.43
99818	RMBup0.41	26-May-11	0.25	1581.43	9.67
99819	RMBup0.41	26-May-11	0.24	1110.72	7.06
99820	RMBmid0.42	26-May-11	0.30	1077.34	6.11
99821	RMBmid0.42	26-May-11	0.18	940.93	6.11
99822	RMBmid0.42	26-May-11	0.27	1369.48	7.85
99823	RMBdn0.43	26-May-11	0.21	1138.48	6.29
99824	RMBdn0.43	26-May-11	0.06	848.79	4.03
99825	RMBdn0.43	26-May-11	0.10	595.41	3.88

99846	BDCup0.30	27-May-11	4.58	1258.33	4.57
99847	BDCup0.30	27-May-11	5.33	1407.57	6.12
99848	BDCup0.30	27-May-11	5.24	1499.82	5.39
99849	BDCmid0.38	27-May-11	1.53	673.22	1.89
99850	BDCmid0.38	27-May-11	1.62	674.05	1.86
99851	BDCmid0.38	27-May-11	1.98	858.08	2.22
99852	BDCdn0.45	27-May-11	1.36	946.44	9.44
99853	BDCdn0.45	27-May-11	1.07	790.92	19.65
99854	BDCdn0.45	27-May-11	1.17	889.42	24.96
99871	WHB	31-May-11	3.05	No Value	No Value
99872	WHB	31-May-11	2.62	No Value	No Value
99873	WHB	31-May-11	2.12	No Value	No Value
99874	Lamprey	31-May-11	1.36	No Value	No Value
99875	Lamprey	31-May-11	1.20	No Value	No Value
99876	Lamprey	31-May-11	0.96	No Value	No Value
99946	WHB	7-Jun-11	0.54	603.09	0.27
99947	WHB	7-Jun-11	0.64	740.01	0.05
99948	WHB	7-Jun-11	0.68	778.51	0.26
99949	Lamprey	7-Jun-11	0.16	529.28	5.62
99950	Lamprey	7-Jun-11	0.19	411.29	4.98
99952	BDCup0.30	9-Jun-11	5.79	1453.01	4.87
99953	BDCup0.30	9-Jun-11	12.48	1104.44	3.93
99954	BDCup0.30	9-Jun-11	16.43	768.03	2.68
99955	BDCmid0.38	9-Jun-11	12.80	982.62	0.55
99956	BDCmid0.38	9-Jun-11	9.89	1317.42	0.26
99957	BDCmid0.38	9-Jun-11	8.38	1111.56	0.53
99958	BDCdn0.45	9-Jun-11	6.50	1321.59	12.68
99959	BDCdn0.45	9-Jun-11	5.47	1068.69	39.54
99960	BDCdn0.45	9-Jun-11	4.27	1302.04	14.31
99984	WHB	14-Jun-11	0.82	819.81	4.37
99985	WHB	14-Jun-11	0.74	733.78	3.25
99986	WHB	14-Jun-11	0.79	732.02	3.33
99987	Lamprey	14-Jun-11	0.34	467.25	4.10
99988	Lamprey	14-Jun-11	0.36	484.99	4.72
99989	Lamprey	14-Jun-11	0.22	344.54	3.65
100101	RMBup0.41	20-Jun-11	0.36	1984.33	9.24
100102	RMBup0.41	20-Jun-11	0.29	2221.21	10.56

100104	DNAD	20 km 11	0.00	026 10	7
100104	RIVIBIIIdU.42	20-Jun-11	0.36	936.18	7.58
100105	RIVIBIIIdU.42	20-Jun-11	0.23	1864.32	7.24
100106	RIVIBILIOU.42	20-Jun-11	0.30	1/11.78	7.20
100107	RIVIBONU.43	20-Jun-11	0.27	1288.10	4.14
100108	RIVIBONU.43	20-Jun-11	0.21	1334.36	4.24
100109	RMBdn0.43	20-Jun-11	0.23	1361.40	4.11
100164	WHB	21-Jun-11	0.49	781.24	2.05
100165	WHB	21-Jun-11	0.61	1057.73	2.23
100166	WHB	21-Jun-11	0.62	845.85	2.16
100167	Lamprey	21-Jun-11	0.17	524.25	11.59
100168	Lamprey	21-Jun-11	0.16	508.52	10.40
100169	Lamprey	21-Jun-11	0.27	568.41	8.90
100510	WHBup1.1	29-Jun-11	0.61	740.09	2.02
100511	WHBup1.1	29-Jun-11	0.48	781.60	1.40
100512	WHBup1.1	29-Jun-11	0.51	746.64	1.45
100513	WHBmid1.2	29-Jun-11	1.36	764.73	3.59
100514	WHBmid1.2	29-Jun-11	1.32	774.88	3.92
100515	WHBmid1.2	29-Jun-11	1.55	906.26	4.22
100516	WHBdn1.3	29-Jun-11	1.51	1139.26	3.38
100517	WHBdn1.3	29-Jun-11	1.25	942.40	3.17
100518	WHBdn1.3	29-Jun-11	1.35	841.42	4.33
100460	WHB	29-Jun-11	0.68	756.44	2.78
100461	WHB	29-Jun-11	0.70	571.19	2.52
100462	WHB	29-Jun-11	0.81	497.73	4.13
100463	Lamprey	29-Jun-11	0.17	353.29	4.51
100464	Lamprey	29-Jun-11	0.07	303.80	3.40
100465	Lamprey	29-Jun-11	0.15	423.22	4.69
100563	WHB	5-Jul-11	0.49	837.59	2.57
100564	WHB	5-Jul-11	0.42	818.45	1.92
100565	WHB	5-Jul-11	0.47	732.38	2.18
100566	Lamprey	5-Jul-11	0.02	212.65	5.75
100567	Lamprey	5-Jul-11	0.12	364.57	8.38
100568	Lamprey	5-Jul-11	0.00	115.45	6.30
100632	WHBup1.1	7-Jul-11	0.55	742.97	2.11
100633	WHBup1.1	7-Jul-11	0.43	519.08	1.74
100634	WHBup1.1	7-Jul-11	0.56	649.63	1.98
100635	WHBmid1.2	7-Jul-11	1.56	779.25	5.14

100636	WHBmid1.2	7-Jul-11	1.18	581.54	3.44
100637	WHBmid1.2	7-Jul-11	1.16	574.63	3.30
100638	WHBdn1.3	7-Jul-11	1.33	903.97	3.84
100639	WHBdn1.3	7-Jul-11	1.07	701.30	3.35
100640	WHBdn1.3	7-Jul-11	1.43	874.46	3.93
101158	WHB	12-Jul-11	0.70	929.78	2.05
101159	WHB	12-Jul-11	0.67	791.04	2.03
101160	WHB	12-Jul-11	0.59	695.97	1.79
101161	Lamprey	12-Jul-11	0.26	421.92	6.93
101162	Lamprey	12-Jul-11	0.28	350.41	7.84
101163	Lamprey	12-Jul-11	0.25	396.16	6.69
101164	WHB	19-Jul-11	0.79	890.89	2.04
101165	WHB	19-Jul-11	0.75	1094.22	2.93
101166	WHB	19-Jul-11	0.74	923.00	2.47
101167	Lamprey	19-jul-11	0.18	523.45	10.86
101168	Lamprey	19-Jul-11	0.24	488.87	11.54
101169	Lamprey	19-Jul-11	0.18	360.61	10.26
101219	WHB	26-Jul-11	1.05	1160.51	4.38
101220	WHB	26-Jul-11	0.85	1109.55	3.89
101221	WHB	26-Jul-11	0.76	755.09	3.15
101222	Lamprey	26-Jul-11	0.24	601.34	23.20
101223	Lamprey	26-Jul-11	0.20	591.64	20.91
101224	Lamprey	26-Jul-11	0.30	687.45	23.46
101234	RMBup0.41	27-Jul-11	0.18	1213.89	15.83
101235	RMBup0.41	27-Jul-11	0.19	1320.21	15.68
101236	RMBup0.41	27-Jul-11	0.27	1798.89	17.69
101237	RMBmid0.42	27-Jul-11	0.21	916.75	4.92
101238	RMBmid0.42	27-Jul-11	0.19	1277.44	2.98
101239	RMBmid0.42	27-Jul-11	0.30	1163.73	4.81
101240	RMBdn0.43	27-Jul-11	0.21	603.23	4.03
101241	RMBdn0.43	27-Jul-11	0.43	953.32	4.95
101242	RMBdn0.43	27-Jul-11	0.32	736.50	4.17
101283	BDCup0.30	29-Jul-11	2.74	1117.83	3.40
101284	BDCup0.30	29-Jul-11	2.58	1077.33	3.98
101285	BDCup0.30	29-Jul-11	3.79	1530.84	5.96
101286	BDCmid0.38	29-Jul-11	0.34	1055.26	2.96
101287	BDCmid0.38	29-Jul-11	0.33	1242.33	3.23

101288	BDCmid0.38	29-Jul-11	0.40	1048.70	3.47
101289	BDCdn0.45	29-Jul-11	0.40	959.65	8.80
101290	BDCdn0.45	29-Jul-11	0.35	907.75	9.07
101291	BDCdn0.45	29-Jul-11	0.43	1357.09	34.21
101329	WHB	2-Aug-11	0.68	624.99	2.65
101330	WHB	2-Aug-11	0.56	697.19	2.23
101331	WHB	2-Aug-11	0.54	629.43	2.13
101332	Lamprey	2-Aug-11	0.22	547.54	17.05
101333	Lamprey	2-Aug-11	0.26	568.84	17.67
101334	Lamprey	2-Aug-11	0.21	398.21	15.37
101354	BDC 0	4-Aug-11	1.43	1200.25	172.77
101355	BDC 50	4-Aug-11	0.56	1004.91	19.11
101356	BDC 100	4-Aug-11	0.58	992.92	31.22
101357	BDC 150	4-Aug-11	0.63	1048.74	32.91
101358	BDC 200	4-Aug-11	0.58	1054.23	3.75
101359	BDC 250	4-Aug-11	0.48	727.23	2.47
101360	BDC 300	4-Aug-11	1.50	765.20	3.35
101361	BDC 350	4-Aug-11	5.32	1072.20	4.82
101362	BDC 400	4-Aug-11	29.41	1607.94	18.39
101363	BDC 450	4-Aug-11	21.92	1630.50	3.78
101364	BDC 500	4-Aug-11	0.46	850.28	1.05
101365	BDC 550	4-Aug-11	0.44	1122.61	0.93
101366	BDC 600	4-Aug-11	0.72	2767.08	5.05
101432	WHB source	9-Aug-11	0.27	2179.20	12.03
101433	WHB 100m	9-Aug-11	0.21	1093.08	13.28
101434	WHB 200m	9-Aug-11	0.19	724.68	10.01
101435	WHB 300m	9-Aug-11	0.48	1098.01	6.36
101436	WHB 400m	9-Aug-11	0.46	793.09	4.93
101437	WHB 500m	9-Aug-11	0.70	453.18	2.57
101438	WHB 600m	9-Aug-11	0.66	620.79	7.89
101439	WHB 700m	9-Aug-11	0.32	628.10	2.29
101440	WHB 800m	9-Aug-11	0.72	837.34	7.35
101441	WHB 900m	9-Aug-11	0.78	868.79	4.40
101442	WHB 1000m	9-Aug-11	0.38	701.16	1.50
101443	WHB 1100m	9-Aug-11	0.68	611.34	3.96
101444	WHB 1200m	9-Aug-11	1.58	865.05	3.51
101445	WHB 1300m	9-Aug-11	1.86	1300.64	4.15

101446	WHB 1400m	9-Aug-11	1 74	1605 32	4.88
101447	WHB 1500m	9-Aug-11	1.59	1352.59	5.47
101448	WHB 1600m	9-Aug-11	2.04	1598.12	4.68
101449	WHB 1700m	9-Aug-11	1.33	1128.23	6.00
101450	WHB 1800m	9-Aug-11	0.93	850.94	6.62
101426	WHB	9-Aug-11	0.81	751.70	4.11
101427	WHB	9-Aug-11	0.66	771.26	2.96
101428	WHB	9-Aug-11	0.60	655.01	2.40
101429	Lamprey	9-Aug-11	0.22	441.06	7.14
101430	Lamprey	9-Aug-11	0.24	439.67	7.46
101431	Lamprey	9-Aug-11	0.36	575.85	9.61
101467	WHBup1.1	12-Aug-11	0.44	592.22	1.22
101468	WHBup1.1	12-Aug-11	0.59	699.81	1.72
101469	WHBup1.1	12-Aug-11	0.45	514.55	2.17
101470	WHBmid1.2	12-Aug-11	1.84	838.60	4.85
101471	WHBmid1.2	12-Aug-11	1.97	904.02	4.68
101472	WHBmid1.2	12-Aug-11	2.17	1071.72	5.38
101473	WHBdn1.3	12-Aug-11	2.01	1276.48	5.17
101474	WHBdn1.3	12-Aug-11	1.81	1078.99	6.39
101475	WHBdn1.3	12-Aug-11	1.40	1003.70	4.29
101476	WHB air	12-Aug-11	0.37	234.64	1.45
101599	WHB	16-Aug-11	0.50	587.16	4.52
101600	WHB	16-Aug-11	0.55	640.70	5.41
101601	WHB	16-Aug-11	0.58	751.98	5.20
101602	Lamprey	16-Aug-11	0.26	480.38	8.18
101603	Lamprey	16-Aug-11	0.24	401.60	7.28
101604	Lamprey	16-Aug-11	0.51	211.04	6.96
101965	RMBup0.41	26-Aug-11	0.27	1771.12	20.27
101966	RMBup0.41	26-Aug-11	0.19	1632.16	15.75
101967	RMBup0.41	26-Aug-11	0.77	948.30	2.37
101968	RMBmid0.42	26-Aug-11	0.23	1349.77	8.57
101969	RMBmid0.42	26-Aug-11	0.26	1532.96	6.31
101970	RMBmid0.42	26-Aug-11	0.25	1390.35	8.40
101971	RMBdn0.43	26-Aug-11	0.24	918.59	4.48
101972	RMBdn0.43	26-Aug-11	0.25	923.87	4.85
101973	RMBdn0.43	26-Aug-11	0.17	816.75	4.01
101974	RMB air	26-Aug-11	0.24	149.51	0.92

101979	WHB	30-Aug-11	0.59	652.75	2.84
101980	WHB	30-Aug-11	0.60	709.44	2.98
101981	WHB	30-Aug-11	0.58	612.13	2.98
101982	Lamprey	30-Aug-11	0.27	529.53	4.53
101983	Lamprey	30-Aug-11	0.25	521.53	4.59
101984	Lamprey	30-Aug-11	0.24	538.73	4.77
101986	BDCup0.30	31-Aug-11	0.73	495.40	4.08
101987	BDCup0.30	31-Aug-11	8.16	1187.53	4.45
101988	BDCup0.30	31-Aug-11	6.46	1159.94	3.84
101989	BDCmid0.38	31-Aug-11	1.49	592.22	1.94
101990	BDCmid0.38	31-Aug-11	1.54	614.87	3.08
101991	BDCmid0.38	31-Aug-11	1.48	671.75	1.85
101992	BDCdn0.45	31-Aug-11	0.53	538.84	8.57
101993	BDCdn0.45	31-Aug-11	1.00	663.59	8.32
101994	BDCdn0.45	31-Aug-11	0.96	471.53	8.91
102146	WHBup1.1	9-Sep-11	0.43	611.26	2.88
102147	WHBup1.1	9-Sep-11	0.41	630.28	2.84
102148	WHBup1.1	9-Sep-11	0.33	419.29	2.15
102149	WHBmid1.2	9-Sep-11	0.93	629.50	3.43
102150	WHBmid1.2	9-Sep-11	0.92	629.88	3.44
102151	WHBmid1.2	9-Sep-11	1.33	698.01	4.40
102152	WHBdn1.3	9-Sep-11	0.86	553.91	3.68
102153	WHBdn1.3	9-Sep-11	0.84	659.79	3.30
102154	WHBdn1.3	9-Sep-11	0.91	690.39	3.21
102155	WHB air	9-Sep-11	0.29	254.00	1.40
102245	WHB	13-Sep-11	0.65	781.80	2.40
102246	WHB	13-Sep-11	0.46	583.55	2.16
102247	WHB	13-Sep-11	0.44	602.47	2.08
102248	Lamprey	13-Sep-11	0.14	259.86	3.60
102249	Lamprey	13-Sep-11	0.12	318.41	3.54
102250	Lamprey	13-Sep-11	0.20	555.42	4.20
102572	WHB	20-Sep-11	0.79	716.10	3.13
102573	WHB	20-Sep-11	0.66	602.88	2.70
102574	WHB	20-Sep-11	0.74	733.00	2.90
102575	Lamprey	20-Sep-11	0.27	304.90	5.51
102576	Lamprey	20-Sep-11	0.21	243.57	4.79
102571	Lamprey	20-Sep-11	0.24	237.03	4.57

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102839	WHB	27-Sep-11	0.47	472.56	1.22
102840	WHB	27-Sep-11	0.43	401.27	0.70
102841	WHB	27-Sep-11	0.53	514.96	1.24
102842	Lamprey	27-Sep-11	0.17	324.46	2.79
102843	Lamprey	27-Sep-11	0.22	400.29	3.28
102844	Lamprey	27-Sep-11	0.24	463.88	3.33
102845	RMBup0.41	28-Sep-11	0.15	1267.71	20.73
102846	RMBup0.41	28-Sep-11	0.16	1294.18	21.96
102847	RMBup0.41	28-Sep-11	0.20	1681.04	28.55
102848	RMBmid0.42	28-Sep-11	0.15	984.51	9.47
102849	RMBmid0.42	28-Sep-11	0.20	1031.16	8.61
102850	RMBmid0.42	28-Sep-11	0.18	912.04	10.07
102851	RMBdn0.43	28-Sep-11	0.14	657.07	3.42
102852	RMBdn0.43	28-Sep-11	0.13	621.13	3.19
102853	RMBdn0.43	28-Sep-11	0.27	963.83	5.28
102854	RMB air	28-Sep-11	1.21	587.85	2.36
102904	BDCup0.30	28-Sep-11	8.13	972.32	1.83
102905	BDCup0.30	28-Sep-11	8.67	1122.26	2.14
102906	BDCup0.30	28-Sep-11	9.02	1153.93	2.67
102907	BDCmid0.38	28-Sep-11	2.64	951.75	2.10
102908	BDCmid0.38	28-Sep-11	1.98	754.20	1.48
102909	BDCmid0.38	28-Sep-11	2.23	851.01	1.72
102910	BDCdn0.45	28-Sep-11	0.75	608.05	7.26
102911	BDCdn0.45	28-Sep-11	0.84	688.69	13.81
102912	BDCdn0.45	28-Sep-11	0.79	608.38	6.14
103102	WHB	4-Oct-11	0.52	1353.47	5.28
103103	WHB	4-Oct-11	0.40	1043.09	4.04
103104	WHB	4-Oct-11	0.30	747.62	2.55
103105	Lamprey	4-Oct-11	0.30	596.70	3.95
103106	Lamprey	4-Oct-11	0.12	269.35	1.54
103107	Lamprey	4-Oct-11	0.31	593.47	3.17
103341	WHB	11-Oct-11	0.57	502.30	0.89
103342	WHB	11-Oct-11	0.64	652.79	0.58
103343	WHB	11-Oct-11	0.63	595.57	0.96
103344	Lamprey	11-Oct-11	0.17	277.09	2.17
103345	Lamprey	11-Oct-11	0.21	323.26	1.92
103346	Lamprey	11-Oct-11	0.22	253.60	2.03

103486	WHB	18-Oct-11	0.62	749.38	0.13
103487	WHB	18-Oct-11	0.42	510.59	0.29
103488	WHB	18-Oct-11	0.92	1069.35	2.06
103489	Lamprey	18-Oct-11	0.29	646.07	3.35
103490	Lamprey	18-Oct-11	0.19	505.80	2.33
103491	Lamprey	18-Oct-11	0.20	371.36	1.37
103499	WHBup1.1	19-Oct-11	0.51	645.09	1.24
103500	WHBup1.1	19-Oct-11	0.71	1029.85	1.08
103501	WHBup1.1	19-Oct-11	0.34	513.19	-0.19
103502	WHBmid1.2	19-Oct-11	1.46	948.21	2.39
103503	WHBmid1.2	19-Oct-11	1.07	692.39	1.84
103504	WHBmid1.2	19-Oct-11	1.15	761.43	1.81
103505	WHBdn1.3	19-Oct-11	1.30	965.12	1.82
103506	WHBdn1.3	19-Oct-11	1.02	735.34	1.45
103507	WHBdn1.3	19-Oct-11	1.19	914.97	1.70
103508	WHB air	19-Oct-11	0.36	299.92	1.52
103813	RMBup0.41	24-Oct-11	0.35	1669.66	22.16
103814	RMBup0.41	24-Oct-11	0.23	1112.16	15.16
103815	RMBup0.41	24-Oct-11	0.33	1722.81	20.06
103816	RMBmid0.42	24-Oct-11	0.25	1153.40	10.37
103817	RMBmid0.42	24-Oct-11	0.23	1016.45	8.71
103818	RMBmid0.42	24-Oct-11	0.32	1636.18	15.83
103819	RMBdn0.43	24-Oct-11	0.20	683.78	4.97
103820	RMBdn0.43	24-Oct-11	0.33	1079.21	7.95
103821	RMBdn0.43	24-Oct-11	0.20	844.06	5.92
103822	RMB air	24-Oct-11	0.40	284.88	1.50
103845	BDCup0.30	25-Oct-11	9.45	2193.35	5.30
103846	BDCup0.30	25-Oct-11	9.10	2062.17	5.82
103847	BDCup0.30	25-Oct-11	6.97	1517.85	3.88
103848	BDCmid0.38	25-Oct-11	3.02	851.91	1.52
103849	BDCmid0.38	25-Oct-11	4.35	1412.38	3.97
103850	BDCmid0.38	25-Oct-11	4.75	1498.31	3.55
103851	BDCdn0.45	25-Oct-11	2.21	882.82	6.87
103852	BDCdn0.45	25-Oct-11	1.96	886.14	5.61
103853	BDCdn0.45	25-Oct-11	2.15	581.21	5.73
103854	BDC air	25-Oct-11	0.42	267.23	1.75
103873	WHB	25-Oct-11	0.54	514.43	1.66

103874	WHB	25-Oct-11	0.93	847.41	2.66
103875	WHB	25-Oct-11	0.70	725.16	1.68
103876	Lamprey	25-Oct-11	0.43	733.48	5.67
103878	Lamprey	25-Oct-11	0.30	554.14	4.23
103917	WHB	1-Nov-11	0.72	721.58	1.61
103918	WHB	1-Nov-11	0.79	752.49	2.24
103919	WHB	1-Nov-11	0.84	908.53	2.18
103920	Lamprey	1-Nov-11	0.58	761.37	4.67
103921	Lamprey	1-Nov-11	0.49	613.57	3.88
103922	Lamprey	1-Nov-11	0.57	689.97	4.33
103907	WHBup1.1	2-Nov-11	0.90	817.04	1.68
103908	WHBup1.1	2-Nov-11	0.73	683.86	1.45
103909	WHBup1.1	2-Nov-11	0.61	468.10	1.06
103910	WHBmid1.2	2-Nov-11	1.51	913.47	2.12
103911	WHBmid1.2	2-Nov-11	1.62	936.69	2.26
103912	WHBmid1.2	2-Nov-11	1.64	1012.43	2.40
103913	WHBdn1.3	2-Nov-11	1.26	705.36	1.68
103914	WHBdn1.3	2-Nov-11	1.62	1144.24	2.01
103915	WHBdn1.3	2-Nov-11	1.28	785.18	1.59
103916	WHB air	2-Nov-11	0.48	328.68	1.57
104078	RMBup0.41	6-Nov-11	0.40	1370.94	10.24
104079	RMBup0.41	6-Nov-11	0.51	1577.73	11.98
104080	RMBup0.41	6-Nov-11	0.39	1160.35	9.71
104081	RMBmid0.42	6-Nov-11	0.48	1441.40	8.77
104082	RMBmid0.42	6-Nov-11	0.45	1331.72	8.69
104083	RMBmid0.42	6-Nov-11	0.61	1666.10	10.80
104084	RMBdn0.43	6-Nov-11	0.38	900.75	4.99
104085	RMBdn0.43	6-Nov-11	0.45	1032.23	6.15
104086	RMBdn0.43	6-Nov-11	0.36	926.08	5.07
104087	RMB air	6-Nov-11	0.50	333.64	1.52
104243	WHB	8-Nov-11	0.96	772.59	1.42
104244	WHB	8-Nov-11	0.57	492.57	1.02
104245	WHB	8-Nov-11	0.67	646.53	0.74
104246	Lamprey	8-Nov-11	0.37	464.00	2.63
104247	Lamprey	8-Nov-11	0.34	430.60	2.62
104248	Lamprey	8-Nov-11	0.38	489.08	2.63
104357	WHB	15-Nov-11	0.61	738.91	1.31

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104358	WHB	15-Nov-11	0.34	430.22	0.00
104359	WHB	15-Nov-11	0.42	520.95	0.95
104360	Lamprey	15-Nov-11	0.21	455.05	3.22
104361	Lamprey	15-Nov-11	0.12	337.91	0.64
104362	Lamprey	15-Nov-11	0.11	392.59	2.17
104363	BDCup0.30	19-Nov-11	5.82	1054.93	2.76
104364	BDCup0.30	19-Nov-11	5.68	1098.22	2.51
104365	BDCup0.30	19-Nov-11	6.37	1291.76	3.08
104366	BDCmid0.38	19-Nov-11	2.85	656.75	1.67
104367	BDCmid0.38	19-Nov-11	3.95	995.33	2.26
104368	BDCmid0.38	19-Nov-11	3.94	993.28	2.03
104369	BDCdn0.45	19-Nov-11	2.74	1009.36	5.34
104370	BDCdn0.45	19-Nov-11	2.18	572.83	3.62
104371	BDCdn0.45	19-Nov-11	2.97	945.19	5.42
104372	BDC air	19-Nov-11	0.37	287.68	1.58
104373	WHBup1.1	21-Nov-11	0.73	527.65	1.22
104374	WHBup1.1	21-Nov-11	0.56	372.38	0.93
104375	WHBup1.1	21-Nov-11	0.85	585.87	1.49
104376	WHBmid1.2	21-Nov-11	1.33	499.75	1.25
104377	WHBmid1.2	21-Nov-11	1.23	545.57	1.34
104378	WHBmid1.2	21-Nov-11	1.09	429.51	1.02
104379	WHBdn1.3	21-Nov-11	1.31	666.42	1.50
104380	WHBdn1.3	21-Nov-11	1.12	494.68	1.24
104381	WHBdn1.3	21-Nov-11	1.46	623.02	1.41
104382	WHB air	21-Nov-11	0.83	372.22	2.67
104383	RMBup0.41	21-Nov-11	0.38	808.58	22.68
104384	RMBup0.41	21-Nov-11	0.63	1100.59	32.99
104385	RMBup0.41	21-Nov-11	0.37	729.96	21.76
104386	RMBmid0.42	21-Nov-11	0.54	970.35	28.52
104387	RMBmid0.42	21-Nov-11	0.52	1091.44	39.11
104388	RMBmid0.42	21-Nov-11	0.53	1277.67	42.83
104389	RMBdn0.43	21-Nov-11	0.41	992.53	38.16
104390	RMBdn0.43	21-Nov-11	0.31	780.68	29.67
104391	RMBdn0.43	21-Nov-11	0.35	715.26	29.53
104392	RMB air	21-Nov-11	0.44	213.07	1.65
104489	WHB	29-Nov-11	0.63	402.25	0.99
104490	WHB	29-Nov-11	0.66	355.80	1.18

104491	WHB	29-Nov-11	0.66	372.26	1.01
104492	Lamprey	29-Nov-11	0.50	517.68	3.54
104493	Lamprey	29-Nov-11	0.37	352.63	2.59
104494	Lamprey	29-Nov-11	0.41	427.59	3.14
104525	WHB	6-Dec-11	1.11	643.45	1.85
104526	WHB	6-Dec-11	0.66	405.49	1.17
104527	WHB	6-Dec-11	0.59	413.14	0.92
104528	Lamprey	6-Dec-11	0.29	393.15	2.57
104529	Lamprey	6-Dec-11	0.40	374.98	2.84
104530	Lamprey	6-Dec-11	0.44	521.96	3.12
104836	WHB	13-Dec-11	0.88	552.36	1.10
104837	WHB	13-Dec-11	1.14	575.25	1.45
104838	WHB	13-Dec-11	1.15	756.43	1.50
104839	Lamprey	13-Dec-11	0.58	574.61	4.44
104840	Lamprey	13-Dec-11	0.52	469.31	3.48
104841	Lamprey	13-Dec-11	0.45	593.81	4.11
104886	WHBup1.1	20-Dec-11	1.18	667.09	2.28
104887	WHBup1.1	20-Dec-11	1.05	694.00	1.69
104888	WHBup1.1	20-Dec-11	0.79	465.64	1.21
104889	WHBmid1.2	20-Dec-11	1.49	564.35	1.51
104890	WHBmid1.2	20-Dec-11	0.94	400.57	1.23
104891	WHBmid1.2	20-Dec-11	0.93	412.43	1.19
104892	WHBdn1.3	20-Dec-11	1.20	607.62	1.31
104893	WHBdn1.3	20-Dec-11	1.34	670.78	1.31
104894	WHBdn1.3	20-Dec-11	1.18	323.93	1.39
104895	WHB air	20-Dec-11	0.55	246.47	1.90
104852	WHB	20-Dec-11	0.64	694.45	5.57
104853	WHB	20-Dec-11	0.39	447.63	3.68
104854	WHB	20-Dec-11	0.58	571.49	4.65
104855	Lamprey	20-Dec-11	0.89	572.34	1.21
104856	Lamprey	20-Dec-11	1.31	777.13	1.83
104857	Lamprey	20-Dec-11	1.19	697.81	1.40
104842	RMBup0.41	22-Dec-11	0.64	1002.90	15.88
104843	RMBup0.41	22-Dec-11	0.75	833.59	12.26
104844	RMBup0.41	22-Dec-11	0.87	1002.75	13.74
104845	RMBmid0.42	22-Dec-11	1.23	1293.27	16.44
104846	RMBmid0.42	22-Dec-11	0.63	529.66	9.91

104847	RMBmid0.42	22-Dec-11	0.70	576.00	9.24
104848	RMBdn0.43	22-Dec-11	0.67	792.28	9.10
104849	RMBdn0.43	22-Dec-11	0.74	635.95	8.54
104850	RMBdn0.43	22-Dec-11	0.91	878.33	10.08
104851	RMB air	22-Dec-11	1.44	372.12	2.87
104858	BDCup0.30	22-Dec-11	6.96	1525.06	6.76
104859	BDCup0.30	22-Dec-11	5.02	912.36	4.97
104860	BDCup0.30	22-Dec-11	5.08	952.83	4.95
104861	BDCmid0.38	22-Dec-11	22-Dec-11 4.07		4.31
104862	BDCmid0.38	22-Dec-11	3.67	823.12	3.78
104863	BDCmid0.38	22-Dec-11	3.60	806.24	3.81
104864	BDCdn0.45	22-Dec-11	3.48	927.14	3.87
104865	BDCdn0.45	22-Dec-11	2.99	770.46	3.41
104866	BDCdn0.45	22-Dec-11	4.38	1196.40	4.75
104867	BDC air	22-Dec-11	0.82	242.61	1.83
104824	Lamprey	27-Dec-11	0.71	424.58	3.84
104825	Lamprey	27-Dec-11	0.40	429.08	3.23
104826	Lamprey	27-Dec-11	0.31	308.20	3.34
104827	WHB	27-Dec-11	0.74	453.36	1.12
104828	WHB	27-Dec-11	0.77	441.66	1.06
104829	WHB	27-Dec-11	0.74	289.93	0.84
104830	Lamprey	3-Jan-12	0.42	671.02	3.11
104831	Lamprey	3-Jan-12	0.37	594.23	2.98
104832	Lamprey	3-Jan-12	0.29	1886.33	2.58
104833	WHB	3-Jan-12	0.81	1728.55	1.11
104834	WHB	3-Jan-12	1.16	988.78	1.02
104835	WHB	3-Jan-12	1.14	881.69	0.99
105016	WHB	10-Jan-12	1.02	617.25	0.00
105017	WHB	10-Jan-12	0.81	545.34	0.86
105018	WHB	10-Jan-12	0.97	594.34	0.93
105019	Lamprey	10-Jan-12	0.42	556.19	4.66
105020	Lamprey	10-Jan-12	0.45	548.07	4.45
105021	Lamprey	10-Jan-12	0.53	552.99	4.54
105135	WHB	17-Jan-12	1.77	600.45	1.37
105136	WHB	17-Jan-12	2.17	853.95	1.78
105137	WHB	17-Jan-12	2.12	858.39	1.69
105138	Lamprey	17-Jan-12	1.16	829.68	6.22

105139	Lamprey	17-Jan-12	0.92	658.38	5.25
105140	Lamprey	17-Jan-12	1.19	892.75	6.37
105186	WHBup1.1	23-Jan-12	1.28	522.14	0.84
105187	WHBup1.1	23-Jan-12	1.23	461.87	0.91
105188	WHBup1.1	23-Jan-12	1.27	537.83	0.89
105189	WHBmid1.2	23-Jan-12	2.45	573.97	1.17
105190	WHBmid1.2	23-Jan-12	2.04	480.63	1.02
105191	WHBmid1.2	23-Jan-12	1.91	519.30	0.97
105192	WHBdn1.3	23-Jan-12	1.91	633.79	0.96
105193	WHBdn1.3	23-Jan-12	2.76	855.05	1.18
105194	WHBdn1.3	23-Jan-12	2.71	873.02	1.24
105195	WHB air	23-Jan-12	0.85	262.16	2.00
105247	BDCup0.30	24-Jan-12	4.95	2582.08	7.03
105248	BDCup0.30	24-Jan-12	4.33	2090.60	6.84
105249	BDCup0.30	24-Jan-12	5.82	2952.34	8.56
105250	BDCmid0.38	24-Jan-12	3.52	1876.48	5.26
105251	BDCmid0.38	24-Jan-12	24-Jan-12 3.65 1980.42		5.26
105252	BDCmid0.38	24-Jan-12	3.62	1935.13	5.63
105253	BDCdn0.45	24-Jan-12	4.16	2031.82	6.17
105254	BDCdn0.45	24-Jan-12	2.98	1829.38	4.67
105255	BDCdn0.45	24-Jan-12	3.11	1820.06	4.88
105256	BDC air	24-Jan-12	0.58	362.95	2.24
105345	WHB	24-Jan-12	0.72	606.21	1.61
105346	WHB	24-Jan-12	0.93	634.50	1.60
105347	WHB	24-Jan-12	0.90	594.35	1.58
105348	Lamprey	24-Jan-12	0.61	735.97	4.27
105349	Lamprey	24-Jan-12	0.67	903.17	5.17
105350	Lamprey	24-Jan-12	0.82	1172.84	6.79
105409	RMBup0.41	25-Jan-12	0.65	1177.55	11.61
105410	RMBup0.41	25-Jan-12	0.57	992.90	10.24
105411	RMBup0.41	25-Jan-12	0.61	792.23	9.88
105412	RMBmid0.42	25-Jan-12	0.56	754.49	7.84
105413	RMBmid0.42	25-Jan-12	0.63	842.83	8.26
105414	RMBmid0.42	25-Jan-12	0.47	774.51	7.97
105415	RMBdn0.43	25-Jan-12	0.55	723.49	6.75
105416	RMBdn0.43	25-Jan-12	0.63	821.81	6.33
105417	RMBdn0.43	25-Jan-12	0.76	1140.86	8.77

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105418	RMB air	25-Jan-12	0.66	350.38	2.19
105420	WHB	31-Jan-12	1.01	690.79	2.10
105421	WHB	31-Jan-12	0.79	504.40	0.93
105422	WHB	31-Jan-12	0.94	678.33	1.19
105423	Lamprey	31-Jan-12	0.64	513.74	4.04
105424	Lamprey	31-Jan-12	0.58	722.42	4.11
105425	Lamprey	31-Jan-12 0.62 649.70		3.98	
105511	WHB	7-Feb-12 0.97 577.96		0.64	
105512	WHB	7-Feb-12	0.90	583.46	1.13
105513	WHB	7-Feb-12	1.19	802.79	1.25
105514	Lamprey	7-Feb-12	0.59	679.83	3.87
105515	Lamprey	7-Feb-12	0.64	613.24	3.60
105516	Lamprey	7-Feb-12	0.44	635.01	3.62
105658	WHB	14-Feb-12	1.01	712.24	0.83
105659	WHB	14-Feb-12	1.02	682.90	1.33
105660	WHB	14-Feb-12	1.10	850.41	1.37
105661	Lamprey	14-Feb-12	0.62	747.31	4.92
105662	Lamprey	14-Feb-12	0.60	744.09	5.23
105663	Lamprey	14-Feb-12	0.58	762.17	5.18
105971	WHBup1.1	20-Feb-12	0.87	700.93	0.12
105972	WHBup1.1	20-Feb-12	0.67	515.76	-0.45
105973	WHBup1.1	20-Feb-12	0.73	453.44	-0.35
105974	WHBmid1.2	20-Feb-12	1.10	488.65	-0.23
105975	WHBmid1.2	20-Feb-12	1.27	446.23	-0.35
105976	WHBmid1.2	20-Feb-12	1.96	897.46	0.18
105977	WHBdn1.3	20-Feb-12	1.23	612.77	-0.15
105978	WHBdn1.3	20-Feb-12	1.12	592.99	-0.08
105979	WHBdn1.3	20-Feb-12	1.06	522.95	0.06
105980	WHB air	20-Feb-12	0.53	303.51	1.22
106009	WHB	21-Feb-12	0.96	477.32	-0.31
106010	WHB	21-Feb-12	0.97	583.30	0.61
106011	WHB	21-Feb-12	1.01	578.73	0.07
106012	Lamprey	21-Feb-12	0.44	413.71	1.70
106013	Lamprey	21-Feb-12	0.51	404.55	2.22
106014	Lamprey	21-Feb-12	0.57	188.08	2.04
106016	BDCup0.30	23-Feb-12	3.75	1005.66	3.42
106017	BDCup0.30	23-Feb-12	3.85	1059.67	3.29

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106018	BDCup0.30	23-Feb-12	4.11	1129.35	3.31
106019	BDCmid0.38	23-Feb-12	2.37	693.45	2.34
106020	BDCmid0.38	23-Feb-12	2.36	811.59	2.20
106021	BDCmid0.38	23-Feb-12	2.41	546.79	2.33
106022	BDCdn0.45	23-Feb-12	1.60	619.97	2.01
106023	BDCdn0.45	23-Feb-12	23-Feb-12 1.54		2.05
106024	BDCdn0.45	23-Feb-12	1.60	551.41	1.88
106025	BDC air	23-Feb-12	0.57	349.87	1.90
106026	RMBup0.41	23-Feb-12	0.49	557.68	8.14
106027	RMBup0.41	23-Feb-12	0.38	529.22	7.27
106028	RMBup0.41	23-Feb-12	0.38	583.90	6.88
106029	RMBmid0.42	23-Feb-12	0.34	430.81	5.76
106030	RMBmid0.42	23-Feb-12	0.64	884.97	9.40
106031	RMBmid0.42	23-Feb-12	0.39	452.12	5.70
106032	RMBdn0.43	23-Feb-12	0.38	469.46	4.05
106033	RMBdn0.43	23-Feb-12	0.35	494.15	4.23
106034	RMBdn0.43	23-Feb-12	0.42	458.76	4.68
106035	RMB air	23-Feb-12	23-Feb-12 0.57 344		1.87
106261	WHB .	28-Feb-12	0.78	568.83	0.94
106262	WHB	28-Feb-12	0.98	721.69	1.02
106263	WHB	28-Feb-12	1.13	987.18	1.62
106264	Lamprey	28-Feb-12	0.50	475.73	2.46
106265	Lamprey	28-Feb-12	0.40	260.46	2.27
106266	Lamprey	28-Feb-12	0.50	499.28	2.88
106463	WHB	6-Mar-12	1.35	896.92	3.09
106464	WHB	6-Mar-12	1.11	585.02	1.89
106465	WHB	6-Mar-12	0.93	557.51	1.09
106466	Lamprey	6-Mar-12	0.42	466.69	2.99
106467	Lamprey	6-Mar-12	0.37	347.74	1.82
106468	Lamprey	6-Mar-12	0.46	477.63	2.04
106961	WHBup1.1	8-Mar-12	0.76	539.30	2.62
106962	WHBup1.1	8-Mar-12	0.63	377.64	1.43
106963	WHBup1.1	8-Mar-12	0.42	263.77	1.53
106964	WHBmid1.2	8-Mar-12	0.68	295.51	1.20
106965	WHBmid1.2	8-Mar-12	0.69	338.72	2.33
106966	WHBmid1.2	8-Mar-12	1.30	623.96	1.73
106967	WHBdn1.3	8-Mar-12	1.30	773.34	4.05

106968	WHBdn1.3	8-Mar-12	0.91	366.15	2.69
106969	WHBdn1.3	8-Mar-12	1.33	704.27	0.00
106970	WHB air	8-Mar-12	0.46	252.28	1.62
106971	BDCup0.30	8-Mar-12	3.14	1446.01	2.62
106972	BDCup0.30	8-Mar-12	4.31	1955.44	10.56
106973	BDCup0.30	8-Mar-12	3.53	1657.60	2.82
106974	BDCmid0.38	8-Mar-12	3.35	1293.41	3.85
106975	BDCmid0.38	8-Mar-12	2.69	1300.05	2.57
106976	BDCmid0.38	8-Mar-12	2.88	1313.83	2.47
106977	BDCdn0.45	8-Mar-12	2.38	1254.51	1.65
106978	BDCdn0.45	8-Mar-12	2.38	1165.09	1.21
106979	BDCdn0.45	8-Mar-12	2.57	1177.55	1.92
106980	BDC air	8-Mar-12	0.37	251.55	2.34
106981	RMBup0.41	9-Mar-12	0.48	776.63	6.20
106982	RMBup0.41	9-Mar-12	0.39	647.99	5.51
106983	RMBup0.41	9-Mar-12	0.63	682.01	5.65
106984	RMBmid0.42	9-Mar-12	0.50	660.62	5.55
106985	RMBmid0.42	9-Mar-12	0.72	1116.46	7.16
106986	RMBmid0.42	9-Mar-12	0.40	676.04	6.12
106987	RMBdn0.43	9-Mar-12	0.57	748.57	5.54
106988	RMBdn0.43	9-Mar-12	0.32	588.69	4.79
106989	RMBdn0.43	9-Mar-12	0.49	566.85	5.08
106990	RMB air	9-Mar-12	0.68	183.53	1.89
106816	WHB	13-Mar-12	0.58	323.66	1.00
106817	WHB	13-Mar-12	0.80	285.83	1.18
106818	WHB	13-Mar-12	0.58	413.56	1.56
106819	Lamprey	13-Mar-12	0.45	269.97	2.60
106820	Lamprey	13-Mar-12	0.37	313.05	2.52
106821	Lamprey	13-Mar-12	0.31	462.09	1.90
107862	WHB	20-Mar-12	0.86	545.86	1.22
107863	WHB	20-Mar-12	0.85	629.44	1.38
107864	WHB	20-Mar-12	0.82	578.60	1.17
107865	Lamprey	20-Mar-12	0.49	635.68	3.57
107866	Lamprey	20-Mar-12	0.35	334.92	2.30
107867	Lamprey	20-Mar-12	0.34	432.30	2.35
107253	WHBup1.1	22-Mar-12	0.42	369.15	0.00
107254	WHBup1.1	22-Mar-12	0.46	452.50	0.00

107255	WHBup1.1	22-Mar-12	0.52	506.44	0.00
107256	WHBmid1.2	22-Mar-12	0.87	516.53	0.00
107257	WHBmid1.2	22-Mar-12	1.11	576.76	0.55
107258	WHBmid1.2	22-Mar-12	1.04	561.61	0.00
107259	WHBdn1.3	22-Mar-12	0.97	583.43	0.00
107260	WHBdn1.3	22-Mar-12	1.01	455.90	0.71
107261	WHBdn1.3	22-Mar-12	0.96	462.80	0.51
107262	WHB air	22-Mar-12	0.37	339.88	1.24
107578	BDCup0.30	24-Mar-12	4.81	628.06	1.71
107579	BDCup0.30	24-Mar-12	5.04	658.22	1.64
107580	BDCup0.30	24-Mar-12	4.71	674.05	1.35
107581	BDCmid0.38	24-Mar-12	2.01	476.29	0.75
107582	BDCmid0.38	24-Mar-12	2.02	478.19	0.85
107583	BDCmid0.38	24-Mar-12	2.07	488.72	0.87
107584	BDCdn0.45	24-Mar-12	1.16	431.46	2.28
107585	BDCdn0.45	24-Mar-12	1.19	451.82	2.50
107586	BDCdn0.45	24-Mar-12	1.37	494.29	2.57
107587	BDC air	24-Mar-12	0.38	278.32	2.18
107598	RMBup0.41	24-Mar-12	0.40	854.78	11.81
107599	RMBup0.41	24-Mar-12	0.41	950.50	12.25
107600	RMBup0.41	24-Mar-12	0.42	890.63	12.67
107601	RMBmid0.42	24-Mar-12	0.37	712.13	9.01
107602	RMBmid0.42	24-Mar-12	0.39	789.89	9.40
107603	RMBmid0.42	24-Mar-12	0.23	573.21	7.07
107604	RMBdn0.43	24-Mar-12	0.40	755.11	5.01
107605	RMBdn0.43	24-Mar-12	0.41	598.05	6.05
107606	RMBdn0.43	24-Mar-12	0.45	725.83	5.40
107607	RMB air	24-Mar-12	0.39	211.69	1.18
107563	RMBup0.41	31-Mar-12	0.79	1094.23	16.89
107564	RMBup0.41	31-Mar-12	0.47	900.54	12.52
107565	RMBup0.41	31-Mar-12	0.56	867.18	12.84
107566	RMBmid0.42	31-Mar-12	0.52	801.04	10.98
107567	RMBmid0.42	31-Mar-12	0.52	780.11	9.95
107568	RMBmid0.42	31-Mar-12	0.60	747.81	9.29
107569	RMBdn0.43	31-Mar-12	0.57	702.36	6.29
107570	RMBdn0.43	31-Mar-12	0.48	747.07	6.09
107571	RMBdn0.43	31-Mar-12	0.65	743.02	7.00

107572	RMB air	31-Mar-12	0.44	327.75	1.45
107588	BDCup0.30	2-Apr-12	5.61	703.76	1.56
107589	BDCup0.30	2-Apr-12	5.60	686.24	1.45
107590	BDCup0.30	2-Apr-12	5.51	674.76	1.35
107591	BDCmid0.38	2-Apr-12	2.41	534.49	0.84
107592	BDCmid0.38	2-Apr-12	2.43	450.59	1.22
107593	BDCmid0.38	2-Apr-12	2.64	494.74	0.82
107594	BDCdn0.45	2-Apr-12	1.58	364.69	4.90
107595	BDCdn0.45	2-Apr-12	1.50	403.73	5.93
107596	BDCdn0.45	2-Apr-12	1.59	402.28	5.85
107597	BDC air	2-Apr-12	0.36	245.97	1.17
107874	WHB	3-Apr-12	1.07	684.83	0.94
107875	WHB	3-Apr-12	0.98	609.75	0.98
107876	WHB	3-Apr-12	1.22	710.15	1.05
107877	Lamprey	3-Apr-12	0.36	332.74	2.52
107878	Lamprey	3-Apr-12	0.31	316.83	2.52
107879	Lamprey	3-Apr-12	0.37	408.16	2.79
107620	WHBup1.1	6-Apr-12	0.98	447.21	3.80
107621	WHBup1.1	6-Apr-12	1.07	458.61	1.43
107622	WHBup1.1	6-Apr-12	0.97	456.84	0.95
107623	WHBmid1.2	6-Apr-12	0.39	498.24	2.10
107624	WHBmid1.2	6-Apr-12	0.47	85.53	2.36
107625	WHBmid1.2	6-Apr-12	0.40	204.58	2.09
107626	WHBdn1.3	6-Apr-12	0.91	3107.69	9.77
107627	WHBdn1.3	6-Apr-12	0.78	3013.85	8.75
107628	WHBdn1.3	6-Apr-12	0.60	2572.66	14.34
107629	WHB air	6-Apr-12	0.28	1173.86	8.63
107880	BDCup0.30	7-Apr-12	9.74	1016.26	1.98
107881	BDCup0.30	7-Apr-12	9.32	970.30	1.80
107882	BDCup0.30	7-Apr-12	8.97	1002.78	1.79
107883	BDCmid0.38	7-Apr-12	3.24	602.16	0.76
107884	BDCmid0.38	7-Apr-12	3.23	561.03	0.00
107885	BDCmid0.38	7-Apr-12	3.17	625.54	0.00
107886	BDCdn0.45	7-Apr-12	1.78	372.81	3.55
107887	BDCdn0.45	7-Apr-12	1.65	394.66	3.65
107888	BDCdn0.45	7-Apr-12	1.87	456.56	3.60
107889	BDC air	7-Apr-12	0.47	297.18	1.52

107890	RMBup0.41	7-Apr-12	0.47	681.35	10.92
107891	RMBup0.41	7-Apr-12	0.48	703.21	11.66
107892	RMBup0.41	7-Apr-12	0.46	633.01	11.22
107893	RMBmid0.42	7-Apr-12	0.48	589.54	8.57
107894	RMBmid0.42	7-Apr-12	0.49	625.73	7.95
107895	RMBmid0.42	7-Apr-12	0.44	575.35	7.94
107896	RMBdn0.43	7-Apr-12	0.43	533.62	4.22
107897	RMBdn0.43	7-Apr-12	0.55	575.93	4.35
107898	RMBdn0.43	7-Apr-12	0.64	630.75	4.80
107899	RMB air	7-Apr-12	0.41	257.06	1.30
107856	Lamprey	10-Apr-12	7-Apr-12 0.41 257.06 0-Apr-12 0.33 551.97 0-Apr-12 0.39 632.58		1.35
107857	Lamprey	10-Apr-12	-Apr-120.33551.97-Apr-120.39632.58-Apr-120.27472.47		1.54
107858	Lamprey	10-Apr-12	0.27	472.47	1.41
107859	WHB	10-Apr-12	0.71	682.34	0.00
107860	WHB	10-Apr-12	0.77	750.09	0.00
107861	WHB	10-Apr-12	0.77	646.35	0.00
108019	WHB	17-Apr-12	0.54	406.07	1.04
108020	WHB	17-Apr-12	0.40	280.26	0.73
108021	WHB	17-Apr-12	0.70	616.12	1.20
108022	Lamprey	17-Apr-12	0.20	226.58	1.81
108023	Lamprey	17-Apr-12	0.19	292.03	2.22
108024	Lamprey	17-Apr-12	0.19	277.67	2.41
108460	WHBup1.1	20-Apr-12	0.64	589.62	0.00
108461	WHBup1.1	20-Apr-12	0.59	335.37	0.00
108462	WHBup1.1	20-Apr-12	0.62	491.07	0.00
108463	WHBmid1.2	20-Apr-12	1.62	483.52	1.25
108464	WHBmid1.2	20-Apr-12	1.51	575.22	1.12
108465	WHBmid1.2	20-Apr-12	1.52	552.97	0.96
108466	WHBdn1.3	20-Apr-12	1.56	767.60	1.14
108467	WHBdn1.3	20-Apr-12	1.59	763.77	1.07
108468	WHBdn1.3	20-Apr-12	1.61	783.26	1.16
108469	WHB air	20-Apr-12	0.35	240.83	1.22
108470	BDCup0.30	21-Apr-12	8.34	1121.45	2.94
108471	BDCup0.30	21-Apr-12	8.40	983.23	2.66
108472	BDCup0.30	21-Apr-12	8.30	1042.60	2.44
108473	BDCmid0.38	21-Apr-12	1.54	647.56	0.73
108474	BDCmid0.38	21-Apr-12	1.54	595.12	0.80

108475	BDCmid0.38	21-Apr-12	1.51	692.55	0.70
108476	BDCdn0.45	21-Apr-12	0.83	351.38	8.17
108477	BDCdn0.45	21-Apr-12	0.69	341.01	7.99
108478	BDCdn0.45	21-Apr-12	0.59	348.93	7.63
108480	RMBup0.41	21-Apr-12	0.33	532.99	11.45
108481	RMBup0.41	21-Apr-12	0.40	525.66	10.96
108482	RMBup0.41	21-Apr-12	0.35	317.47	11.18
108483	RMBmid0.42	21-Apr-12	0.28	313.69	7.44
108484	RMBmid0.42	21-Apr-12	0.58	330.34	7.09
108485	RMBmid0.42	21-Apr-12	0.36	338.15	7.88
108486	RMBdn0.43	21-Apr-12	0.42	332.78	3.43
108487	RMBdn0.43	21-Apr-12	0.41	310.71	3.50
108488	RMBdn0.43	21-Apr-12	0.41	371.04	3.24
108489	RMB air	21-Apr-12	0.34	219.67	0.99

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Appendix B

Average Monthly Transect Station Samples

		N₂O-N	CO₂-C	CH₄-C	NO ₃ ⁻	DOC	Temp
Site	Date	μg/L	μg/L	µg/L	mg N/L	mg C/L	(C°)
WHBdn1.3	5/20/2011	0.92	696.40	1.94			9.96
WHBmid1.2	5/20/2011	0.89	629.32	2.13			
WHBup1.1	5/20/2011	0.52	471.47	2.47			11.35
RMBdn0.43	5/26/2011	0.12	860.90	4.73	0.02	7.59	16.65
RMBmid0.42	5/26/2011	0.25	1129.25	6.69	0.00	7.76	
RMBup0.41	5/26/2011	0.25	1460.39	9.05	0.02	7.87	16.39
BDCdn0.45	5/27/2011	1.20	875.59	18.02	0.58	11.15	16.34
BDCmid0.38	5/27/2011	1.71	735.11	1.99	0.61	10.95	16.34
BDCup0.30	5/27/2011	5.05	1388.58	5.36	0.62	11.01	16.3
BDCdn0.45	6/9/2011	5.41	1230.77	22.18	1.88	8.92	17.87
BDCmid0.38	6/9/2011	10.35	1137.20	0.45			
BDCup0.30	6/9/2011	11.57	1108.49	3.83	2.08	8.75	17.31
RMBdn0.43	6/20/2011	0.24	1327.95	4.16	0.08	6.93	17.63
RMBmid0.42	6/20/2011	0.29	1504.09	7.34	0.00	6.72	
RMBup0.41	6/20/2011	0.32	2102.77	9.90	0.02	6.64	17.59
WHBdn1.3	6/29/2011	1.37	974.36	3.62	1.24	2.56	12.99
WHBmid1.2	6/29/2011	1.41	815.29	3.91	1.16	2.74	13.08
WHBup1.1	6/29/2011	0.53	756.11	1.62	0.70	3.65	13.94
WHBdn1.3	7/7/2011	1.27	826.58	3.71	1.32	2.43	14.99
WHBmid1.2	7/7/2011	1.30	645.14	3.96	1.24	2.59	
WHBup1.1	7/7/2011	0.51	637.23	1.95	0.72	3.32	16.66
RMBdn0.43	7/27/2011	0.32	764.35	4.38			20.15
RMBmid0.42	7/27/2011	0.24	1119.31	4.24			
RMBup0.41	7/27/2011	0.21	1444.33	16.40			19.76
BDCdn0.45	7/29/2011	0.39	1074.83	17.36	2.52	2.81	17.91
BDCmid0.38	7/29/2011	0.36	1115.43	3.22	3.06	2.48	17.73
BDCup0.30	7/29/2011	3.03	1242.00	4.45	4.41	2.30	16.97
WHBdn1.3	8/12/2011	1.74	1119.72	5.28	1.31	1.93	13.87
WHBmid1.2	8/12/2011	1.99	938.11	4.97	1.22	2.01	13.89
WHBup1.1	8/12/2011	0.49	602.19	1.70	0.73	2.89	15.37
RMBdn0.43	8/26/2011	0.22	886.40	4.45	0.07	5.84	19.82
RMBmid0.42	8/26/2011	0.25	1424.36	7.76	0.06	5.97	19.86
RMBup0.41	8/26/2011	0.23	1701.64	18.01	0.08	5.78	19.41

BDCdn0.45	8/31/2011	0.83	557.99	8.60	0.68	3.73	17.78
BDCmid0.38	8/31/2011	1.51	626.28	2.29	0.61	3.72	18.18
BDCup0.30	8/31/2011	7.31	1173.74	4.12	0.36	4.26	17.4
WHBdn1.3	9/9/2011	0.87	634.69	3.40	0.50	2.43	14.41
WHBmid1.2	9/9/2011	1.06	652.46	3.76	0.76	4.99	14.53
WHBup1.1	9/9/2011	0.39	553.61	2.62	0.36	6.43	15.37
BDCdn0.45	9/28/2011	0.79	635.04	9.07	1.57	14.87	17.08
BDCmid0.38	9/28/2011	2.28	852.32	1.76	1.56	15.29	17.13
BDCup0.30	9/28/2011	8.61	1082.83	2.21	1.84	15.90	17.09
RMBdn0.43	9/28/2011	0.18	747.34	3.96	0.03	11.60	17.37
RMBmid0.42	9/28/2011	0.18	975.91	9.38	0.03	11.19	17.47
RMBup0.41	9/28/2011	0.17	1414.31	23.75	0.05	11.75	17.42
WHBdn1.3	10/19/2011	1.17	871.81	1.66	0.91	3.04	10.3
WHBmid1.2	10/19/2011	1.23	800.68	2.01	1.00	2.70	10.32
WHBup1.1	10/19/2011	0.52	729.38	0.71	0.44	3.74	10.38
RMBdn0.43	10/24/2011	0.24	869.02	6.28	0.04	11.31	8.32
RMBmid0.42	10/24/2011	0.27	1268.67	11.64	0.04	10.68	8.29
RMBup0.41	10/24/2011	0.30	1501.54	19.13	0.04	10.16	8.25
BDCdn0.45	10/25/2011	2.10	783.39	6.07	0.73	10.91	9.18
BDCmid0.38	10/25/2011	4.04	1254.20	3.01	0.76	11.50	9.08
BDCup0.30	10/25/2011	8.51	1924.46	5.00	0.74	11.49	9.09
BDCdn0.45	11/19/2011	2.63	842.46	4.79	0.92	7.35	4.97
BDCmid0.38	11/19/2011	3.58	881.78	1.98	0.95	7.79	
BDCup0.30	11/19/2011	5.96	1148.31	2.78	0.99	8.74	4.79
WHBdn1.3	11/21/2011	1.30	594.70	1.38	0.75	2.04	7.3
WHBmid1.2	11/21/2011	1.22	491.61	1.20	0.90	2.41	7.26
WHBup1.1	11/21/2011	0.71	495.30	1.21	0.54	2.80	7
RMBdn0.43	11/21/2011	0.36	829.49	32.45	0.12	5.83	6.94
RMBmid0.42	11/21/2011	0.53	1113.15	36.82	0.12	5.91	6.96
RMBup0.41	11/21/2011	0.46	879.71	25.81	0.12	6.01	6.94
WHBdn1.3	12/20/2011	1.24	534.11	1.34	1.36	1.92	2.52
WHBmid1.2	12/20/2011	1.12	459.11	1.31	1.31	2.02	2.31
WHBup1.1	12/20/2011	1.01	608.91	1.72	1.04	2.10	1.56
BDCdn0.45	12/22/2011	3.62	964.67	4.01	1.03	6.12	1.44
BDCmid0.38	12/22/2011	3.78	864.61	3.96	1.08	6.56	1.32
BDCup0.30	12/22/2011	5.69	1130.08	5.56	1.09	5.81	1.15
RMBdn0.43	12/22/2011	0.78	768.85	9.24	0.24	4.40	1.06
RMBmid0.42	12/22/2011	0.85	799.64	11.87	0.23	4.29	1.04
RMBup0.41	12/22/2011	0.75	946.41	13.96	0.23	4.28	1
WHBdn1.3	1/23/2012	2.46	787.28	1.13	1.29	1.30	2.2

WHBmid1.2	1/23/2012	2.13	524.63	1.05	1.36	1.33	2.02
WHBup1.1	1/23/2012	1.26	507.28	0.88	0.92	1.44	0.95
BDCdn0.45	1/24/2012	3.42	1893.75	5.24	0.78	5.71	-0.08
BDCmid0.38	1/24/2012	3.60	1930.68	5.38	1.09	6.69	-0.09
BDCup0.30	1/24/2012	5.03	2541.67	7.47	1.07	6.98	-0.06
RMBdn0.43	1/25/2012	0.65	895.39	7.28	0.25	4.19	0.23
RMBmid0.42	1/25/2012	0.55	790.61	8.02	0.24	4.13	0.21
RMBup0.41	1/25/2012	0.61	987.56	10.57	0.25	4.25	0.14
WHBdn1.3	2/20/2012	1.14	576.24	0.02	1.53	1.40	3.05
WHBmid1.2	2/20/2012	1.44	610.78	0.06	1.37	1.54	2.94
WHBup1.1	2/20/2012	0.76	556.71	0.04	1.19	1.61	2.16
BDCdn0.45	2/23/2012	1.58	600.89	1.98	1.73	5.39	2.42
BDCmid0.38	2/23/2012	2.38	683.94	2.29	1.78	5.69	2.24
BDCup0.30	2/23/2012	3.90	1064.90	3.34	1.84	5.71	1.85
RMBdn0.43	2/23/2012	0.39	474.12	4.32	0.26	3.10	3.24
RMBmid0.42	2/23/2012	0.45	589.30	6.95	0.26	3.10	3.37
RMBup0.41	2/23/2012	0.42	556.93	7.43	0.24	2.36	3.26
BDCdn0.45	3/8/2012	2.44	1199.05	1.59	1.17	6:20	0.34
BDCmid0.38	3/8/2012	2.97	1302.43	2.96	1.29	6.01	0.3
BDCup0.30	3/8/2012	3.66	1686.35	5.33	1.35	6.14	0.47
WHBdn1.3	3/8/2012	1.18	614.58	2.25	1.00	2.96	4.56
WHBmid1.2	3/8/2012	0.89	419.40	1.75	0.96	3.16	4.54
WHBup1.1	3/8/2012	0.60	393.57	1.86	0.84	3.30	4.44
RMBdn0.43	3/9/2012	0.46	634.70	5.14	0.22	4.84	4.08
RMBmid0.42	3/9/2012	0.54	817.70	6.28	0.22	4.80	3.88
RMBup0.41	3/9/2012	0.50	702.21	5.79	0.22	4.84	3.71
WHBdn1.3	3/22/2012	0.98	500.71	0.41	1.15	2.39	10.26
WHBmid1.2	3/22/2012	1.01	551.63	0.18	0.92	2.47	10.17
WHBup1.1	3/22/2012	0.46	442.70	0.00	0.83	2.89	10.27
BDCdn0.45	3/24/2012	1.24	459.19	2.45	0.80	7.92	8.73
BDCmid0.38	3/24/2012	2.03	481.06	0.82	0.84	7.94	8.83
BDCup0.30	3/24/2012	4.85	653.44	1.56	0.87	8.10	8.8
RMBdn0.43	3/24/2012	0.42	692.99	5.49	0.19	5.44	10.17
RMBmid0.42	3/24/2012	0.33	691.74	8.49	0.19	5.71	10.27
RMBup0.41	3/24/2012	0.41	898.64	12.24	0.19	5.19	10.36
WHBdn1.3	4/6/2012	0.76	2898.07	10.95	1.35	1.74	7.02
WHBmid1.2	4/6/2012	0.42	262.78	2.18	0.98	1.68	7.09
WHBup1.1	4/6/2012	1.01	454.22	2.06	0.91	2.18	6.86
BDCdn0.45	4/7/2012	1.76	408.01	3.60	1.42	6.18	5.8
BDCmid0.38	4/7/2012	3.21	596.24	0.25	1.51	6.51	5.02

BDCup0.30	4/7/2012	9.34	996.45	1.85	1.52	6.44	5.01
RMBdn0.43	4/7/2012	0.54	580.10	4.46	0.27	3.73	8.38
RMBmid0.42	4/7/2012	0.47	596.87	8.15	0.26	3.60	8.52
RMBup0.41	4/7/2012	0.47	672.52	11.27	0.28	3.73	8.53
WHBdn1.3	4/20/2012	1.58	771.54	1.12	1.39	1.58	11.89
WHBmid1.2	4/20/2012	1.55	537.24	1.11	1.36	1.74	12.01
WHBup1.1	4/20/2012	0.62	472.02	0.00	0.85	2.23	12.81
BDCdn0.45	4/21/2012	0.70	347.11	7.93	1.79	7.44	14.55
BDCmid0.38	4/21/2012	1.53	645.08	0.74	1.96	7.49	13.98
BDCup0.30	4/21/2012	8.35	1049.09	2.68	2.04	7.67	13.72
RMBdn0.43	4/21/2012	0.41	338.18	3.39	0.25	4.21	15.83
RMBmid0.42	4/21/2012	0.41	327.39	7.47	0.23	4.09	16.5
RMBup0.41	4/21/2012	0.36	458.71	11.20	0.22	4.13	16.58

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Appendix C

Average Monthly Stream Sample Chemistry

Site	Date	N₂O-N µg/L	CO₂-C µg/L	CH₄-C μg/L	NO₃ ⁻ mg N/L	DOC mg C/L	рН	Temp (C°)	Q (L/S)
BDC	8/31/11	3.22	786.00	5.00	0.55	3.90	6.83	17.79	
BDC	9/28/11	3.89	856.73	4.35	1.66	15.35	6.74	17.10	
BDC	10/25/11	4.88	1320.68	4.69	0.74	11.30	7.01	9.12	
BDC	11/19/11	4.06	957.52	3.19	0.95	7.96	7.12	4.88	0.71
BDC	12/22/11	4.36	986.45	4.51	1.07	6.16	6.78	1.30	7.47
BDC	1/24/12	. 4.02	2122.03	6.03	0. 9 8	6.46	6.14	-0.08	13.71
BDC	2/23/12	2.62	783.24	2.54	1.78	5.60	6.33	2.17	3.38
BDC	3/8/12	3.03	1395.94	3.30	1.27	6.12	5.22	0.37	22.36
BDC	3/24/12	2.71	531.23	1.61	0.84	7.99	5.79	8.79	
BDC	4/7/12	4.77	666.90	1.90	1.48	6.38	6.51	5.28	
BDC	4/21/12	3.53	680.43	3.78	1.93	7.53	7.51	14.08	
BDC	5/27/11	2.65	999.76	8.46	0.61	11.04	6.73	16.33	2.19
BDC	6/9/11	9.11	1158.82	8.82	1.98	8.83	7.17	17.59	0.18
BDC	7/29/11	1.26	1144.09	8.34	3.33	2.53	6.89	17.54	
WHB	5/20/11	0.78	599.06	2.18			7.18	10.66	25.55
WHB	7/7/11	1.03	702.98	3.20	1.09	2.78	7.55	15.83	6.62
WHB	8/12/11	1.41	886.68	3.98	1.09	2.28	7.15	14.38	3.30
WHB	9/9/11	0.77	613.59	3.26	0.54	4.62	6.61	14.77	7.28
WHB	10/19/11	0.97	800.62	1.46	0.79	3.16	6.74	10.33	5.10
WHB	11/21/11	1.07	527.20	1.27	0.73	2.42	6.56	7.19	7.23
WHB	12/20/11	1.12	534.04	1.46	1.23	2.02	6.93	2.13	13.48
WHB	1/23/12	1.95	606.40	1.02	1.19	1.35	6.36	1.72	3.75
WHB	2/20/12	1.11	581.24	0.04	1.36	1.52	6.23	2.72	10.07
WHB	3/8/12	0.89	475.85	1.95	0.93	3.14	6.80	4.51	35.90
WHB	3/22/12	0.82	498.35	0.20	0.97	2.58	6.74	10.23	11.23
WHB	4/6/12	0.73	1205.02	5.06	1.08	1.86	7	6.99	5.80
WHB	4/20/12	1.25	593.60	0.74	1.20	1.85	7.20	12.24	2.24
WHB	6/29/11	1.10	848.59	3.05	1.03	2.98	7.40	13.34	8.52
RMB	5/26/11	0.21	1150.18	6.83	0.01	7.74	6.67	16.52	140.8
RMB	7/27/11	0.26	1109.33	8.34			6.86	19.96	6.60
RMB	8/26/11	0.23	1337.47	10.07	0.07	5.86	6.41	19.70	1.25
RMB	9/28/11	0.18	1045.85	12.36	0.03	11.51	6.14	17.42	10.92
RMB	10/24/11	0.27	1213.08	12.35	0.04	10.72	5.95	8.29	42.47
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RMB	11/21/11	0.45	940.78	31.69	0.12	5.92	6.57	6.95	69.92
RMB	12/22/11	0.79	838.30	11.69	0.24	4.32	5.72	1.03	92.62
RMB	1/25/12	0.60	891.19	8.63	0.25	4.19	6.17	0.19	81.97
RMB	2/23/12	0.42	540.12	6.23	0.25	2.85	6.15	3.29	61.40
RMB	3/9/12	0.50	718.20	5.73	0.22	4.83	6.20	3.89	216.2
RMB	3/24/12	0.39	761.12	8.74	0.19	5.44	5.91	10.27	33.50
RMB	4/7/12	0.49	616.50	7.96	0.27	3.69	6.49	8.48	27.84
RMB	4/21/12	0.39	374.76	7.35	0.23	4.14	7.29	16.30	14.39
RMB	6/20/11	0.28	1644.94	7.13	0.03	6.77	6.66	17.61	23.42

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Appendix D

Monthly Gaseous Flux Estimates

Site	Date	$N_2O \ \mu g \ N \ m^{-2} \ day^{-1}$	$CO_2 \ \mu g \ C \ m^{-2} \ day^{-1}$	CH₄µg C m ⁻² day ⁻¹
BDC	8/31/11	2161.46	437309.89	2798.03
BDC	9/28/11	2659.42	486388.66	2298.26
BDC	10/25/11	3321.20	785508.69	2295.13
BDC	11/19/11	2650.73	488342.75	982.35
BDC	12/22/11	2826.65	482005.30	1779.14
BDC	1/24/12	2544.54	1298139.15	2808.27
BDC	2/23/12	1556.13	344178.08	396.77
BDC	3/8/12	1893.61	812491.79	1086.56
BDC	3/24/12	1702.58	205059.05	5.97
BDC	4/7/12	3190.86	280849.65	69.07
BDC	4/21/12	2364.08	345186.03	1803.86
BDC	5/27/11	1733.56	588186.43	5303.06
BDC	6/9/11	6533.84	712564.68	5620.13
BDC	7/29/11	711.65	698924.79	5253.67
WHB	5/20/11	674.19	619168.33	1450.48
WHB	7/7/11	1238.15	866664.48	3618.77
WHB ·	8/12/11	1883.67	1170529.53	4896.04
WHB	9/9/11	767.23	699792.95	3653.36
WHB	10/19/11	1016.36	967304.55	168.03
WHB	11/21/11	1100.78	436736.54	-472.24
WHB	12/20/11	1014.37	353840.28	-664.89
WHB	1/23/12	2453.85	463994.88	-1522.55
WHB	2/20/12	1018.90	448069.94	-3084.44
WHB	3/8/12	692.35	300231.06	474.10
WHB	3/22/12	732.49	435637.06	-2073.63
WHB	4/6/12	492.63	1620622.26	6202.78
WHB	4/20/12	1552.58	632400.28	-939.77
WHB	6/29/11	1321.15	1092533.70	3197.11
RMB	5/26/11	-297.26	2227751.98	13350.57
RMB	7/27/11	-91.92	2179244.97	17112.59
RMB	8/26/11	-157.38	2700058.51	21085.99
RMB	9/28/11	-353.26	1996445.40	26218.30
RMB	10/24/11	-422.26	2237479.02	25355.53
RMB	11/21/11	-56.39	1578418.11	69944.10

RMB	12/22/11	475.52	1203823.68	22880.65
RMB	1/25/12	-37.28	1295177.39	15621.40
RMB	2/23/12	-271.42	583924.59	10653.06
RMB	3/9/12	-68.03	1000676.70	9527.74
RMB	3/24/12	-73.62	1230045.88	17222.85
RMB	4/7/12	121.02	865350.88	15243.14
RMB	4/21/12	139.65	435238.91	14564.98
RMB	6/20/11	-87.21	3386227.69	14146.48

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Appendix E

Reaeration Experiment Results

Site	Date	K _{sf6}	Sc SF6	Sc CO2	Temp	K(CO₂)	Avg Depth (m)	k (m/day)
RMB	7/27/2011	12.94	963.18	602.09	19.91	10.23	0.06	0.62
RMB	11/6/2011	31.33	2672.06	1591.66	2.95	24.18	0.17	3.99
RMB	3/31/2011	31.44	2248.35	1356.13	5.54	24.42	0.10	2.32
WHB	7/7/2011	30.71	1200.85	749.34	15.67	24.26	0.09	2.06
WHB	11/2/2011	1 9 .12	2386.42	1433.28	4.64	14.81	0.10	1.43
BDC	6/9/2011	36.21	1066.23	666.57	17.89	28.63	0.03	0.78
BDC	11/19/2011	13.12	2306.66	1388.76	5.15	10.18	0.06	0.51
BDC	4/2/2012	28.85	1797.94	1100.96	8.95	22.57	0.04	0.90

Site	Date	K _{sf6}	Sc sf6	Sc N2O	Temp	K(N₂O)	Avg Depth (m)	k (m/day)
RMB	7/27/2011	12.94	963.18	608.12	19.91	10.28	0.06	0.63
RMB	11/6/2011	31.33	2672.06	1687.30	2.95	24.89	0.17	4.11
RMB	3/31/2011	31.44	2248.35	1419.75	5.54	24.99	0.10	2.37
WHB	7/7/2011	30.71	1200.85	758.28	15.67	24.41	0.09	2.07
WHB	11/2/2011	19.12	2386.42	1506.93	4.64	15.19	0.10	1.46
BDC	6/9/2011	36.21	1066.23	673.27	17.89	28.77	0.03	0.79
BDC	11/19/2011	13.12	2306.66	1456.57	5.15	10.42	0.06	0.52
BDC	4/2/2012	28.85	1797.94	1135.33	8.95	22.92	0.04	0.92

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Site	Date	K _{sf6}	Sc sf6	Sc CH4	Temp	K(CH₄)	Avg Depth (m)	k (m/day)
RMB	7/27/2011	12.94	963.18	618.38	19.91	10.37	0.06	0.63
RMB	11/6/2011	31.33	2672.06	1588.30	2.95	24.15	0.17	3.99
RMB	3/31/2011	31.44	2248.35	1359.44	5.54	24.45	0.10	2.32
WHB	7/7/2011	30.71	1200.85	764.84	15.67	24.51	0.09	2.08
WHB	11/2/2011	19.12	2386.42	1434.48	4.64	14.82	0.10	1.43
BDC	6/9/2011	36.21	1066.23	682.71	17.89	28.97	0.03	0.79
BDC	11/19/2011	13.12	2306.66	1391.19	5.15	10.19	0.06	0.51
BDC	4/2/2012	28.85	1797.94	1110.54	8.95	22.67	0.04	0.91

Appendix F

Calculations

Bunsen Solubility Coefficients

Linx II Project (S.K. Hamilton, professor, Michigan State University, unpublished)

Bsc (N₂O) = $2.7182818^{(-165.8806 + (222.8743* (100/(temperature)))) + (92.0792*LN((temperature)/100)) + (-1.48425*((temperature)/100)^2))*0.0821*273.15$

Bsc (CO₂) = $(2.7182818^{-58.0931+(90.5069*(100/temperature))} + (22.294 *LN (temperature/100))) * ((0.0821*273.15) + ((-1636.75+(12.0408*273.15) - (3.27957*0.01*273.15*273.15) + (3.16528*0.00001*273.15*273.15*273.15))/1000))$

Bsc (CH₄) = $(2.7182818^{-58.0931+(90.5069*(100/temperature)) + (22.294 * LN (temperature/100))) * ((0.0821*273.15) + ((-1636.75+(12.0408*273.15) - (3.27957*0.01*273.15*273.15) + (3.16528*0.00001*273.15*273.15*273.15))/1000))$

Calculated Schmidt Numbers

(Wanninkhof, 1992)

Sc CO₂ = 1911.1 - (118.11*(17.89)) + (3.4527 * (17.89^2)) - (0.04132 * (17.89^3)) Sc N₂O = 2055.6-(137.11*(17.89)) + (4.3173*(17.89^2)) - (0.05435*(17.89^3))

Sc $CH_4 = 1897.8 - (114.28*(17.89)) + (3.2902*(17.89^2)) - (0.039061*(17.89^3))$

Sc SF₆ = $3255.3 - (217.13*(17.89)) + (6.837*(17.89^2)) - (0.08607*(17.89^3))$

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