METHYL BROMIDE DEGRADATION IN SOUTHERN OCEAN SEA ICE

by

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(Under the Direction of Patricia Yager)

ABSTRACT

Methyl bromide utilization in sea ice, brine, and under-ice seawater was measured from four stations in the Amundsen Sea using a ^{14}C isotope technique during the Icebreaker *Oden's* 2008-09 austral summer route through the Pacific sector of the Southern Ocean. Increases in ^{14}C measured on 0.2 µm filter membranes and CO_2-trapping wicks are attributed to microbial incorporation and respiration due to the dehalogenating activity of cold-adapted bacteria. Respiration rate constants were >50-fold higher than incorporation constants, reaching 0.51 day^{-1} in sea ice samples, 0.23 day^{-1} in brine samples, and 0.15 day^{-1} in under-ice seawater. These rate constants did not correlate with overall bacterial abundance and suggest that dehalogenating populations are not proportional to the overall microbial communities in the sample types examined. These data show evidence of microbial degradation of methyl bromide in sea ice, brine, and under-ice seawater of the Amundsen Sea, and may help to explain the under-saturation of methyl bromide in the Southern Ocean.

INDEX WORDS: Methyl Bromide, MeBr, Southern Ocean, Amundsen Sea, Sea Ice, Microbial, Bacterial, Degradation, Ice Core, Brine, Seawater, Halocarbon, Organohalogen, Polar, Marine, Methyl Halide, Halogen, Bromine

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BS, Bucknell University, 2007

A Thesis Submitted to the Graduate Faculty of the University of Georgia in Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2010

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May 2010

DEDICATION

For Ian,

who would have been thoroughly amused that I made it to Antarctica,

and for Maripat, Brittany, Amanda, Nikki, and Dunn,

who will be proud of wherever I end up next.

ACKNOWLEDGEMENTS

This thesis includes environmental site data from the collaboration of many scientists onboard the Oden Southern Ocean 2008-09 research cruise, funded by NSF Grant ANT-0836144. The crew and logistical support staff onboard the Oden were invaluable in ensuring the smooth operation of our experiments, as well as providing an extremely welcoming environment to conduct research at the ends of the earth. A National Oceanic and Atmospheric Administration/ Georgia Oceans and Human Health Initiative graduate fellowship covered one year of research support, and Kevin Bakker, Karie Sines, Brett Heimlich, Erin Lipp, Tim Hollibaugh, and Patricia Yager all contributed logistical, laboratory, or other support for this research.

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1.1 Introduction

Anthropogenic halogenated organic compounds synthesized as pesticides, solvents, degreasers and fire retardants have resulted in aquatic and terrestrial contamination due to their toxicity and environmental persistence (Haggblom and Bossert 2003a). Methyl bromide (MeBr) is one of the most abundant halocarbons present in the environment and stratosphere, is 2,400-fold more potent as a greenhouse gas than CO_2 (Oremland 2003), and has been suggested as the most toxic halocarbon to humans (Castro 2003). In addition to industrial production as a soil fumigant, MeBr is produced naturally by marine algae (Gribble 2000), while certain bacteria can degrade it to carbon dioxide in soil, freshwater, estuarine, marine, and hypersaline/alkaline environments (Connell et al. 1997). Predictions of its global budget are therefore complicated by its combination of anthropogenic and biogenic sources and multiple microbial degradation pathways. Since current estimates of MeBr emissions do not balance known sinks, additional sinks need to be identified and incorporated into global models (Rhew et al. 2003). While many halocarbons are primarily broken down in proximity to their biogenic source, MeBr is degraded by soil methylotrophs (Bartnicki and Castro 1994) and marine nitrifiers (Rasche et al. 1990) from ambient concentrations enough to affect its global biogeochemical budget. Biodegradation in various environments may serve as a sink for more than 30% of MeBr's 150 x 10^3 ton atmospheric burden (Butler 1996; Harper 2000). Thus, many microbial degradation pathways are

currently being investigated for their potential value in bioremediative applications. The processes responsible for biological dehalogenation and halocarbon degradation are extremely varied and include metabolic, cometabolic and 'fortuitous' reactions taking place in a variety of different environmental media (Castro 2003). The breadth of degradative processes and environmental media capable of supporting dehalogenating populations therefore need to be identified in order to describe and isolate the most efficient microbial populations and enzyme systems for use in remediative processes.

1.2 Chemical Characteristics of Halocarbons

Halocarbons constitute a diverse class of compounds, produced anthropogenically and biogenically and identified by their carbon-halogen bond. As the molecular weight of a halogen increases, carbon-halogen bond strengths decrease such that the strength of the carbon-fluorine bond is greater than the carbon-chlorine, carbon-bromine, carbon-iodine, and carbon-astatine bonds, respectively. Carbon-fluorine bond energies are among the highest found in natural compounds and are more polar than carbon-chlorine or carbon-bromine bonds. With the increasing ionic radius of heavier halogens and the number of halogen substituents per compound, the metabolic pathways capable of biodegradation and biotransformation become increasingly limited (Commandeur and Parsons 1994). Halogens are strongly electronegative and the electron-withdrawing effect of a halogen substituent increases the electrophilicity of the central carbons, increasing stability (and thus persistence) particularly in aromatic compounds. The 'purest' form of halogens is often the highly reactive diatomic state, and halogens tend to form ionic compounds with metals (such as sodium chloride) and covalent compounds (ie. halocarbons) with non-metals. Naturally occurring halocarbons include 2,320 organochlorines,

2,050 organobromines, 115 organoiodines and 34 organofluorines. Astatine (At), the fifth and heaviest halogen element, is radioactively unstable and not found in nature (Gribble 2004).The presence of halogens and degree of halogenation generally reduce the water solubility and vapor pressure, increase lipid solubility and sorption potential, and often increase the toxicity of a compound. Increased lipophilicity may reduce biodegradation due to decreased bioavailability or the effect of biomagnification in the food chain, as the non-degraded halocarbons are sequestered into the fatty tissue of higher animals or partition more readily onto organic surfaces. These general characteristics, in addition to the high specific density and low vapor pressure of halocarbons, can all act to increase their mobility and persistence in the environment (Haggblom and Bossert 2003b).

1.3 Anthropogenic Production, Uses, and Environmental Fate

Halocarbons have been produced anthropogenically as solvents, degreasing agents, dyes, pharmaceuticals, heat transfer fluids, biocides, plasticizers, and the by-products of disinfection for the last eighty years. The harmful effects of these compounds can be both biological, in their toxicity towards organisms, or abiotic, in the case of the destruction of stratospheric ozone by atmospheric halocarbons (Haggblom and Bossert 2003b).The majority of these halocarbons are chlorinated compounds, but brominated, fluorinated, and iodinated compounds are also used in industrial applications (Haggblom and Bossert 2003b).

Table 1- List of referenced compounds and abbreviations.

Common Chemical Name	Abbreviation	Chemical Formula
2,4-dichlorophenoxyacetic acid	2,4-D	$C_8H_6Cl_2O_3$
Ammonium	---	NH_4+
Astatine	At	At
Bromine	Br	Br
Bromoform	---	$CHBr_3$
Carbon Dioxide	CO_2	CO_2
Chlorine	Cl	Cl
Chlorofluorocarbons	CFCs	CCl_3F, CCl_2F_2, etc.
Dichloro-diphenyl-trichloroethane	DDT	$C_{14}H_9Cl_5$
Dimethyl Sulfide	DMS	C_2H_6S
Fluorine	F	F
Iodine	I	I
Methane	---	CH_4
Methyl Bromide (Bromomethane)	MeBr	CH_3Br
Methyl Chloride (Chloromethane)	MeCl	CH_3Cl
Methyl Fluoride (Fluoromethane)	MeFl	CH_3F
Methyl Iodide (Iodomethane)	MeI	CH_3I
Ozone	---	O_3
Perchloroethylene	PCE	C_2Cl_4
Persistant Organic Pollutants	POPs	
Polybrominated Biphenols	PBBs	$C_{12}H_{10-x}Br_x$
Polychlorinated Biphenols	PCBs	$C_{12}H_{10-x}Cl_x$
Polyvinylchloride	PVC	CH_2=CHCl units repeating
Trichloroethylene	TCE	C_2HCl_3
Volatile Organic Compounds	VOCs	

Chloroethane (C_2H_5Cl) and ethylene dichloride ($C_2H_4Cl_2$), the two primary precursors of polyvinylchloride (PVC) production, have a combined annual production of over 20 million tons and comprise the top two halocarbon compounds produced industrially (American Chemical Society 2002). Approximately 1.4 billion pounds of polychlorinated biphenols (PCBs) have been manufactured, of which several hundred million pounds were released into the environment and now reside in aquatic sediments (Hutzinger and Veerkamp 1981; National Resource Council 1979). Perhaps the two most controversial man-made halocarbons are the insecticide DDT (dichloro-diphenyl-trichloroethane), used to great effect in World War II to drastically reduce

vector-borne disease-induced fatality (ATSDR 2002) and the herbicide 2,4-D (2,4-dichlorophenoxyacetic acid), which was used in the Vietnam War-era defoliant Agent Orange (Gribble 2004). Both of these compounds have been greatly criticized for their effects and persistence in the environment. Halocarbons are also generated by the degradation of organic matter in soil (Keppler and Scholer 2002) as well as by combustion processes (Tiernan et al. 1983) such as forest fires and municipal waste incineration (Karasek and Dickson 1987). Volcanic emissions associated with high temperature and pressure conditions where halogen salts combine with organic molecules (Ahling and Lindskog 1982; Jordan et al. 2000) also naturally create compounds such as PCE (perchloroethylene), TCE (trichloroethylene) and PCBs (Pereira et al. 1980; Isidorov 1990). Combustion processes greatly increase the global airborne transport of anthropogenic halocarbons as the compounds volatilize or sorb onto fly ash (Salkinoja-Salonen et al. 1984). Halocarbons are present in higher concentrations in the Northern hemisphere than the Southern hemisphere because of anthropogenic production on the continents (Iwata et al. 1993). Volatility and atmospheric circulation, however, sequester many of these compounds at the poles (AMAP 1998).

1.4 Biological Production

Approximately 4,500 naturally produced organohalides have been identified to date, with chlorinated and brominated compounds produced most abundantly, iodinated compounds less frequently, and fluorinated compounds quite rarely (Key et al. 1997; O'Hagan and Harper 1999). The toxicity of biologically produced halocarbons is used for protection against competition and predation (Hay 1996; Hay and Fenical 1996). Additional uses include incorporation in sex pheromones (Berger 1972) and growth/regulatory hormones in insects and plants (Gribble 2004).

Many of these compounds are produced by oxidation of the halide with heme-containing haloperoxidases (Hewson and Hager 1979), iron porphyrin-containing enzymes, and certain enzymes with vanadium centers (Castro 2003).

Biogenic halocarbon production has been found in both terrestrial and marine environments, including insects (Karasek and Dickson 1987), bacteria, fungi, lichens, plants, and mammals (Faulkner 1980; Gribble 1999). Marine organisms are the largest source of biogenic halocarbons (Gribble 2004), and volatile halocarbons are thought to be responsible for the general smell of the ocean (Gribble 1998). Methyl chloride (MeCl), the single most abundant volatile halocarbon in the atmosphere (Coulter et al. 1999), is biogenically produced up to 8 million tons per year (de Jong and Field 1997) with 5 million tons contributed from marine systems alone (Harper 1985). This dominance may be explained by the relative concentrations of halide ions in seawater (Cl:Br:I / 5400:8.1:0.004 mol) which keeps chloride ions the most bioavailable (Harper 2000). Kelp (Giese et al. 1999) and other marine algae (Pederson et al. 1974) are the largest producers of halocarbons, while mollusks (Baker and Duke 1973), polychaetes (Simonich and Hites 1995; Fieldman et al. 2001), jellyfish (White and Hager 1977), sponges (Schmitz and Gopichand 1978; Garson et al. 1994), soft corals, and blue-green algae (Alexandraander 1994, Gribble 1994) are also marine contributors. Marine macroalgae produce volatile chlorinated, brominated and iodinated halocarbons, a selection of which are listed in Table 2. Bromoform has the highest biological production of all brominated halocarbons, with an annual budget of 2 million tons/year, with 70,000 tons produced by Arctic ice microalgae alone (Gribble 2000).

Table 2- Simple Haloalkane Compounds Produced by Marine Algae (Gribble 1998)

CH_2Cl_2	$CHCl_3$	CCl_4	CH_3Cl	CH_2ClBr
CH_2Br_2	$CHBr_3$	CBr_4	CH_3Br	CH_2BrI
CH_2I_2	CHI_3		CH_3I (Gribble 1996)	CH_2ClI
	$CHClBr_2$	$CHCl_2Br$	CH_3CH_2Br	$BrCH_2CH_2I$
	$CHBr_2I$	$CHBr_2I$	CH_3CH_2I	$BrCH_2CH_2Br$
	$CHClBrI$	$CHBrI_2$	$CH_3CH_2CH_2Br$	

Significant contradictions exist between studies that report that oceans are a source for halocarbons to the atmosphere (Gribble 1998), and those that report that oceans are a sink due to mass transfer from air to seawater (Iwata et al. 1993). This disagreement is likely due to generalizations about halocarbons as a compound class and the specific saturation of each compound in water and air; ocean production of bromoform exceeds atmospheric concentrations (Gribble 1999), yet many complex anthropogenic compounds such as PCBs are transferred from the atmosphere to the ocean (Iwata et al. 1993). Methyl chloride and methyl bromide are supersaturated in low latitude oceans with respect to atmospheric concentrations, yet undersaturated in high latitude seawater beyond the expected increase in gas solubility at colder temperatures (Tokarczyk et al. 2003a; Yvon-Lewis et al. 2004).

1.5 Halocarbon Toxicity and Public Policy

The negative and environmentally persistent characteristics of halocarbons were first recognized in the 1960s due to their increased use and the publicity of Rachel Carson's outcry against the environmentally persistent pesticide DDT in her layman-accessible book 'Silent Spring' (Carson 1962; Haggblom and Bossert 2003a). Mechanisms of toxicity for halocarbons include dissolution of cell membrane, enzyme inhibition, decoupling of electron transport, and carcinogenicity via secondary metabolite halogen radicals, each of which vary considerably between similar compounds (Haggblom and Bossert, 2003b). Nervous system damage,

hemorrhage, and respiratory failure are all toxic effects of MeBr, which has a lowest observed effect level (LOEL) of 34ppm for inhalation exposure to humans (EPA 2000) and a determined threshold limit value (TLV) of 5ppm; more toxic even than carbon monoxide or hydrogen cyanide (Lide 1999; Castro 2003). Since halocarbons are often applied as pesticides and fumigants, inhalation toxicity is most dangerous near their sites of application. While MeBr fumigators are required to wear masks to avoid direct inhalation of the gas, agricultural/industrial neighborhoods can have ambient MeBr concentrations above 1.2ppb well away from the fields/factories themselves (EPA 2000). MeBr has been suggested as a comparative 'benchmark' for human toxicity as the most toxic halocarbon due to its strong alkylating capacity, permeation characteristics, (Castro 2003) and its ability to bind to heme iron (Wade and Castro 1985).

Methyl halides, particularly MeBr and MeCl, represent the largest source of halogen atoms to the stratosphere and have direct effects on both global warming of the troposphere and degradation of stratospheric ozone. The extent to which a given halocarbon affects each parameter is measured by its global warming potential (GWP) and its ozone depletion potential (ODP) set relative to CO_2 and CCl_3F, respectively. A halocarbon's ability to absorb infrared energy as well as its degree of halogenation, reactivity with atmospheric oxidants, susceptibility to photolysis, residence time in troposphere, and global budget of sources and sinks all contribute to the determination of these values. The primary sink for halocarbons in the troposphere is oxidation with hydroxyl radicals created by the photochemical reaction of ozone (O_3) with water vapor (Coulter et al. 1999). The longer a halocarbon persists in the troposphere undegraded, the likelier its chance of breaking through the tropopause into the stratosphere, where photolysis breaks the halogen bond and causes free halogens, primarily chlorine and bromine, to react with and break down ozone (Mina and Rowland 1974). MeBr has a tropospheric mixing ratio of

0.01ppb, a tropospheric residence time of 0.7 years, yet an ozone depletion potential of 0.7 (relative to CCl_3F at 1.0; EPA 2009a) and a global warming potential of 2,400 (relative to CO_2 at 1.0). This reflects the high affinity of bromide species for ozone (50-100 times greater than the affinity of Cl; Oremland et al. 1994) even though bromine species are ~400-fold less-abundant than chlorine (Oremland 2003). MeBr is responsible for approximately 15% of all halogen-catalyzed ozone depletion in the stratosphere (Harper 2000), and 10% of total stratospheric ozone destruction (Goodwin et al. 2001).

Acknowledgement of the deleterious effects of multi-halogenated halocarbons resulted in efforts to replace them with less-halogenated forms, and in the 1990s industrial and agricultural facilities used trifluoromethyl iodide (CF_3I) as a replacement for chlorofluorocarbons (CFCs) to fight fires, and methyl iodide (CH_3I) and MeBr as less-halogenated insecticides and fumigants. Initially these compounds were used because of their shorter atmospheric residence time, believed to be due to photolysis with sunlight, but the previously underestimated ozone depletion potential of MeBr caused the US EPA to issue a monitored phaseout of MeBr initially scheduled for completion in 2005 (Oremland 2003, EPA 2009b). This phaseout has now been delayed to 2015 due to high demand for MeBr use and lack of an inexpensive alternative. *Nonessential* use of MeBr was banned by the EPA in 2004, although 'critical use' requests for use as a fumigant still allow production in the US, and MeBr production constituted 91% of the total allowances requested by the United States to the Montreal Protocol for 2007 (Morrissey 2006). The controversy over whether or not the United States 'critically needs' to use MeBr was a significantly contributing factor to President Bush's threat to leave the treaty in 2006, (Morrissey 2006), while the US EPA is currently proposing an absolute ban on its anthropogenic production for 2015 (USC 2003).

The ‘global distillation effect’ distributes halocarbons through volatilization and condensation mechanisms that result in a greater accumulation at higher latitudes, and polar regions serve as environmental sinks for many halocarbons due to meteorological and geographical characteristics that trap contaminants in these areas (Majewski and Capel 1995; AMAP 1998; Barrie et al. 1998; de March et al. 1998; Stringer and Johnston 2001). The Arctic Monitoring and Assessment Programme’s (AMAP) 2002 assessment identified brominated fire retardants as ‘high concern’ chemical compounds in polar environments due to their environmental persistence and long-range air transport, travelling over 2,000km from their point source of release. The atmospheric concentration of MeBr is highest at high latitudes (Berg et al. 1984; Rasmussen and Khalil 1984).

The twelve most hazardous compounds defined by the 2001 Stockholm Convention’s global treaty to protect human health and the environment from persistant organic pollutants (POPs) are all organochlorine compounds, (Stockholm Convention 2001) and the Montreal Protocol instituted several constraints on anthropogenic halocarbon releases including many brominated halocarbons such as MeBr and halons (brominated fire retardants, Oremland 2003). While the United States and 195 of 196 United Nations countries have adhered to the Montreal Protocol (UN 2009), the restricted use of many halocarbon compounds was one of the reasons why the United States and Russia both refused to ratify the Stockholm convention, which was signed by 153 other nations, or the Aarhus Convention on the Long-Range Transport of Air Pollutants (AMAP 2009). For MeBr specifically, many studies (Gribble 2000; Castro 2003; Oremland 2003) propose that banning anthropogenic production of the chemical may have little environmental effect due to the large contribution of biogenic sources to total global budgets. Rapeseed (canola) plants produce 6.6×10^3 tons of MeBr per year, which is akin to nearly 15%

of anthropogenic production (Table 3; Gribble 2004). Added to the uncertainty in the amount of marine biogenic production, MeBr has been forced to the front of an ongoing debate concerning how substantially governmental control and human activity can truly affect environmental change (Castro 2003).

1.6 Characterization of Methyl Bromide

MeBr is an aliphatic haloalkane (CH_3Br), a toxic, odorless gas at room temperature with significant ozone-depleting characteristics (Oremland 2003) that has been suggested as the most toxic halocarbon to humans (Castro 2003). At 1.1°C, MeBr has a solubility (mol l^{-1}:atm) of 0.493 in pure water, 0.399 in seawater, and 0.397 in 35% NaCl (De Bruyn and Saltzman 1997). Its atmospheric concentration is highest at high latitudes (Berg et al. 1984; Rasmussen and Khalil 1984). Approximately 20-50 thousand tons of MeBr are produced annually by burning biomass (Gribble 1999), while industrially it is used as a biocide and pre-planting soil fumigant (66 thousand tons /yr; Morrissey 2006) for strawberries, vegetables and flowers (Oremland 2003). Industrially it is manufactured by reacting methanol with hydrogen bromide in the reaction:

$$CH_3OH + HBr \rightarrow CH_3Br + H_2O$$ (Haggblom and Bossert 2003a)

It is biogenically produced by rice (Harper 2000), kelp (Manley 1987) and Antarctic ice algae (Sturges et al. 1993). Bromoperoxidase (BPO) enzymes thought to be responsible for the production of MeBr have been found in over 100 species of marine algae (red, green, and brown), phytoplankton, and bacteria (Gribble 2000). Bacterial production of MeBr is not considered to be significant to ambient or global concentrations (Hoeft et al. 2000). Experiments

with MeBr-producing unialgal phytoplankton cultures yielded peak concentrations of 0.6 to 2.5nM MeBr after 35-day incubations, suggesting that it is unlikely for these primary producers alone to support bacteria using MeBr as a sole source of energy or carbon (Moore et al. 1996). Bacteria have been found to degrade MeBr to carbon dioxide in soil, freshwater, estuarine, marine, and hypersaline/alkaline environments (Connell et al. 1997). Estimates of significant MeBr sources and sinks are listed in Table 3.

Table 3- Global budget of Methyl Bromide

Average concentrations:		Source
Air above open ocean	10-12 pptv (0.14pM)	(4, 7)
Air above land	25 pptv (0.34pM)	(10)
Air in industrial/ agricultural areas	1200 pptv (16.25pM)	(10)
Seawater	0.3pptv (3.16pM)	(4, 7, 10)
Estimated fluxes:	**Amount Produced (10^3 metric tons yr^{-1})**	**Source**
Methyl Bromide Sources		
Soil Fumigant	66	(1)
Marine Emissions	56	(2)
Burning biomass	20-50	(3)
Salt Marshes	14	(4)
Canola/ Rapeseed emissions	6.6	(5)
Wetlands	5	(4)
Automobile Emissions	1.5	(4)
'Best Estimate' of **Total Production**	**185**	(4)
Degradation in soils	-42 (10^3 metric tons yr^{-1} consumed)	(6)
Atmospheric burden:		Source
Total stratospheric MeBr	150 x10^3 metric tons	(11)
Total stratospheric Br	167 x10^3 metric tons	(8, 9)
Atmospheric residence time	0.7 yrs	(4)

Table data from [1]Morrissey 2006, [2]Gribble 2000, [3]Gribble 1999, [4]Harper 2000, [5]Gribble 2004, [6]Shorter et al. 1995, [7]Goodwin et al. 2001, [8]Tanhua et al. 1996, [9]Oremland 2003, [10]EPA 2000, and [11]Butler 1996. Ocean/air concentrations change depending on location. Note that due to the variability in sources used and the lack of identified MeBr sinks, this budget is not a fully balanced model.

While MeBr has been found to hydrolyze abiotically, particularly in the presence of light (Castro and Belser 1981), these rates are very low compared to production (Castro 2003). Significant uncertainty in the global MeBr budget is fueled by the variation in production levels reported by different studies (Oremland 2003a; Castro 2003; Gribble 2004) and estimates of how much of this production contributes to stratospheric bromine. While marine production of bromoform can exceed 2 million tons/yr (Gribble 1999) and is greater than tropospheric MeBr levels, MeBr contributes nearly 85% of all bromine in the stratosphere due to its chemical characteristics, relatively long atmospheric residence time compared to other brominated

methanes and methyl halides (Schaefer and Oremland 1999), and its ability to cross the tropopause (Mina and Rowland 1974). Biological production and degradation of MeBr occur simultaneously in the oceans resulting in a net sink for atmospheric MeBr (Goodwin et al. 2001). However, these microbial sinks tend to rely on very specific degradative pathways for individual compounds, so while biodegradation is a major sink for methyl halides, it is fairly minor for the degradation of many CFCs (Oremland 2003).

1.7 Biological Degradation of Halocarbons

Microorganisms play a significant role in the biogeochemical cycling of halogens both in and out of organic phases and through various metabolic intermediate products, contributing to their ultimate environmental fate (Kluyver and van Niel 1956). Biodegradation of anthropogenic chemicals may occur when the compounds can feed into the enzymatic pathways already present for the degradation of similar natural compounds (Dagley 1972), and dehalogenation reactions have been found in both bacteria and eukarya (El Fantroussi et al., 1998; Fetzner 1998). The overwhelming majority of research on the transformation and degradation of halocarbons has focused on chloroorganic compounds, often due to their frequent industrial application (Reineke 2001). However, other halogenated compounds present environmental concern (Castro 2003), can serve as carbon and energy sources for bacteria (Leisinger and Braus-Stromeyer 1995), and require further study (Giesy and Kannan 2001; Key, Howell and Criddle 2001).

1.8 Environmental Constraints to Biodegradation

Biodegradation is often limited by bioavailability regardless of the overall concentration of a given halocarbon in the environment. Bioavailability is determined mainly by the physical

state, solubility, and chemical structure of the compound and surrounding environment (Bossert and Bartha 1986; Volkering et al. 1992), and as halocarbons are typically hydrophobic they tend to sequester / sorb onto organic material. The solubility of halocarbons is directly proportional to their rates of biotransformation, (not necessarily biodegradation, as the transformation may alter other components of the chemical formula) in part due to ease of access to transformational reactions, and experimental studies have increased biodegradation of insoluble compounds by adding surfactants during soil application (Focht 2003). Halocarbons with an octanol/water partition coefficient (log K_{ow} -3 to 7; 7 indicating a high likelihood of partitioning into organic matter) closest to 1 are capable of being degraded in a broader range of matrices and tend to have a shorter environmental residence time due to ease of degradation (Castro 2003). MeBr, with a log K_{OW} of 1.19, is more polar and less lipophilic than many other halocarbons, and therefore likelier to remain more bioavailable in the environment (Hertel and Kielhorn 1995). A reduction in mass transfer of the contaminant from the sorbent (such as soil) to degradative microorganisms is a prominent cause of reduced bioavailability of halocarbons (Nam and Kim 2002). Halocarbons are most bioavailable in the aqueous phase (Ogram et al. 1985; Harmansson and Marshall 1985; Rijnaarts et al. 1990; Robinson et al. 1990; Bossert and Compeau 1995; Bosma et al. 1997) while desorption rates can control bioavailability in other matrices. Thus the highly persistent nature of halocarbons applied as pesticides is partly due to sequestration into the soil matrices that render these compounds unavailable to degradative microorganisms. Reduced bioavailability is often accompanied, however, by a reduction in the apparent toxicity of a compound (Nam and Kim 2002).

The specific metabolic strategy used in dehalogenation varies between aerobic and anaerobic environments, the availability of electron donors and acceptors (particularly H_2,

stimulating microbiota to use halogenated compounds as electron acceptors), and both the substituent and class of halogenated compound (eg. aromatic vs. aliphatic compounds). Thus the rate and breadth of dehalogenation can often be enhanced by manipulating the environmental characteristics of a given site through pH control, fertilization, or addition of secondary substrates (Madsen and Aamand 1992; Rhee et al. 1993; Lovley et al. 1994; Kuo and Genther 1996; Mohn et al. 1997; Scherer et al. 1998; Sun, Cole and Tiedke 2001). Since all biologically-mediated dehalogenations release protons in addition to the halide, dehalogenation is an acidifying process which may decrease pH in environments with low buffering capacity (Loffler et al. 2003). Dehalogenating bacteria isolated on methyl halides as a growth substrate decreased their growth rates after a fall in pH, but were capable of continuing growth if the environmental pH was sustained (Coulter et al. 1999). Biological dehalogenation appears most efficient at neutral pH for most species (Young and Gossett 1997), often decreases with the presence of toxic organic co-contaminants such as chloroform and cyanide (Carney 1996), decreases in the presence of heavy metals (Fennel and Gossett 2003), yet often increases with the presence of petroleum hydrocarbons, acetone, and methanol, which may act as electron donor substrates to support reductive dehalogenation (Major et al. 1991; Sewell and Gibson 1991; Cozzarelli et al. 1995). Environmental characteristics will also control the viability of dehalogenating populations, and high concentrations of nitrate and sulfate appear to impede the enrichment of dehalogenators by increasing the viability of sulfate-reducing and other bacteria competing for hydrogen sources (Townsend and Suflita 1997). In addition, large imbalances in the ratio of nitrate to nitrite or sulfate to sulfide would make those reactions more thermodynamically favorable as electron acceptors when the concentration of halogenated substrates and lesser-halogenated products is relatively similar (Bossert et al. 2003).

1.9 Thermodynamics and Strategies of Biodegradation

The defining step in the degradation of halocarbons is cleavage of the carbon-halogen bond; the dehalogenation step requiring enzymes under physiological conditions (Haggblom and Bossert 2003a). Microorganisms have evolved a number of dehalogenation mechanisms for metabolic processes including oxidation, reduction, substitution, dehydrohalogenation, hydration, and methyl transfer reactions, utilizing dehalogenases including oxygenases and peroxidases, (Duddleston et al. 2000), B_{12} (van Eekert et al. 1999), myoglobin, hemoglobin, hemeproteins in G-conformation, and cytochrome P_{450} (Castro, Wade and Belser 1985; Castro 1998). In general, as the degree of halogenation increases, a compound will more likely undergo reductive, rather than oxidative, dehalogenation (Alexandraander 1965). Dehalogenation may occur as a detoxification mechanism, cometabolic reaction, a method to break the carbon backbone to serve as an energy source for aerobic microorganisms, as part of acetogenic fermentation, or in halorespiration when halocarbons serve as alternate electron acceptors for anaerobic respiration.

The amount of energy released from dehalogenation increases with increasing atomic number of the halogen substituent such that Fl<Cl<Br<I, and also depends on the nature of neighboring groups (Dolfing 2003). Microorganisms in anaerobic conditions are often opportunistic in choosing to break the bonds that provide the greatest net energy gain in mixed halocarbons, and thus the preferred transformation route of CFCs is dechlorination rather than defluorination (Sonier et al. 1994; Oremland et al. 1996; Hageman et al. 2001), while debromination is preferred in mixes with lighter halogen groups. In fact, since the addition of polybrominated biphenyls (PBBs) has been found to ‘prime’ dechlorination in PCB-contaminated sediments (Bedard et al. 1993; Bedard et al. 1996; van Dort et al. 1997), PBBs are

successfully being used in an attempt to stimulate high-energy degradation and 'wean' microorganisms onto continued degradation of PCBs (Bedard et al. 1998; Wu et al. 1999). Consumption of MeBr is inhibited by MeI, and MeCl consumption is inhibited by MeBr (Schaefer and Oremland 1999). In multi-halogen organic compounds, the halogen substituent with the most neighboring halogen substituents is the one most likely to be removed, and the energy released often decreases with decreasing degree of halogenation (Dolfing 2003). While metabolic degradation pathways have not been found for all halocarbons, co-metabolic transformations by bacteria can change compounds into secondary forms that are either more likely (in the case of chloroform, $CHCl_3$ gratuitously oxidized to dichloromethane, CH_2Cl_2) or less likely (in the oxidation of DDT to DDD, which is less bioavailable to microorganisms) to be further transformed (Leisinger and Braus-Stromeyer 1995).

1.10 Routes of Biological Dehalogenation

Reductive dehalogenation (hydrogenolysis) occurs in anaerobic (Kuhn and Suflita 1989; Mohn and Tiedje 1992; Holliger et al. 1999), methanogenic, and denitrifying conditions (Van den Tweel et al. 1987), but is somewhat rare aerobically (Apajalahti and Salkinoja-Salonen 1987). Aliphatic halocarbons, primarily haloalkanes, are far more commonly reductively dehalogenated than aromatic halocarbons. Reductive dehalogenation often uses corrinoid-containing dehalogenases, and the broad spectrum of bacteria capable of this process (including methanogenic, acetogenic, sulfate-reducing and iron-reducing bacteria) suggests that alkyl reductive dehalogenation is a cometabolic activity with no benefit to the organism (Holliger et al. 2003). Anoxic basins are an identified sink of many halocarbons, and microbially mediated reactions are thought to cause degradation of chlorinated and brominated methanes in the Black

Sea (Tanhua et al. 1996). MeBr and to a lesser extent MeCl can undergo nucleophilic substitution with sulfide to form dimethylsulfide, which in turn can lead to microbially-mediated methanogenesis and sulfate reduction (Oremland et al. 1994).

Dehalorespiration is another process in anaerobic bacteria, used by chloroflexi, δ- and ε-proteobacteria, and Gram-positives with a low G+C content (Holliger et al. 2003), and is catalyzed by vitamin B_{12} in methanogenic systems (van Eekert et al. 1999) with the halocarbon as electron acceptor (Reineke 2001). In addition, anaerobic homoacetogenic bacteria have been isolated that are capable of growing on chlorinated methanes as sole energy sources, converting C_1 to CO_2 (Traunecker, Preuss and Diekert 1991; Magli et al. 199) during a methyl transfer reaction.

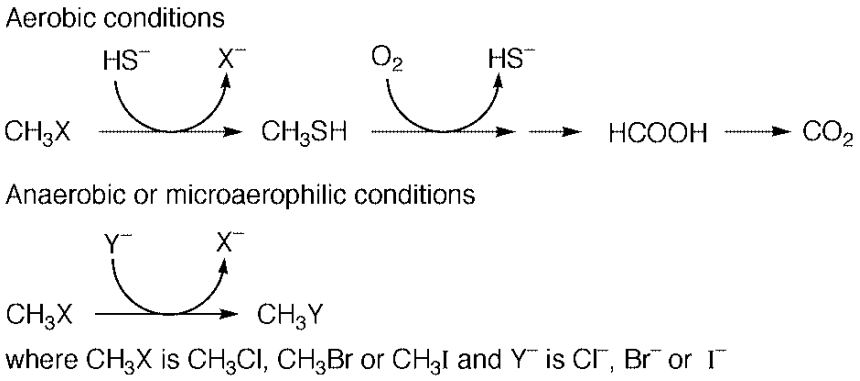


Figure 1- Diagram of degradation and transhalogenation reactions of strain CC495 reprinted from Gribble 2000.

In aerobic and nitate-reducing conditions, oxidative and hydrolytic dehalogenation are more common (Dolfing 1995; Fetzner 1998). In oxidative dehalogenation, the mono- or dioxygenases of methanotrophs and nitrifying bacteria can cause aerobic degradation of MeBr and MeCl (Colby et al. 1975) as a cometabolic process, serving as competitive inhibitors of methane and ammonia (Oremland and Culbertson 1992; Matheson et al. 1997). Substitutive dehalogenation is most commonly a hydrolytic process catalyzed by halidohydrolases, although

a thiolytic mechanism with glutathione can also occur. The greatest number of described dehalogenases are hydrolytic in nature. Finally, in dehydrohalogenase-catalyzed dehalogenation, elimination of the halide causes double bond formation (Fetzner 1998).

1.11 Bacterial Degradation of Methyl Bromide

The transhalogenation of MeBr to MeCl (Fig. 1) may represent a significant biological sink for atmospheric MeBr both from soil and marine environments, and experiments with seawater indicate microbial degradation of MeBr occurs at concentrations up to ~100-fold above ambient levels. Bacteria able to cooxidize MeBr include terrestrial methanotrophs, nitrifiers, and certain marine methylotrophs that grow on dimethyl sulfide (DMS) or methanesulfonate (Goodwin et al. 2001). In Mono Lake, California, oxidation of MeBr to carbon dioxide was unaffected by methyl fluoride (MeF), MeCl, methanol or glucose, but was stimulated by trimethylamine, suggesting that MeBr is degraded by a cometabolic reaction from trimethylamine- or dimethylamine-utilizing methylotrophs (Connell et al. 1997; Hoeft et al. 2000). Increased MeBr degradation after 'priming' additions of MeBr over time suggests that MeBr may serve as a growth substrate for certain microorganisms (Miller et al. 1997; Oremland 2003), and so far the facultative methylotroph α-proteobacteria strains IMB-1 (soil), CC495 (soil), and MB2 (marine) have been isolated capable of growing on and degrading MeBr, MeCl, and MeI. Species IMB-1 and CC495 are very closely related to the new genus *Pseudoaminobacter*, related to *Rhizobium* spp. Strain CC-495 catalyzes methyl transfer from these methyl halides to Iodide, Hydrogen Sulfide, Chloride, Bromide, Nitrite, Cyanide, and Thiocyanate (I^-, HS^-, Cl^-, Br^-, NO_2^-, CN^-, and SCN^-, respectively) in order of decreasing efficacy (Coulter et al. 1999), using HS^- as the physiological acceptor ion. While not capable of

surviving on all three compounds, strains MC1, CM2, and CM4 can also grow on one or more methyl halides as the sole carbon source (Hartmans et al. 1986; Oremland 2003).

Strains CC495, IMB-1 and $MB2^T$ each consume MeBr at levels mimicking the tropospheric mixing ratio for MeBr (12pptv) at equilibrium with surface waters (~2pM), exhibiting first-order uptake with no indication of threshold values (Goodwin et al. 2001). Seawater strain $MB2^T$ has an experimental K_s of 2.4µM MeBr and a V_{max} of 1.6 nmol h^{-1} using micromolar concentrations of MeBr. (Comparatively, terrestrial IMB-1 has an apparent K_s of 190nM and V_{max} of 210 pmol $10^6 cells^{-1}$ h^{-1} for MeBr degradation in Schaefer and Oremland's 1999 study.) The presence of glucose during the uptake-phase analysis did not inhibit MeBr uptake, and growth was not dependent on previous exposure to MeBr, although MeBr uptake rates were highest in cultures grown solely on MeBr previous to the uptake-phase analysis. However, soil samples exhibited an 80% decrease in MeBr oxidation in the presence of glucose in Miller et al.'s 1997 study, which the authors suggest is due to overcompetition with bacteria metabolizing the glucose. Similar to the apparent MeBr toxicity threshold of 0.3mM for CC495 (Coulter et al. 1999), 0.5mM concentrations used by Goodwin as well as Hoeft et al. (2000) appeared toxic and caused a decline in MeBr consumption and growth. The MeBr consumption by coastal marine methylotrophs studied by Hoeft et al. was greatly enhanced by the presence of dimethylsulfide (DMS), although consumption stopped when DMS concentrations exceeded 5mM.

'Priming' bacteria with increasing doses of MeBr to initiate degradation and induction patterns in which degradation occurs after a lag time are both common patterns seen in degradation studies. Miller et al.'s 1997 study of bacterial oxidation in fumigated agricultural soils found that the highest rates of MeBr oxidation occurred 1-2 days after fumigation, while

oxidation rates tripled with repeated MeBr addition. No oxidation occurred in heat-killed soils, indicating that microbes and not abiotic factors were the source of degradation. Schaefer and Oremland (1999) found that oxidation rates were 3.5-fold greater for IMB-1 cells previously exposed to MeBr and an 8-hr induction occurred before MeBr uptake when cells were grown on glucose. Dark incubations did not inhibit IMB-1 MeBr consumption, ruling out cobalamin compound/ B_{12}-mediated methyltransferase reactions. Dehalogenation by IMB-1 was constitutive at low concentrations (<20nM) but induced by very low concentrations of MeBr to consume MeBr at >100μM. Goodwin's examinations with other related strains to IMB-1 and CC495 suggested that the ability to consume ambient ratios of MeBr was limited to C_1 compound oxidizing bacteria, possibly because the monooxygenases of methanotrophs and nitrifiers oxidize analogs of methane, including MeBr. Since atmospheric concentrations of MeBr are low and degradation at high concentrations requires induction, Goodwin et al. (2001), Schaefer and Oremland (1999), and Hoeft et al. (2000) suggest that facultative marine methylotrophs degrading methyl halides may consume MeBr from the atmosphere as a cometabolic process while their growth is supported by other, more commonly available substrates in their environment such as DMS or trimethylamine (TMA).

In order to track the utilization of MeBr in different laboratory and field experiments, certain studies (Visscher et al. 1994; Bradley and Chapelle 1998; Bradley 2000; Bradley and Chapelle 2000; Goodwin et al. 2001) have introduced ^{14}C-labeled MeBr to examine degradation and possible subsequent CO_2 formation by bacteria. Schaefer and Oremland (1999) incubated samples with ^{14}C-MeBr, halted incubation with acidification with hydrochloric acid (HCl) driving mineralized carbon to CO_2, and detected $^{14}CO_2$ concentrations from the headspace of samples by gas chromatography. Miller et al. (1997) used similar techniques for soil bacteria and

found that complete removal of ^{14}C-MeBr occurred within 3 days, with 47-67% of the added MeBr oxidized to $^{14}CO_2$ while the remainder was associated with the solid phase. Neither nitrifying nor methane-oxidizing bacteria were sufficiently active in studied soil samples to account for the observed oxidation of MeBr, nor could the degradation be linked to any cooxidation with exogenously supplied electron donors, but the authors isolated gram-negative aerobic bacteria capable of growing solely on MeBr as an electron donor for growth.

1.12 Identifying Dehalogenating Bacteria

While the types of dehalogenation and the enzymes used by different microorganisms vary greatly, main investigative foci for bioremediative purposes include isolating dehalogenating bacteria and identifying dehalogenases with broad substrate specificity (Baker 1990) in order to make them applicable to different conditions in the field. Many dehalogenating reactions are highly specific to environmental conditions, and successfully isolating dehalogenating bacteria using halocarbons as the sole source of carbon in laboratory conditions is a coveted, if not rare, achievement. In addition to the methyl-halide utilizing proteobacteria discussed previously, bacteria capable of growing on organochlorines, the most studied group of halocarbons, include species in the α- (Fulthorpe et al. 1995; Kamagata et al. 1997), β- (Don and Pemberton 1981), γ- (Maltseva et al. 1996), δ- (Krumholtz 1997; Loffler et al. 1997), and ε- (Scholz-Muramatsu et al. 1995; Smidt et al. 2000) proteobacteria subdivisions, low (Gerritse et al. 1996; Chang et al. 2000) and high (Rogoff and Reid 1956; Loos et al. 1967) G+C gram positive bacteria, the Bacteroides-Cytophaga-Flexibacter (CFB) group (Chaudhry and Huang 1988; Mannisto et al. 1999), and chloroflexi/ green non-sulfur bacteria (Maymo-Gatell et al. 1997; Loffler et al. 2000). These isolations have primarily been with compounds such as

chlorobenzoates, 2,4-dichlorophenoxyacetic acid (2,4-D), or pentachlorophenol (PCP) as the sole carbon source, while DDT and many other commonly used products have not yielded the same success. In part the difference in successful isolations appears related to the water solubility and residence time of a given halocarbon in the environment- while DDT is highly water insoluble and persists in contaminated soils for decades, the slightly more water soluble 2,4-D and methyl halides degrade within a year of application (Focht 2003).

Difficulty in identifying dehalogenating bacteria arises from the varied enzyme systems used even within the same bacterial subdivisions. Certain enzymes appear to be shared by various bacteria capable of degrading the same compound, such as the case of DCM-dehalogenase shared by apparently all aerobic dichloromethane (DCM)-utilizing bacteria (Leisinger and Braus-Stromeyer 1995), while other compounds such as MeBr and 2,4-D may be degraded by different enzymes and specific or unknown gene sequences independent in related species/ dehalogenation pathways. Schaefer and Oremland (1999) suggest that methyl halide oxidation proceeds through a single enzyme system specific for methyl halides (not including methyl fluoride) which runs through formaldehyde to CO_2, and the methane-analog oxidation discussed in section 1.10 suggests broad oxygenase applicability, but many other studies of degradation studies (review in Haggblom and Bossert 2003a) disagree with the single-enzyme theory, suggesting that it must be some other characteristic that enables only certain species that have monooxygenases to actually apply them towards the cooxidation of halocarbons.

1.13 Bioremediative Applications for Dehalogenation

The priming of contaminated sediments with more thermodynamically favorable halocarbons (biostimulation) and the addition of dehalogenating microbiota to contaminated

environments (bioaugmentation) are the two main strategies for *in situ* remediation, although the sheer volume of contamination, limited bioavailability of certain contaminants, and toxicity of co-contaminants to dehalogenating organisms all pose significant challenges. In agriculture, tear gas (chloropicrin; CCl_3NO_2) traditionally composes one third of MeBr fumigant mixtures and inhibits the growth of MeBr utilizing organisms, which can limit their bioremediative application in treated fields. If chloropicrin can be removed or otherwise degraded before dehalogenating bacteria are introduced to soils, they may have significant bioremediative implications by drastically increasing methyl halide consumption (Fennell and Gossett 2003). Site Reactivity Probes (SRPs) have been developed that can determine the reactivity of terrestrial sites for their oxidative, reductive, and substitutive dehalogenating capacities using nuclear magnetic resonance, and rates determined by these probes can be assessed for each target contaminant (Castro 2003). However, the rate-limiting step in microbial dehalogenation appears to be dependent on the organism and its ability to access bioavailable reactive sites rather than the mechanism of dehalogenation (Castro 1998), and thus SRPs can only determine the maximum plausible rate of dehalogenation, not the current ongoing rates.

1.14 Halocarbon Degradation in Polar Climates and Sea Ice

Sea ice covers 13% of the Earth's surface at its maximum extent, with the largest expanse in the Southern Ocean, spanning $18 \times 10^{16} km^2$. The freezing of seawater results in the expulsion of dissolved halogens from the ice crystal matrix, leading to increased ionic strength of brine trapped within the ice (Macdonald et al. 2005). Ambient concentrations of halocarbons in the Southern Ocean include 10-20pM bromoform and~0.2-0.25pM chloroiodomethane (CH_2ClI) per liter of sea ice, and ~0.9pM bromoform and 0.2pM CH_2ClI in snow (Abrahamsson, unpublished

data). MeBr and MeCl are both undersaturated in the Southern Ocean with respect to atmospheric concentrations (Yvon-Lewis et al. 2004), refuting earlier suppositions that methyl halides may be supersaturated in polar waters.

Sea ice and brine provide a diverse ecological habitat that is becoming increasingly recognized for its role in biogeochemical cycles, but significant spatial heterogeneity can make conclusive measurements of these cycles difficult. Microbial community composition in Southern Ocean brines include ciliates, dinoflagellates, diatoms, and bacteria. Primary productivity within sea ice is maximal during the December-January austral summer, decreasing after the 24-hour photoperiod wanes toward 24-hour darkness in austral winter. (Papadimitriou et al. 2007). Production from the autotrophic community and associated heterotrophic community responses modify the chemical composition of brines within the sea ice, including reducing the concentration of nitrite and dissolved inorganic phosphate, decreasing aqueous CO_2, and increasing pH (Gleitz et al. 1995). In the Southern Ocean, bromoform (Gribble 2000), bromochloromethane (290–400 pmol l^{-1} seawater), tribromomethane (7.2–47 pmol l^{-1}), trichloroethene (2.5–7.5 pmol l^{-1}) and diiodomethane (110–170 pmol l^{-1}) (Abrahamsson 2004) are the five most common halocarbons produced by marine algae, but to date only the net production or *in-situ* concentrations of these compounds have been examined; not the rates of production by these ice algae. The contribution of sea algae to total global concentrations is now believed to be much more significant than previously thought (de Jong and Dijkstra 2003).

Climate change may have a significant impact on environmental concentrations of halocarbons in polar environments, and the AMAP 2009 Arctic Pollution assessment found that, in contrast to general global trends, levels of PCBs, DDT and other anthropogenically produced halocarbons have increased in the Arctic since 2002, despite the decreased production of many

of these compounds in the last few decades. The AMAP assessment suggests that climate change, the decrease in ice cover in the Arctic, and subsequent increase in open water has allowed POPs that have previously been trapped in ocean water to escape to the air. While the Arctic and Southern Oceans have served as a sink for the global emission of many POPs and halocarbons, a continual decline in sea ice cover may serve to release many of these 'stored' compounds to the atmosphere long after direct releases into the environment have stopped. The contaminant load in glaciers is also being released via meltwater and calving.

Bacteria in polar environments capable of dehalogenating methyl halides and other halocarbon groups are most frequently in or closely related to the genus *Pseudomonas*, (γ-proteobacteria) and all dehalogenating species identified in Master and Mohn's 1998 study of psychrotolerant bacteria were gram-negative, catalase-positive obligately aerobic motile rod bacteria. (Characteristics of proteobacteria; comparatively, the species identified by Coulter et al. 1999 and Goodwin et al. 2001 for temperate dehalogenating bacterial isolations were α-proteobacteria.) Temperature had no affect on dehalogenation and cogener specificity, suggesting that the temperature extreme itself is not responsible for dehalogenating activity, but Master and Mohn propose that the increased cell membrane fluidity and other cold adaptations of psychrotolerant bacteria better equip these species to take up larger halocarbons for degradation. Since psychrotolerant bacteria can degrade methyl halides and PCBs at high initial rates without heating, Master and Mohn suggest that these bacteria would be the most applicable and cost-effective bioremediative species in both polar and temperate climates due to physiological and genetic adaptations to cold environments that enhance pollutant degradation activity. Since bromocarbons can prime certain bacterial dehalogenation of similar chlorocarbons (Bedard et al.

1998; Wu et al. 1999), psychrotolerant bacteria capable of debromination may prove to be some of the most valuable in bioremediative applications.

1.15 Conclusions

As the global budget of MeBr is continuously refined by the identification of additional sources and sinks, the scale of biological production and degradation of this compound is becoming more pronounced, and the identification of microbial dehalogenation pathways has significant implications in the field of bioremediation. MeBr has significant ozone-depleting characteristics (Oremland 2003) and its degradative pathways in sea ice are poorly understood. Since sea ice covers 13% of Earth's surface, including $18 \times 10^{16} km^2$ in the Southern Ocean alone, polar regions may play an important role in the biochemical cycle of halocarbons. Biological degradation within sea ice may serve as a sink for halocarbons and contribute to the identified undersaturation of MeBr in Southern Ocean surface water beyond the expected gas solubility and air-sea exchange dynamics of polar waters (Yvon-Lewis et al. 2004).

CHAPTER 2- METHODS

Field Measurement of Methyl Bromide Degradation in an Antarctic Sea Ice Ecosystem

Methyl bromide (MeBr) is one of the most abundant halocarbons present in the environment and stratosphere, is 2,400-fold more potent as a greenhouse gas than CO_2 (Oremland 2003), and has been suggested as the most toxic halocarbon to humans (Castro 2003). In addition to industrial production as a soil fumigant, MeBr is produced naturally by marine algae (Gribble 2000), while certain bacteria can degrade it to carbon dioxide in soil, freshwater, estuarine, marine, and hypersaline/alkaline environments (Connell et al. 1997). Since sea ice covers 13% of Earth's surface, including $18 \times 10^{16} km^2$ in the Southern Ocean alone, polar regions may play an important role in the biogeochemical cycle of halocarbons. Biological degradation within sea ice may serve as a sink for halocarbons and contribute to the identified undersaturation of MeBr in Southern Ocean surface water beyond the expected gas solubility and air-sea exchange dynamics of polar waters (Yvon-Lewis et al. 2004). Using a ^{14}C tracer method, this study analyzed bacterial utilization of MeBr in sea ice, brine, and under-ice seawater of the Southern Ocean to identify sites containing dehalogenating communities, analyze rates of utilization, and assess saturation kinetics of MeBr incorporation and respiration in each sample type. In addition to analyses of the bacterial utilization of MeBr, data obtained from this study may help to elaborate the complex biogeochemical cycling and global budget of MeBr by identifying additional environmental sinks.

2.1 Sampling Methods

Samples of ice core, brine, and under-ice seawater were collected from four sea-ice stations (#16, 21, 39 and 41) in the Amundsen Sea on December 17, 20, 29 2008 and January 1, 2009, respectively, during the Icebreaker *Oden*'s 2008-9 austral summer route to McMurdo station seen in Fig. 2.

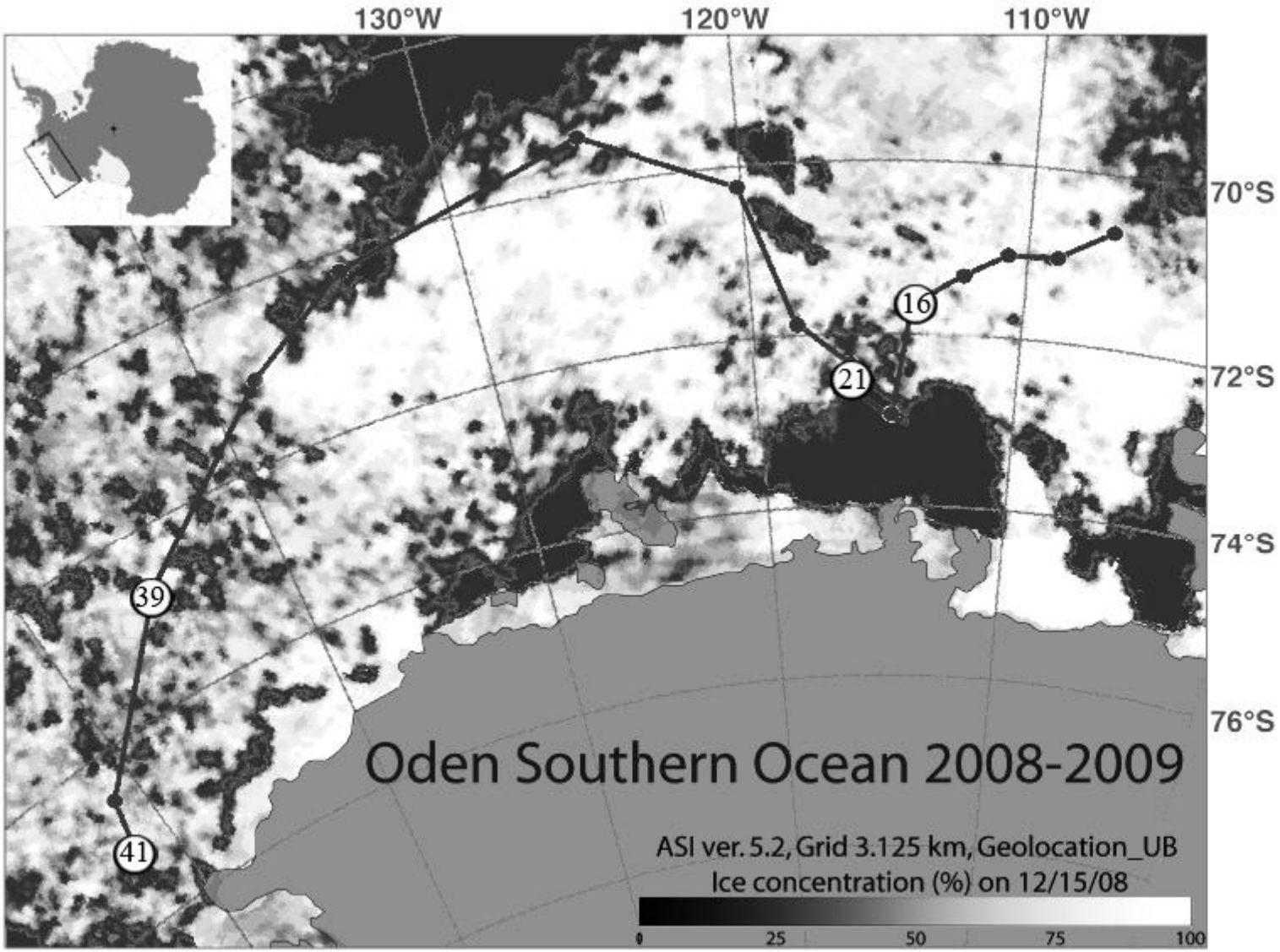


Figure 2- Route of the Icebreaker Oden's field stations and course to McMurdo Sound December 2008- January 2009, overlaid on the ice concentration from December 15, 2008.

All samples (with the exception of under-ice seawater from Station 41 which was collected 18hrs after ice core and brine extraction) were collected at relative midmorning 7am-2pm local time.

Table 4- Station Coordinates and Time of Arrival

Station	Date	Lat°	Latitude Minutes	Latitude Decimal	Long.°	Longitude Minutes	Longitude Decimal	Universal Time	Local Time of Arrival
16	Dec. 17	71	50.35	71.84	114	6.86	114.11	17:26	9:26am
21	Dec. 20	72	35.98	72.60	116	1.48	116.02	11:15	3:15am
39	Dec. 29	72	30.62	72.51	144	43.78	144.73	14:08	4:08am
41	Jan. 1	75	24.08	75.40	151	13.87	151.23	14:31	3:31am

At each station environmental characteristics including nutrient content, salinity, bacterial abundance, and meteorological data were measured in collaboration with other scientists onboard the Oden Southern Ocean 2008-09 research cruise. Two ice cores were collected from each station using a 14cm diameter CRREL-type fiberglass barrel ice auger, and 10cm of the high-chlorophyll colored layer with biomass was cut from each core and placed in an acid-washed plastic container. Immediately upon return to the ship each core slice was diluted 1:1 with 0.2µm-filtered seawater, placed on a shaker table under low light at room temperature for approximately 24 hours until just melted, then stored at -1°C under low light until processed. Seawater was sampled from directly beneath the ice by pumping water through the ice core hole into 10L acid-washed plastic bottles. Brine was sampled from sackholes made by drilling additional ice cores without penetrating to seawater levels, removing the partial ice cores, letting the sackholes fill with brine and hand-pumping the brine into 10L plastic bottles. All samples were stored at -1°C under low light until processed. Experiments using brine and seawater were conducted as soon as field procedures were completed for each station, while the experiments

using melted cores began approximately 24 hours later once the ice was completely melted. Collected samples were submitted to one of two procedures outlined below in order to investigate the rates of MeBr utilization by bacteria as well as the saturation concentrations and kinetics of MeBr utilization.

2.2 Time-course Analysis of Methyl Bromide Utilization (Part A)

The method used by Yager and Deming (1999) for measuring bacterial incorporation and respiration of ^{14}C-radiolabeled organic matter was modified for this MeBr analysis. Each of the sample types from Stations 16, 21 and 39 were poured into 1L sterile plastic bottles, removed from the incubation room and set into ice baths with continuous magnetic stir bars over a stir plate. A subsample volume of 30mL was dispensed aseptically into ashed, sterilized 50mL glass serum bottles by a Brinkman dispensette, and capped with sterilized silicone rubber stoppers. All bottles were stored in ice baths throughout the inoculation phase of this experiment, and serum bottles were chilled to -1°C. Subsamples were divided into either non-enriched or glucose-enriched treatments. Bottles were assigned to time-points at 0, 6, 12, 18 and 24 hours with duplicates, in addition to two killed controls per sample and enrichment type. The glucose-enriched treatments received 10µM glucose, and 1.5mL formalin was added to the killed controls for each enrichment type. All subsamples were then carried in ice baths to the radiation laboratory, where a final concentration of 47.5nM of ^{14}C-MeBr was added to each bottle, and the bottles were sealed with aluminum crimp caps and shaken vigorously. Bottles were incubated in the dark at 1°C for the duration of their time-course, while 0-hr bottles were processed immediately. The killed controls were incubated separately for 24 hours in parallel with the 24-hour live samples.

At the end of incubation, CO_2-trapping wicks (fluted 2x5cm strips of Whatman No.1 filter paper) were each saturated with 0.2mL phenethylamine and inserted into a Kontes plastic center well fitted with a silicone rubber cap. The bottle crimps and stoppers were removed with pliers, the plastic wells were inserted quickly into the headspace of each bottle and the bottles were re-sealed. The wick/wells were assembled to remain above the sample liquid level of each bottle, but if sample touched the wick assembly, it was replaced immediately and noted. Sulfuric acid (0.4 mL 4-N H_2SO_4) was then added to each sample (avoiding the wick assembly) with a 1-cc syringe through the bottle caps to reduce pH and outgas carbon dioxide for trapping by the carbon wick. The silicone caps were coated with rubber cement to prevent gas leaks through the syringe puncture site. Bottles were left to sit for twelve hours, after which the bottles were opened, the wicks were removed with forceps (rinsed with ethanol after each sample) and placed into capped 7mL plastic scintillation vials. The remaining liquid from each bottle was then vacuum filtered onto a 0.2µm Millipore membrane filter, both the bottles and filtration tower were rinsed three times with filtered seawater, and the filters were removed with sterile forceps into additional scintillation vials. Ultima Gold-F scintillation cocktail (7mL) was added via Brinkman dispensette to all vials 36-48 hours prior to counting on a Packard liquid scintillation counter at McMurdo Station, Antarctica at the end of the Oden research cruise. The liquid scintillation counter intended for onboard use during this study malfunctioned in transit to the Oden, so ^{14}C activity was measured after the cruise track was completed. This meant that the 6-hr measurement interval and 24-hr endpoints were chosen during the cruise without being able to adjust future time course experiments according to incoming results, and the time intervals were kept consistent throughout all Part A experiments without pilot study adjustments.

2.3 Kinetic Analysis of Methyl Bromide Utilization (Part B)

Samples collected from Station 41 were dispensed into serum bottles following the methods described in Part A, but assigned as either 0-hr or 24-hour endpoint incubations receiving MeBr in concentrations corresponding to 0.1, 0.5, 1, 5, or 10-fold the final concentration of 47.5nM used in part A (^{14}C-MeBr concentrations of 4.75, 23.75, 47.5, 237.5, and 475nM, respectively), with duplicates for each sample and enrichment type. Once inoculated the remainder of this experiment followed the procedure outlined in part A. Glass scintillation vials (7mL) were used for all samples in this experiment.

2.4 Stock preparation

Throughout these experiments, 'filtered seawater' refers to under-ice seawater taken from each station, 0.2µm vacuum-filtered, and stored at -1°C until use. The MeBr originated from a 52.6mCi/mmol, 260µCi/mL stock solution in 1.5mL ethanol. From this primary stock, 0.25mL was then pipetted into 25mL of filtered seawater at the beginning of the Oden research cruise, and 2.5mL of secondary stock was prepared into a final 1:1000 dilution in 25mL filtered seawater for each ice station. Final concentrations of 47.5nM (0.289mL of 1:1000 stock) were then used to inoculate all bottles in part A, and measured additions in part B were adjusted accordingly using a 1:1000 stock. An additional 1:100000 stock using 0.25mL of 1:1000 MeBr and 25mL filtered seawater was used as the final stock for the 1% (475pM MeBr) quench analysis.

The glucose solution was prepared by mixing 100g glucose with 1L milipore water before all experiments, then pipetting 0.2mL into 50mL of filtered seawater for a 222µM secondary stock made during each station. 1.35mL of secondary stock (10µM final concentration

in 30mL sample per bottle) was used for all glucose enrichments. Both the glucose and MeBr stocks were stored in 2-4°C refrigerators throughout the duration of this study. The formalin was taken from a 37% stock solution buffered with borate and filtered through 0.2µm filters before addition to the killed controls. The 4-N sulfuric acid was prepared for each station from 12mL of 18-N solution with 42mL Millipore water, stored in crimped serum bottles. The phenethylamine was stored in opaque, sealed glass serum bottles and removed without introducing air into the headspace via syringe for use on CO_2-trapping wicks.

2.5 Quench Curves

Quench was measured on sample blanks following the method of Part A for 24-hour filter collection, using MeBr additions to processed filters at 0.01, 0.1, and 1-fold of the 47.5nM dose with duplicates for each sample and treatment type, and 0.01, 0.1, and 1-fold doses applied directly to phenethylamine-coated carbon wicks. Since plastic scintillation vials were used for all samples from Stations 16, 21 and 39 while glass scintillation vials were used for all samples from Station 41, a complete quench analysis was completed with each sample and treatment type from Station 39 for plastic vials, and Station 41 for glass vials. These quench analyses were carried out after each corresponding station on a timeline comparable to the primary experiments. In addition, samples of each MeBr stock solution and MeBr in concentrations at 0.01, 0.1, 0.5, 1, 5 and 10-fold the 47.5nM dose were pipetted into both glass and plastic vials with duplicates to compare known DPM (disintegrations per minute) to sample vials. Transforming data with quench slope estimates did not improve the statistical relationship between measured and expected DPM. Thus, DPM measured directly by the liquid scintillation counter and adjusted for background CPM (counts per minute) were used for pM conversions according to the following formula (where 0.0526 is the specific activity):

$$pM = \frac{DPM}{30\ ml} \times \frac{1\ nCi}{2220\ DPM} \times \frac{1\ pmol}{0.0526\ nCi} \times \frac{1000\ ml}{L} \quad \text{(Eq. 1)}$$

2.6 Rate Calculations

Optimum incorporation and respiration rates for stations 16, 21 and 39 were calculated using the earliest identifiable pM increase within the 24-hour time course and subtracting the values of 0hr or killed control samples in order to determine the rate above abiotic or blank values. If any 0hr datapoint was identified as irregular/inconsistent with 24-hr killed controls, the 24-hr killed controls were substituted for 0hr data in rate calculations (Appendix D). If any time-courses exhibited a delayed response before incorporation or respiration (induction), rates were determined by the increase in activity over a particular time step and the pattern was noted in Table 6. Time-courses without a consistent increasing pattern in pM ^{14}C measured over time before bottle effects decreased overall rates were determined to have no identifiable rate. Rates from station 41 were calculated by substracting the ^{14}C concentrations collected on 0-hr samples from each 24-hr data point, and the 47.5nM MeBr-inoculated rates comparable to stations 16, 21 and 39 were included in Table 6. Rate constants for the degradation or turnover of MeBr were calculated by multiplying the identified $pM \cdot hr^{-1}$ rates by the pM ^{14}C-MeBr introduced into each sample, and converting hourly rates to 24-hour spans in order to represent rates as the proportion of total MeBr introduced that may be degraded per day. For stations 16, 21 and 39, this rate constant was calculated based on the *optimum* $pM \cdot hr^{-1}$ rate span identified within each incubation and converted to a daily rate, while station 41 rates were calculated based on the fixed 24-hr incubation intervals and adjusting for the variable concentrations of MeBr administered. The

chlorophyll content, bacterial abundance, and measured rates of all ice core melt samples were multiplied by 2 in order to adjust for the 1:1 filtered seawater dilution of those samples.

Nonlinear modeling of MeBr first-order uptake saturation kinetics was fit with SAS modified Gauss-Newton nlin procedures using all identified rates. If the sample's 24-hr endpoint was lower than the 0-hr, the sample was determined to have no observable rate and was not included in the nonlinear models.

3. RESULTS

Meteorological data from each station and the ice core depths used for melt sample analysis are included in Table 5 below.

Table 5- Meteorological Data for Each Station

Station	True Wind°	Mean Wind (m/s)	Gust (m/s)	Barometer Pressure (hPa)	Air Temp (°C)	Water Temp (°C)	Relative Humidity %	Visibility (km)	Ice Thickness (cm)	Snow Depth (cm)	Draft (cm)	Chlorophyll/ Biocore Sample Depth in Ice (cm)	Brine Fraction of Biocore Sample
16	142	10.4	11.5	974.2	-1.8	-2.0	76	99.9	157	28	26	135-145	20%
21	248	8.2	9.2	974.5	-6.0	-1.6	81	37.4	105	8	12	45-55	16%
39	67	0.9	1.7	984.4	-1.9	-1.6	91	99.9	154	74	Nd	75-85	13%
41	77	2.0	2.4	983.3	-1.9	-1.3	94	18.7	144	3	Nd	55-65	19%

Incorporation and respiration of ^{14}C-MeBr were observed in all sample types, although occasionally not detectable in a given sample type at a particular station (Table 6). Total MeBr utilization (incorporation plus respiration) was dominated by respiration of MeBr. Respiration rates were 50-400-fold higher than incorporation rates, suggesting that little of the MeBr taken up by cells was incorporated into biomass and was instead used for energy. For this reason incorporation and respiration rates were analyzed separately rather than using a total measure of MeBr utilization (incorporation plus respiration) to identify patterns emerging from each respective rate scale. All mention of respiration, incorporation, and utilization hereafter refers to the incorporation or respiration of ^{14}C-MeBr.

Table 6- MeBr Incorporation and Respiration Rates and for Each Sample Type (47.5nM MeBr additions)

Sample Type		Respiration					Incorporation					
Station	Sample type	Timespan for rate	Rate ($pM \cdot hr^{-1}$)	Cell-specific Rate ($pmol \cdot hr^{-1} \cdot 10^9$ cells^{-1})	R^2	Rate Constant (d^{-1})	Timespan for rate	Rate ($pM \cdot hr^{-1}$)	Cell-specific Rate ($pmol \cdot hr^{-1} \cdot 10^9$ cells^{-1})	R^2	Rate Constant (d^{-1})	10^3 cells$\cdot mL^{-1}$
Unamended treatments												
16	Core melt	0-12hrs	247	467	0.65	0.12	0-18hrs	1.25	2.38	0.55	0.0006	2112
21	Core melt	0-6hrs	110	115	0.86	0.06	0-12hrs	3.60	3.75	0.85	0.0018	3883
39	Core melt	0-6hrs	760	1966	0.99	0.38	6-12hrs, induction	1.82	4.71	0.80	0.0009	1547
41	Core melt	0-24hrs (fixed)	90	379	0.97	0.05	0-24hrs (fixed)	3.17	13.28	0.86	0.0016	955
16	Brine	12-18hrs, induction	265	1213	0.90	0.13	0-6hrs	2.47	11.32	0.92	0.0012	218
21	Brine	6-12hrs, induction	220	310	0.99	0.11	no observable rate	nd	Nd			710
39	Brine	6-12hrs, induction	447	1352	0.99	0.23	0-12hrs	1.30	3.92	0.95	0.0007	331
41	Brine	0-24hrs (fixed)	43	183	0.96	0.02	0-24hrs (fixed)	0.40	1.72	0.82	0.0002	233
16	UI Seawater	no observable rate	nd	nd			0-6hrs	1.01	6.27	0.71	0.0005	161
21	UI Seawater	no observable rate	nd	nd			6-12hrs, induction	0.67	1.47	0.70	0.0003	456
39	UI Seawater	0-12hrs	136	526	0.69	0.07	6-12hrs, induction	1.85	7.15	0.77	0.0009	259
41	UI Seawater	0-24hrs (fixed)	27	76	0.51	0.01	no observable rate	nd	nd			350
Glucose-amended treatments												
16	Core melt + glu	0-6hrs	160	304	0.95	0.08	0-6hrs	4.13	7.82	0.90	0.0021	2112
21	Core melt + glu	0-6hrs	112	117	0.96	0.06	6-24hrs, induction	1.70	1.77	0.87	0.0009	3883
39	Core melt + glu	no observable rate	nd	nd			12-24hrs, induction	3.18	8.22	0.69	0.0016	1547
41	Core melt + glu	0-24hrs (fixed)	110.	462	0.88	0.06	0-24hrs (fixed)	2.26	9.47	0.99	0.0011	955
16	Brine + glu	0-6hrs	164	752	0.55	0.08	0-6hrs	2.22	10.16	0.84	0.0011	218
21	Brine + glu	0-24hrs	64	90	0.51	0.03	no observable rate	nd	nd			710
39	Brine + glu	0-6hrs	412	1244	0.99	0.21	6-12hrs, induction	2.23	6.74	0.67	0.0011	331
41	Brine + glu	0-24hrs (fixed)	43	185	0.93	0.02	0-24hrs (fixed)	0.69	2.95	0.59	0.0003	233
16	UI Seawater + glu	no observable rate	nd	nd			no observable rate	nd	nd			161
21	UI Seawater + glu	0-6hrs	168	368	0.62	0.08	no observable rate	nd	nd			456
39	UI Seawater + glu	0-12hrs	296	1145	0.86	0.15	12-24hrs, induction	1.67	6.45	0.85	0.0008	259
41	UI Seawater + glu	0-24hrs (fixed)	54	154	0.98	0.03	0-24hrs (fixed)	0.72	2.05	0.86	0.0004	350

UI is'under-ice' seawater, 'glu' refers to 10µM glucose additions. Rate constants represent the proportion of introduced MeBr degraded per day.

3.1 MeBr Incorporation

Incorporation rates in unamended samples ranged from not detectable to 3.6 $pM \cdot hr^{-1}$. The highest rates were exhibited by brine and melt samples, but overlap occurred between the incorporation rate ranges of all three sample types. A delayed response before incorporation (induction) was exhibited in two out of four seawater incubations, as well as one core melt incubation. In each of these cases the incorporation rate following induction remained within the same range as non-induced samples of the same water type.

Glucose did not have a consistent effect increasing or decreasing incorporation rates in the samples, and all glucose-addition rates remained within the same range as the other incubations, from not detectable to 4.13 $pM \cdot hr^{-1}$. Like the unamended samples, ice core melt exhibited the highest incorporation rates, while seawater had the lowest rates. At Stations 16 and 39, the addition of glucose significantly increased the MeBr incorporation rates of ice core melt, whereas rates decreased with additions at Stations 21 and 41. Glucose amendments triggered a delayed incorporation response for Station 39 brine (Fig. 3) and Station 21 ice core melt (Fig. 4) that was not evident in unamended samples. This induction did not increase or decrease incorporation rates beyond the range exhibited by the rest of each sample type. All seawater types other than unamended brine exhibited an induction pattern in at least one station. However, no environmental variables or patterns could be identified in either unamended or glucose added samples to explain why induction occurred in only certain samples.

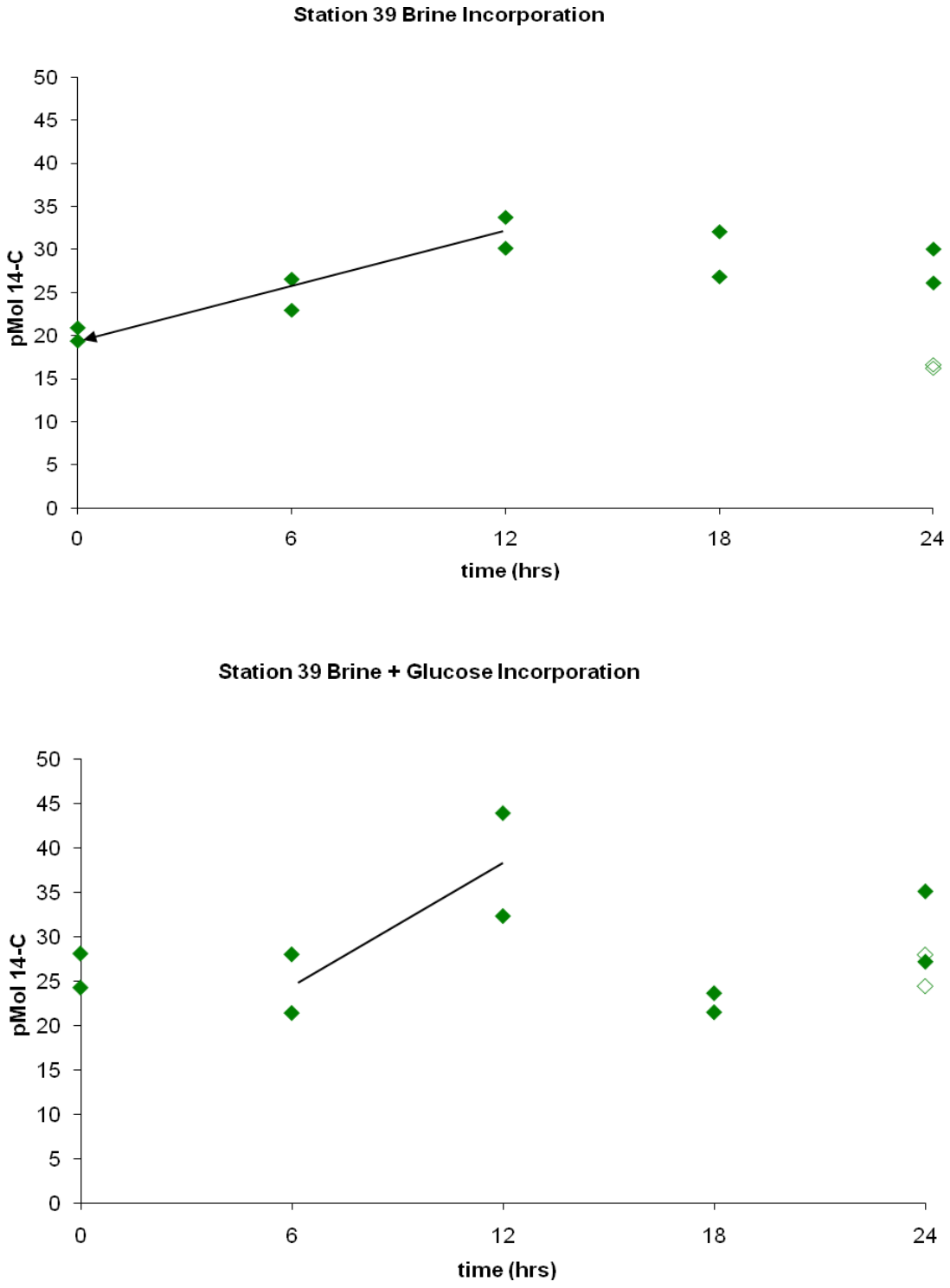


Figure 3- Immediate incorporation (top; 1.30pM·hr^{-1}, R^2=0.95) and induced incorporation (bottom; 2.23 pM·hr^{-1}, R^2=0.67) of ^{14}C from MeBr in brine samples. Solid and open markers represent live samples and killed controls, respectively. Straight regression lines represent rates calculated including each intervening data point, while capped (arrow) regression lines represent rates more statistically significant when killed controls were used in place of 0-hr data.

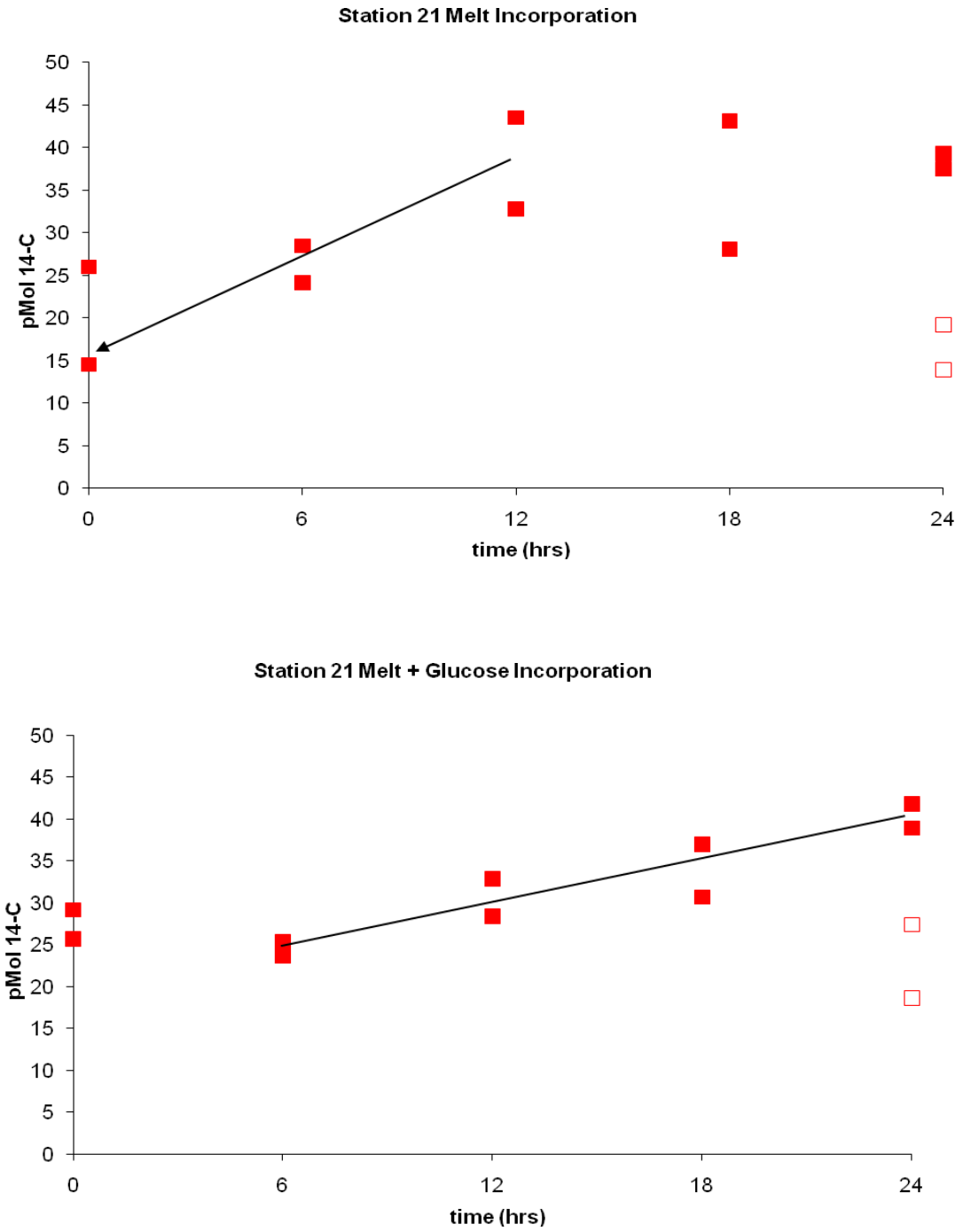


Figure 4- Immediate incorporation (top; 3.60pM·hr^{-1}, R^2=0.85) and induced incorporation (bottom; 1.70pM·hr^{-1}, R^2=0.87) of ^{14}C from MeBr in ice core melt samples. Solid and open markers represent live samples and killed controls, respectively. Straight regression lines represent rates calculated including each intervening data point, while capped (arrow) regression lines represent rates more statistically significant when killed controls were used in place of 0-hr data. While Figures 3 and 4 both illustrate delayed incorporation in glucose samples, glucose did not have a consistent influence on induction patterns across all incorporation rates.

3.2 Respiration

In unamended samples, ice core melt from station 39 produced the highest respiration rate (760 $pM \cdot hr^{-1}$), while all other samples were under 448 $pM \cdot hr^{-1}$. Interestingly, the glucose-added treatment of Station 39 ice core melt exhibited no observable rate. Significant overlap occurred between the respiration ranges of all three sample types in the 26-448 $pM \cdot hr^{-1}$ range, and the lowest observed rate (26.6$pM \cdot hr^{-1}$) was from under-ice seawater. Under-ice seawater yielded the most variable results overall, including three time-courses (one unamended and two glucose) with no observable rate. All unamended station 16, 21 and 39 brine samples required a 6-12 hour period before respiration could be induced, while the addition of 10µM glucose to brine samples removed the induction period but reduced the overall respiration rate measured. Neither ice melt nor under-ice seawater samples exhibited induction of MeBr respiration.

For stations 16, 21 and 39, respiration rates in brine (Fig.5) and ice melt were consistently lower in samples with glucose, but these rates still remained within the same range of variability exhibited by each sample type overall. Brine produced the highest respiration rate in glucose-added samples (412 $pM \cdot hr^{-1}$), very similar to the 448 $pM \cdot hr^{-1}$ highest brine respiration rate in unamended samples. Station 41 produced the lowest measurable respiration rates for all sample and treatment types, as well as many of the weakest statistical relationships. This is likely due to the fixed 24-hr interval between data points used for station 41 samples, during which bottle effects and cell death may have decreased the overall degradation rate.

While the pattern of which sample type had the highest and lowest rates was similar for both incorporation and respiration, (ice core melt producing the highest rate and under-ice seawater the lowest or undetectable rates) this pattern did not correspond directly to the same sample types from specific stations or treatment types. This may be due to the difference in scale

between incorporation and respiration; the variability between duplicates in respiration samples often exceeded the total rate calculated for incorporation, and the time-scales used to calculate each rate varied from one time-course to the next. Due to the low activity of incorporation measurements, the pattern exhibited by different respiration rates is more likely a better assessment of differences in MeBr utilization.

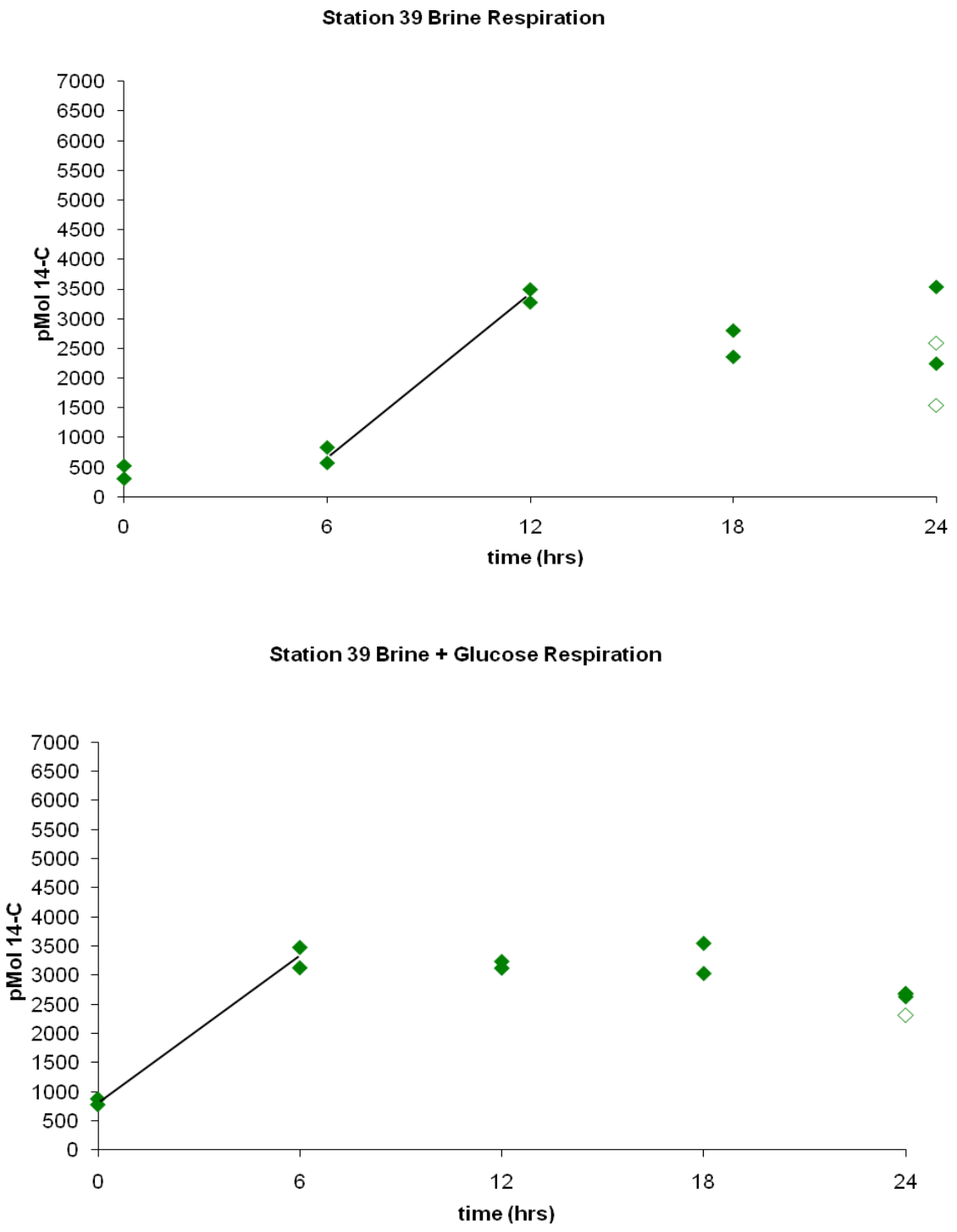


Figure 5- Respiration of ^{14}C from MeBr in brine after a 6-hr delay (top; 447.3pM·hr^{-1}, R^2=0.99) and immediate respiration (bottom; 411.6pM·hr^{-1}, R^2=0.99) in glucose-added samples. Solid and open markers represent live samples and killed controls, respectively, and a regression line spans the interval identified for rate calculations.

3.3 Kinetic Analysis of Rates

The incorporation and respiration rates for each sample type at Station 41 were compared with the concentration of MeBr administered in order to assess the kinetics and possible saturation level of MeBr utilization.

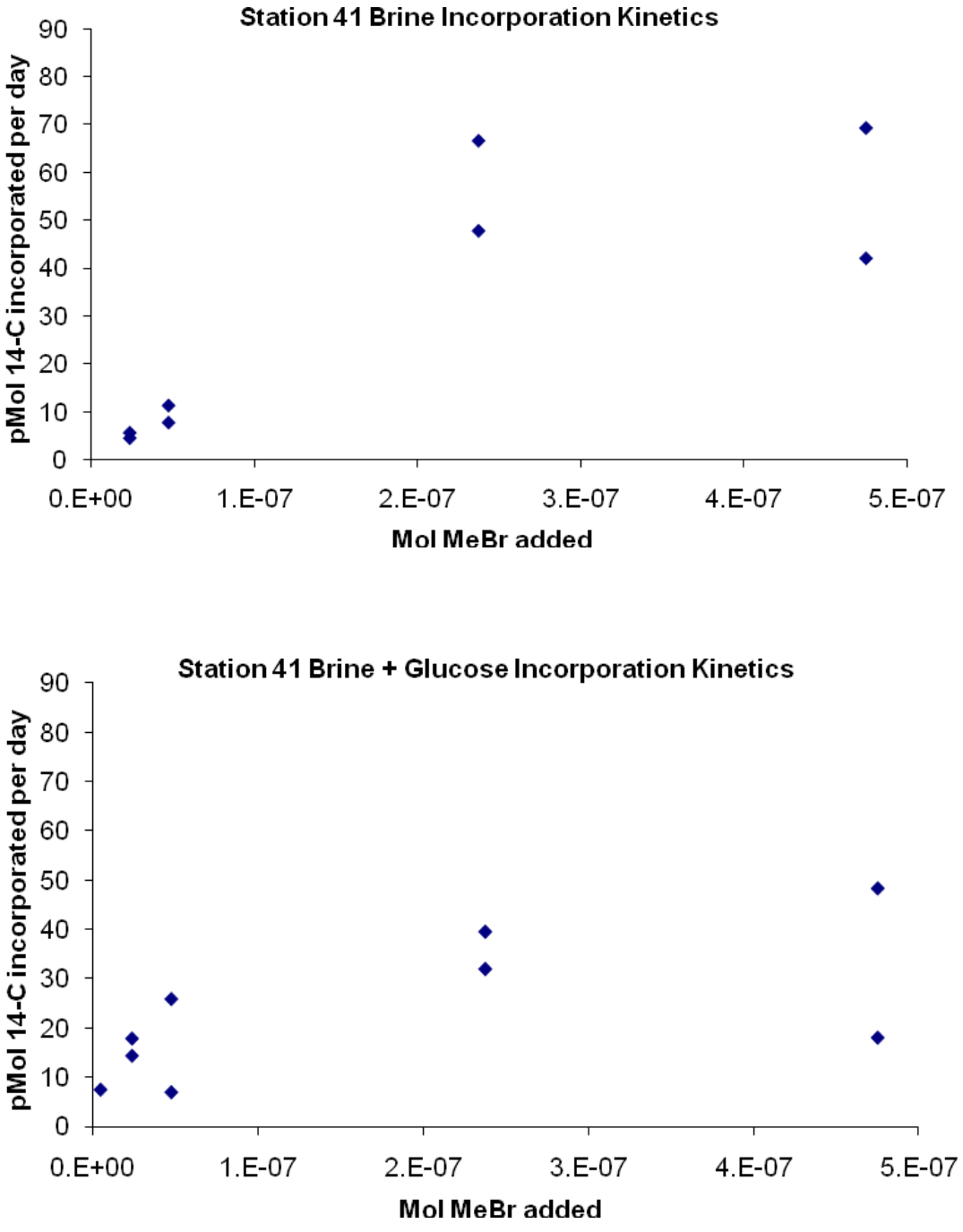


Figure 6- Kinetic analysis of MeBr incorporation in brine samples from station 41.

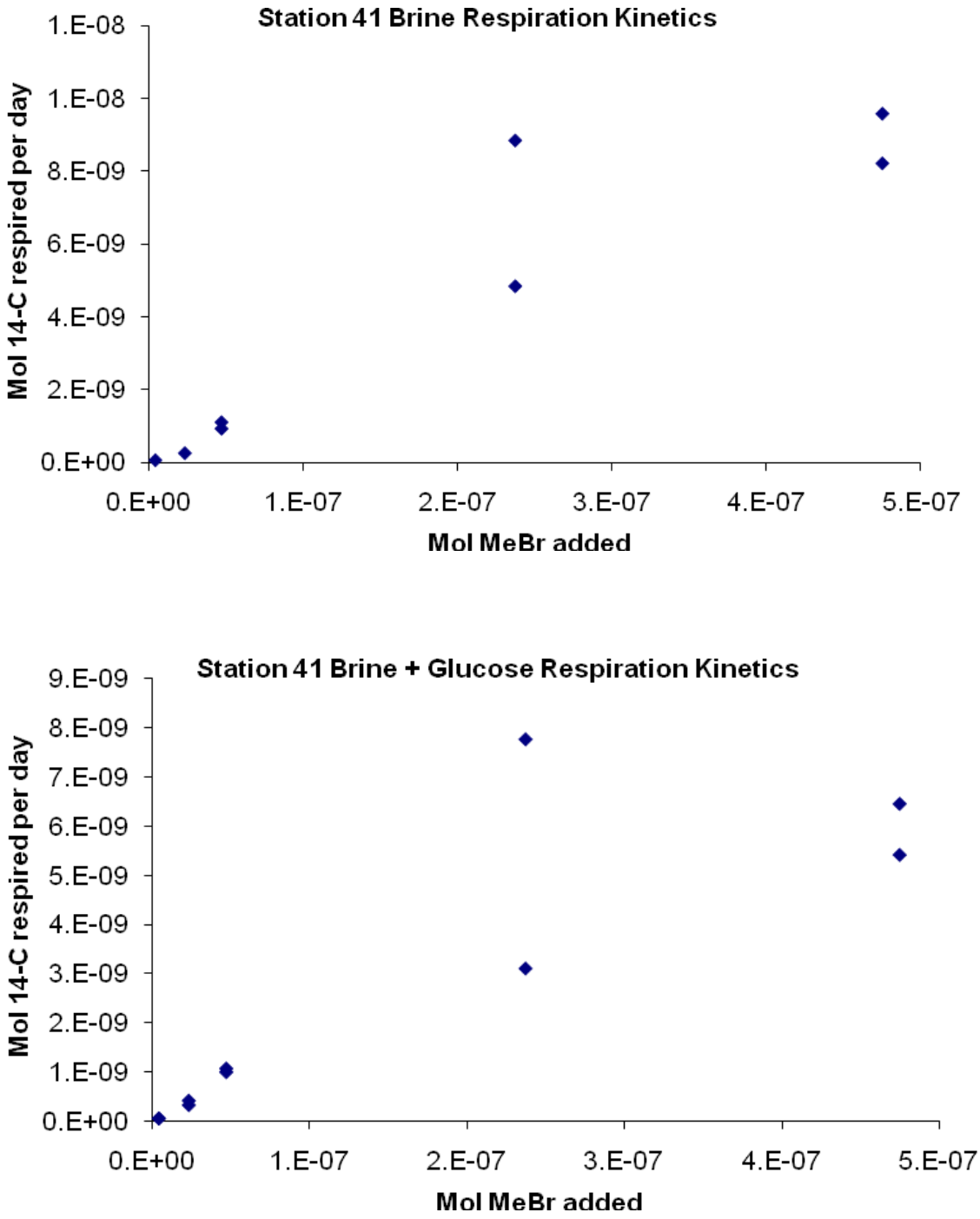


Figure 7- Kinetic Analysis of MeBr respiration in brine samples from station 41.

Brine and ice core melt samples (all graphs available in Appendix E) displayed similar results; with respiration rates continuing to increase beyond the 475nM concentrations used in this experiment. Under-ice seawater provided the least conclusive patterns due to very few 24-hr data points above the rate of 0-hr controls. Incorporation rates, however, do appear to suggest that MeBr saturation may have been reached in certain samples. Data from glucose-amended samples were very similar in patterning to each un-amended counterpart, and ice core melt samples displayed the steepest kinetic slopes for both incorporation and respiration (Fig. 8) suggesting that much more MeBr may be needed to reach a point of saturation.

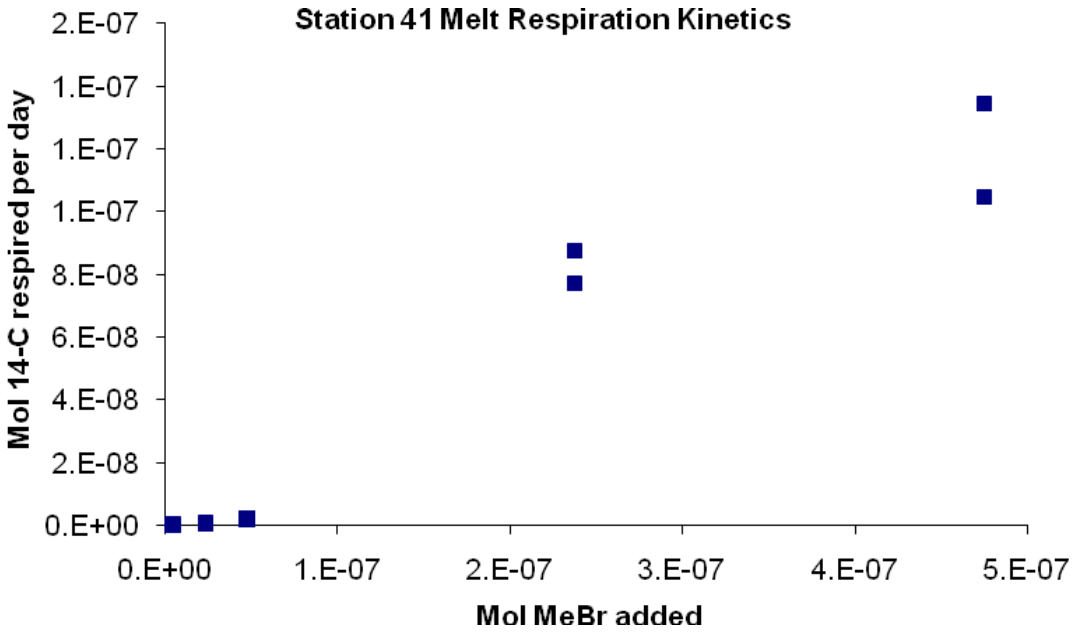


Figure 8- Kinetic analysis of MeBr respiration in melt samples from station 41. Graphs for all sample and rate types are included in Appendix E.

3.4 Saturation Kinetics

SAS-approximated models of the saturation kinetics for methyl bromide degradation are shown in Table 7.

Table 7- Nonlinear Modeling Predictions of MeBr Saturation Kinetics from Station 41.

Station 41 Nonlinear curve fit	n	V_{max} M·day^{-1}	K_m M	R^2 of model fit
Incorporation				
Ice core melt	10	7.65E-10	2.37E-07	0.87
Ice core melt + glucose	10	1.33E-09	6.05E-07	0.87
Brine	8	8.76E-11	2.06E-07	0.82
Brine + glucose	9	3.82E-11	4.16E-08	0.54
UI Seawater	6	2.34E-11	2.58E-08	0.43
UI Seawater + glucose	5	3.22E-11	4.25E-08	0.40
Respiration				
Ice core melt	10	3.94E-07	1.05E-06	0.95
Ice core melt + glucose	10	4.93E-07	9.34E-07	0.96
Brine	8	1.75E-08	4.32E-07	0.91
Brine + glucose	10	9.70E-09	2.54E-07	0.82
UI Seawater	4	*not enough data to fit		
UI Seawater + glucose	7	8.84E-09	3.17E-07	0.98

Note that V_{max} is represented by M·day^{-1}, as opposed to previous rates calculated from stations 16, 21 and 39 per hour. V_{max} is represented in M rather than grams cells since it is the total sample volume, rather than a specific microbial isolate, that is being examined for utilization rates and bacterial abundance did not correlate with rates measured.

Ice core melt rates yielded the strongest statistical models and both the highest estimates of rate V_{max} and half-saturation K_m for incorporation and respiration. Among all sample types V_{max} ranged from 2.34x10^{-11} to 1.33x10^{-9} M·day^{-1} for incorporation and 8.84x10^{-9} to 4.93x10^{-7} M·day^{-1} for respiration, yielding respiration rates 120-550-fold higher than incorporation rates. K_m ranged from 2.58x10^{-8} to 6.05x10^{-7} M for incorporation and 2.54x10^{-7} to 1.05x10^{-6} M for respiration, estimating the saturation for respiration to be 1.5-10-fold higher than the concentrations utilized for incorporation. Under-ice seawater provided the poorest model fits due to the variability in calculated rates and the high number of undetectable rates.

3.5 Rate Constants

Degradation or turnover rate constants were calculated to eliminate the variable of MeBr quantity administered in order to represent rates as the proportion of total MeBr introduced that may be degraded per day. While rate constants for the 47.5nM ^{14}C incubations from all stations are represented in Table 6, the varying quantities of ^{14}C-MeBr used at Station 41 were used to analyze patterns and identify the concentration of introduced MeBr that could generate the quickest proportional degradation (Table 8).

Table 8- Rate Constants for Incorporation and Respiration at Station 41.

		Unamended Samples				**Glucose-amended Samples**			
Water type	nM added	Respiration pM·day^{-1}	Respiration constant·day^{-1}	Incorporation pM·day^{-1}	Incorporation constant· day^{-1}	Respiration pM·day^{-1}	Respiration constant·day^{-1}	Incorporation pM·day^{-1}	Incorporation constant· day^{-1}
melt	4.75	176	0.037	33.7	7.10E-03	325	0.068	25.0	5.27E-03
melt	4.75	218	0.046	31.7	6.68E-03	319	0.067	25.7	5.41E-03
melt	23.75	819	0.034	40.7	1.71E-03	1015	0.043	53.4	2.25E-03
melt	23.75	650	0.027	38.3	1.61E-03	673	0.028	32.2	1.35E-03
melt	47.50	2006	0.042	54.3	1.14E-03	3330	0.070	54.0	1.14E-03
melt	47.50	2332	0.049	97.6	2.06E-03	1961	0.041	54.7	1.15E-03
melt	237.50	87527	0.369	428.3	1.80E-03	120218	0.506	264.1	1.11E-03
melt	237.50	77205	0.325	472.4	1.99E-03	108120	0.455	539.3	2.27E-03
melt	475.00	104836	0.221	609.0	1.28E-03	155035	0.326	701.1	1.48E-03
melt	475.00	134604	0.283	342.5	7.21E-04	168011	0.354	448.9	9.45E-04
brine	4.75	67	0.014	nd	nd	57	0.012	nd	nd
brine	4.75	nd	nd	nd	nd	57	0.012	7.5	1.59E-03
brine	23.75	nd	nd	5.7	2.40E-04	328	0.014	17.9	7.54E-04
brine	23.75	262	0.011	4.6	1.93E-04	419	0.018	14.4	6.08E-04
brine	47.50	934	0.020	11.4	2.40E-04	1000	0.021	7.0	1.48E-04
brine	47.50	1111	0.023	7.8	1.65E-04	1073	0.023	25.9	5.46E-04
brine	237.50	8847	0.037	66.6	2.80E-04	7766	0.033	39.6	1.67E-04
brine	237.50	4846	0.020	47.8	2.01E-04	3107	0.013	32.1	1.35E-04
brine	475.00	8219	0.017	42.1	8.86E-05	6454	0.014	18.1	3.81E-05
brine	475.00	9582	0.020	69.2	1.46E-04	5417	0.011	48.4	1.02E-04
under ice	4.75	26	0.005	nd	nd	151	0.032	2.1	4.47E-04
under ice	4.75	61	0.013	1.4	3.03E-04	59	0.012	nd	nd
under ice	23.75	nd	nd	14.8	6.23E-04	480	0.020	nd	nd
under ice	23.75	nd	nd	5.7	2.41E-04	321	0.014	nd	nd
under ice	47.50	648	0.014	nd	nd	1165	0.025	13.0	2.73E-04
under ice	47.50	631	0.013	nd	nd	1426	0.030	21.5	4.53E-04
under ice	237.50	nd	nd	nd	nd	3772	0.016	nd	nd
under ice	237.50	nd	nd	37.9	1.59E-04	nd	nd	nd	nd
under ice	475.00	nd	nd	19.6	4.12E-05	nd	nd	48.8	1.03E-04
under ice	475.00	nd	nd	10.2	2.15E-05	nd	nd	10.3	2.17E-05

The highest rate constants for respiration at Station 41 were found with additions of 237.5nM MeBr; producing rates of 0.506 day^{-1} in ice core and 0.037 day^{-1} in brine samples. (Fig. 9).Under-ice seawater (not shown) produced respiration constants of up to 0.030 day^{-1} in 4.75nM additions , but many higher concentrations did not produce any observable constants above the noise of 0-hr and killed controls. This is partially due to the low number of successful under-ice seawater incubations that produced positive rates, leaving far fewer data points available to calculate rate constants.

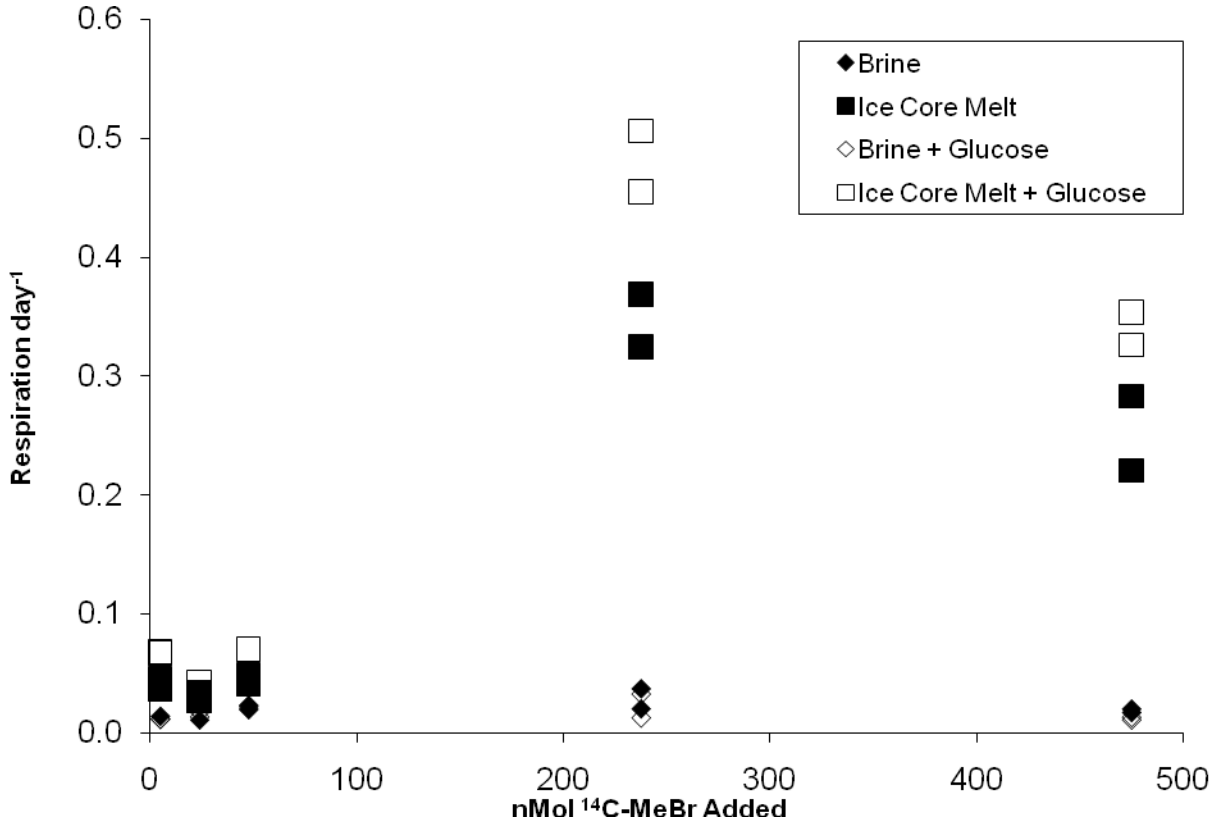


Figure 9- Respiration constants of ^{14}C from MeBr in Station 41 brine and ice core melt using increasing concentrations of MeBr.

In all station 41 ice core melt and under-ice seawater samples, respiration rate constants were higher with glucose additions, but the majority of brine respiration constants were lower in samples with glucose. Rate constants for respiration measured from the other three stations did not exceed station 41 levels for ice core melt, but brine and seawater from station 39 reached 0.23 day^{-1} and 0.15 day^{-1}, respectively (Table 6). Like the pattern exhibited at Station 41, glucose-amended samples for stations 16, 21 and 39 yielded higher respiration rate constants in under-ice seawater and most ice core melt samples, while lower constants in brine samples.

Incorporation rate constants did not exhibit as clear of a pattern as those for respiration, which may be partially attributed to the amount of noise in samples measuring rate constants of less than 0.003 day^{-1} (Fig. 10).

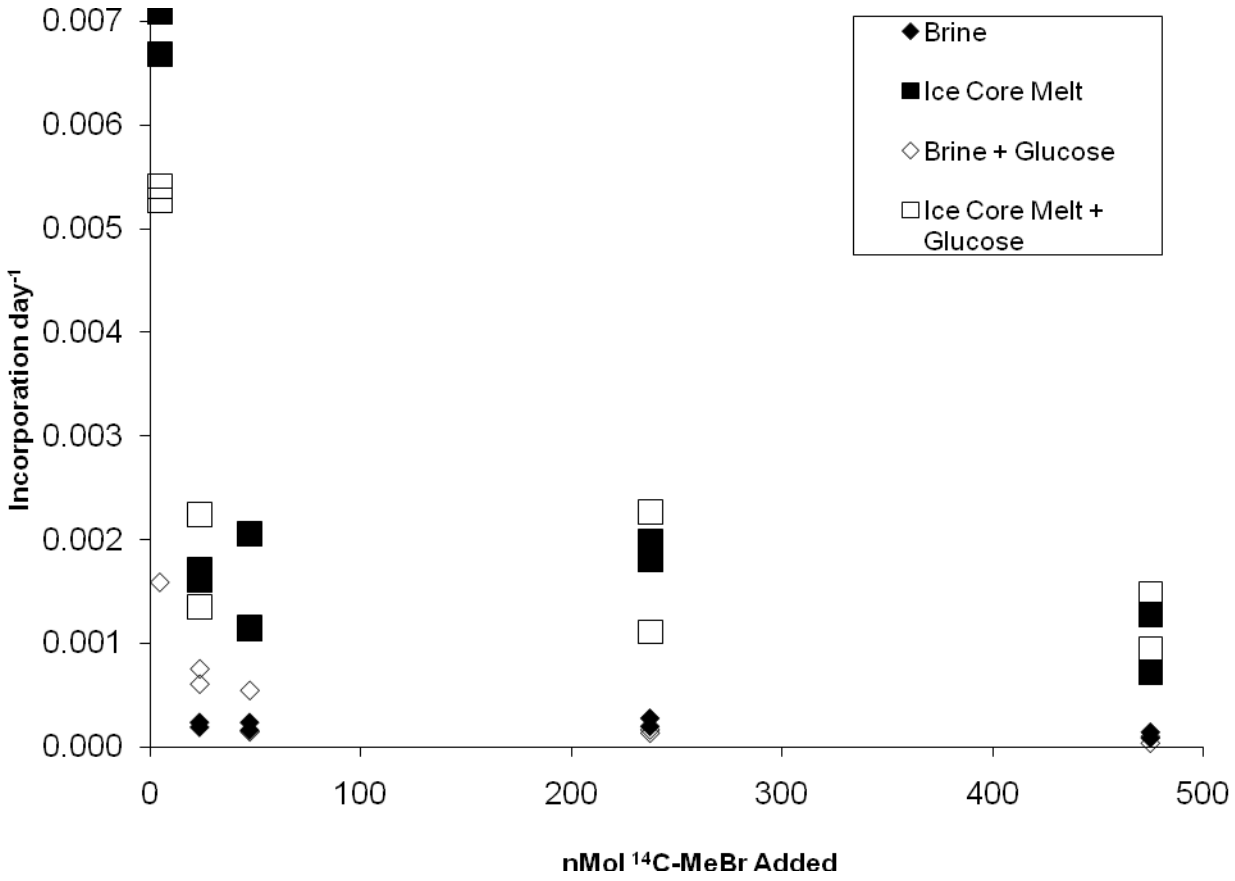


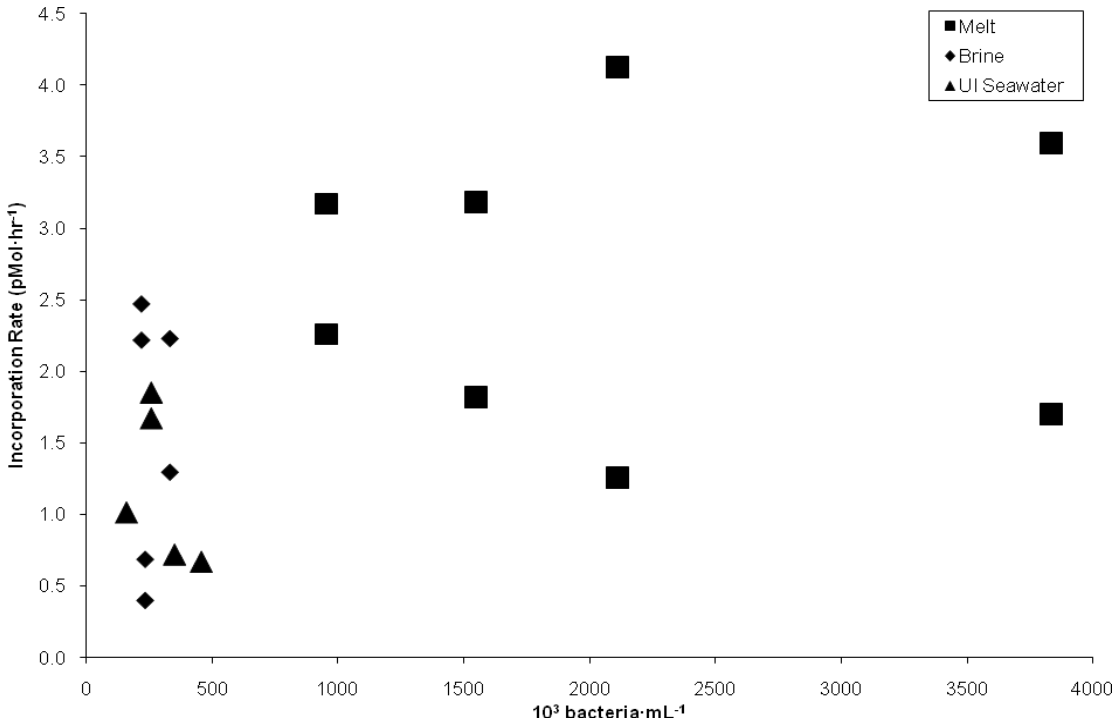
Figure 10- Incorporation rate constants of ^{14}C from MeBr in Station 41 brine and ice core melt using increasing concentrations of MeBr.

The highest degradation rate constants for incorporation at Station 41 were found with additions of 4.75nM MeBr, producing rates of 0.0071 day^{-1} for ice core melt and 0.0016 day^{-1} for brine (Fig. 10). Above 4.75nM concentrations, the rate constants for both ice core melt and brine incubations remain relatively constant, with average rate constants of 0.0015 (+/- 0.00047 1 standard deviation; STD) for ice core melt and 0.00025 (+/- 0.0002 1STD) for brine samples. Interestingly glucose-amended samples had the opposite effect on incorporation than respiration for each water type's highest rate constant; while glucose additions produced lower brine respiration constants, it produced higher brine incorporation constants. Likewise, glucose

additions produced higher ice core melt respiration constants and lower ice core melt incorporation constants. Overall, patterns within incorporation are much less conclusive than those for respiration due to the lack of identifiable patterns in incorporation constants and the large differences in the scale of respiration to incorporation rates. Under-ice seawater (not shown) produced incorporation constants of up to 0.00045 day^{-1} in 4.75nM and 47.5nM additions, but 9 out of 20 seawater incubations did not produce any observable constants above the noise of 0-hr controls. While no incorporation constants for ice core melt or brine from stations 16, 21 or 39 exceeded the rates calculated at station 41, under ice seawater exhibited higher constants at stations 16 and 39, reaching up to 0.0009 day^{-1}.

3.6 Environmental Characteristics

Bacterial abundance varied by more than an order of magnitude in ice core melt samples (Table 6), while mean rates for incorporation in ice core melt remained roughly consistent at approximately 2.64pM·hr^{-1} (+/- 1.02 STD). No patterns were observed between respiration rates and bacterial abundance. Samples with the highest bacterial abundances did not necessarily produce the highest rates in either incorporation or respiration (Fig. 11), and no statistical relationships were found between rates and abundance. (Rates in pmol·hr^{-1}·10^9 $cells^{-1}$ were higher at stations 16 and 39, both of which had lower counts of bacterial abundance than the other stations. Thus adjusting for bacterial abundance may skew the rate data by comparing rates to the size of bacterial populations in which not all species are capable of dehalogenation.) Since bacterial abundance was not directly correlated with incorporation or respiration and it is likely that only a small percentage of the overall bacterial community is capable of MeBr degradation, rates were thus compared in pM·hr^{-1} for further analysis.



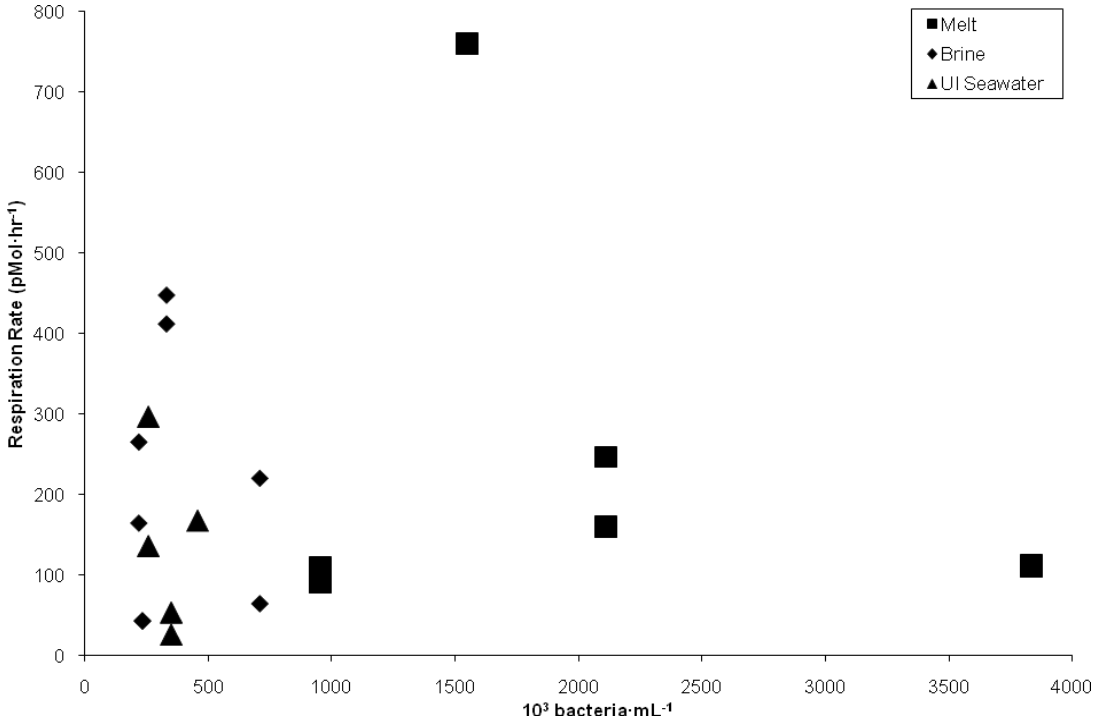


Figure 11- ^{14}C Rates of incorporation and respiration with the bacterial abundance in brine, ice core melt, and under-ice seawater from each station.

All rates were compared against environmental characteristics measured at each station for each sample type before the addition of glucose. Environmental characteristics were compared to incorporation and respiration rates represented both in $pM \cdot hr^{-1}$ (Table 9) and $pmol \cdot hr^{-1} \cdot 10^{9}$ $cells^{-1}$ (Appendix G) in order to assess the relationship that environmental factors may have had on degradation rates independent of the possible correlation between these variables and bacterial population counts.

Table 9- Chemical Characteristics of All Water Types

Station	Water type or Correlation	Resp. Rate ($pM \cdot hr^{-1}$)	(+Glu) Resp. Rate	Incorp. Rate ($pM \cdot hr^{-1}$)	(+Glu) Incorp. Rate	Chl a ($mg \cdot L^{-1}$) (A)	DMSP (nM) (A)	PO_4 (µM) (B)	N+N (µM) (B)	DON (µM)	TDN (µM)	DOC (µM)	DIC (µM) (B)	pH (B)	Total Alkalinity ($\mu mol \cdot kg^{-1}$) (B)	Salinity (B)	10^3cells $\cdot mL^{-1}$ (C)
16	Melt	246.8	160.3	1.25	4.13	34.94	227.5	1.49	5.13				273.6	8.0	270	8.6	2112
21	Melt	110.3	111.9	3.60	1.70	13.53	208.1	0.35	-0.09				262.2	8.9	160	6.3	3883
39	Melt	760.3	nd	1.82	3.18	8.6	110.0	0.06	1.40				191.5	8.4	210	4.4	1547
41	Melt	90.4	110.2	3.17	2.26	1.72	175.2	0.00	3.43				521.2	8.1	510	5.9	955
	Melt Resp. corr.					-0.07	-0.81	-0.19	-0.16				-0.65	0.01	-0.39	-0.56	-0.30
	Melt + glu Resp. corr.					**0.95**	0.80	**0.98**	0.73				-0.49	-0.55	-0.24	**0.99**	-0.09
	Melt Incorp. corr.					-0.65	**0.99**	-0.63	-0.63				0.45	0.60	0.16	-0.32	0.37
	Melt + glu Incorp. corr.					0.72	**-0.99**	0.71	0.74				-0.34	-0.69	-0.07	0.46	-0.38
16	Brine	264.9	164.3	2.47	2.22	0.02	14.5	0.56	0.84	8.3	9.3	87.5	2151.1			42.0	218
21	Brine	219.9	64.2	nd	nd	0.46	29.3	1.33	22.63	9.0	9.8	86.3	1407.3			34.6	710
39	Brine	447.3	411.6	1.30	2.23	0.11	26.5	0.00	0.00	3.4	3.4	65.7	1917.5			37.9	331
41	Brine	42.6	43.2	0.40	0.69	0.13	74.1	0.00	0.00	6.3	6.3	74.2	1811.1			31.1	233
	Brine Resp. corr.					-0.15	-0.76	-0.06	-0.09	-0.49	-0.41	-0.33	0.25			0.66	0.07
	Brine + glu Resp. corr.					-0.40	-0.48	-0.46	-0.43	-0.79	-0.73	-0.65	0.42			0.51	-0.23
	Brine Incorp. corr.					**-0.96**	**-0.92**	**0.90**	**0.90**	0.48	0.57	0.67	**0.99**			**0.98**	-0.20
	Brine + glu Incorp.corr.					-0.64	**-0.98**	0.49	0.49	-0.11	0.00	0.12	0.74			**0.93**	0.40
16	UI Seawater	nd	nd	1.01	nd	0.26	5.3	1.92	27.96	0.0	25.0	45.0	2194.9			33.6	161
21	UI Seawater	nd	167.7	0.67	nd	6.05	70.5	1.38	15.66	3.7	21.3	60.5	2109.2			33.4	456
39	UI Seawater	136.2	296.3	1.85	1.67	0.14	11.2	1.76	30.96	8.4	39.7	38.4	2170.7			33.5	259
41	UI Seawater	26.6	54.0	nd	0.72	0.41	13.8	1.80	29.77	11.6	41.7	34.6	2165.5			33.3	350
	UI-SW Resp. corr.					*not enough rates											
	UI-SW + glu Resp. corr.					-0.08	-0.07	-0.05	0.11	-0.37	-0.05	0.10	0.11			**0.99**	-0.49
	UI-SW Incorp. corr.					-0.74	-0.67	0.50	0.84	0.74	**0.99**	-0.89	0.51			0.28	-0.46
	UI-SW + glu Incorp. corr.					*not enough rates											

'Corr.' abbreviates correlations between environmental characteristics and the degradation rates for each water type. Environmental characteristics were measured from different sources of ice core melt depending on availability. (A) represents characteristics measured from ice core melt 1:1 diluent, (B) represents characteristics measured directly from a 10cm slice of ice core corresponding to the depth used in each analysis, and for bacterial abundance (C), the cell counts from 1:1 diluent were subsequently doubled to represent an estimate of cell counts in the original undiluted core. Dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC) were not measured in ice core samples, while pH and total alkalinity were only measured in ice cores.

No correlations were found using either rate representation for dissolved organic nitrogen (DON) or pH. Due to the low number of stations examined, correlations between environmental characteristics and one particular rate may not be as conclusive as the overall trend between rates and characteristics measured. Environmental characteristics that correlated with more than one rate represented both in pM·hr and pmol·hr·10^9 cells included Chlorophyll-a, Dimethylsulfoniopropionate (DMSP), Phosphate (PO_4), and salinity. However, closer inspection of these relationships revealed contradicting trends within water types for Chlorohpyll-a and DMSP, while phosphate yielded positive relationships with incorporation and salinity exhibited positive relationships with both incorporation and respiration rates across different water types. In brine samples, incorporation correlated with salinity in both unamended and glucose-added incubations (Fig. 12).

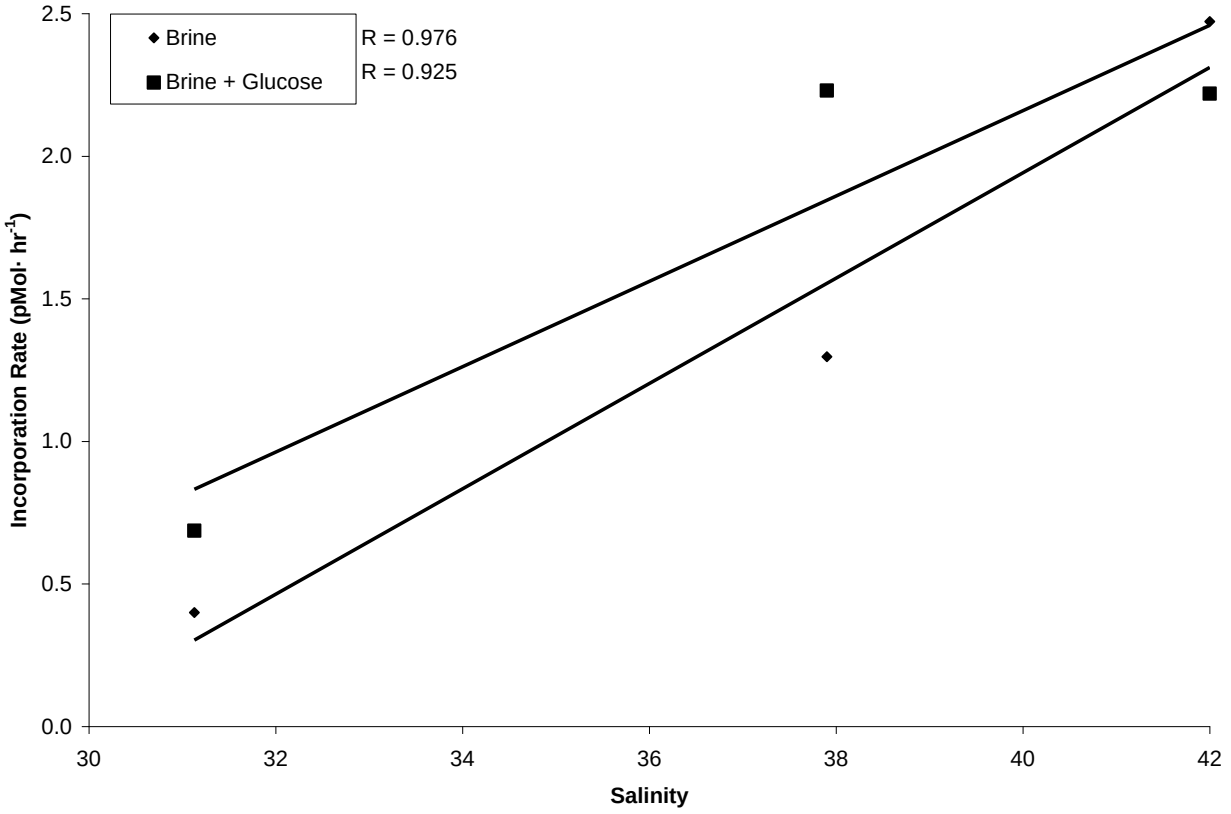


Figure 12- Incorporation rates and salinity of brine and under-ice seawater.

However, no consistently significant correlations existed between ice core melt rates and salinity, nor the brine fraction within the ice core (Table 5) and ice core melt incorporation or respiration rates. Meteorological site characteristics including air and water temperature as well as ice thickness also revealed no correlations to respiration or incorporation rates. Unexpectedly, depth of the ice core slice used in the analysis did correlate to melt incorporation rates; revealing a negative correlation for unamended samples and a positive correlation for glucose-added samples (Fig. 13).

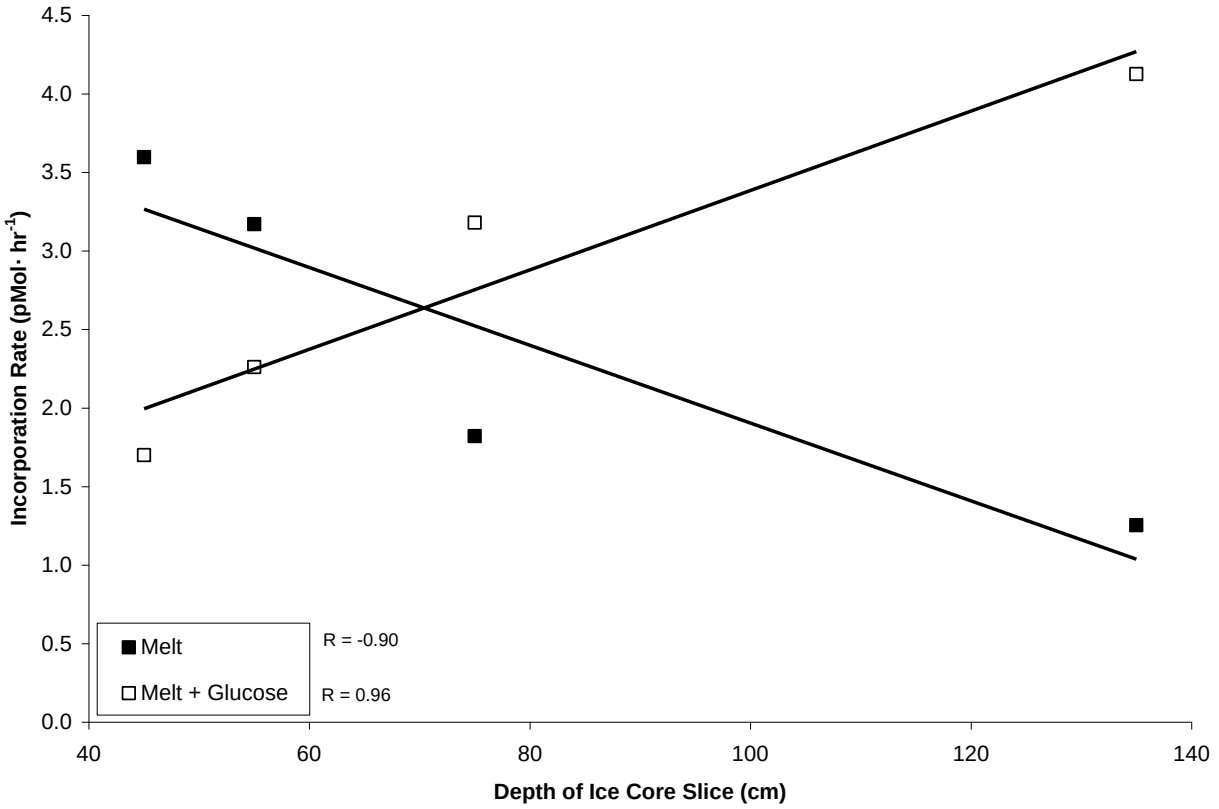


Figure 10- Melt incorporation rates and the depth of the ice slice used in each analysis.

4. DISCUSSION

4.1 No Evidence for Abiotic Degradation

The increase in ^{14}C measured on incorporation filters and respiration wicks over time, in addition to comparison against killed control samples, suggests that abiotic transformation of MeBr due to changes in pH (from the sulfuric acid step to initiate CO_2 outgassing), temperature changes, or other abiotic degradation is not likely, and the rates calculated here are attributed to microbial processes. The rate of MeBr hydrolysis can be enhanced by light, and Castro and Belser's 1981 study found a 7-fold increase in the rate of hydrolysis with UV lights ($k_\lambda = 1.4 \times 10^{-4}\ s^{-1}$) releasing methanol, bromide ions, and protons as a direct reaction of photoexcited MeBr. However, the rate of MeBr hydrolysis in laboratory light conditions is negligible over a 24-hour incubation, and the MeBr used in this study was stored in dark conditions to prevent degradation. In addition, chemical loss rates for MeBr are negligible in the Southern Ocean due to low temperatures (Tokarczyk et al. 2003a). Since all rates in this study were calculated by first subtracting 0-hr or killed controls and all experiments were carried out in dark, airtight conditions below the 3.6°C boiling point of MeBr, the increased activity on cell filters and carbon wicks is attributed to microbial incorporation and respiration of ^{14}C from ^{14}C-MeBr.

Since this study traced the movement of ^{14}C specifically, no data can conclude whether the carbon incorporated into cells has already been cleaved from MeBr or if it is incorporated as a halocarbon, but previous research on microbial utilization and dehalogenation of halocarbons (review in Haggblom and Bossert 2003a) suggests that MeBr is cleaved by dehalogenases and

the carbon atoms may be incorporated into the cell for use in cell growth. Compounds loosely associated with the cell membrane would dissociate upon addition of sulfuric acid and filtration, so the rates calculated here apply specifically to cellular incorporation. However, the >50-fold higher rates of respiration measured in this study suggest that the carbon in MeBr is used cometabolically in respiration (~50-760pM·hr^{-1} in 47.5nM MeBr) while very little (~2pM·hr^{-1} in 47.5nM MeBr) is incorporated in cells. A comparison of environmental conditions, the bacterial community of sea ice, and the significantly higher rates of ^{14}C respiration than incorporation of MeBr suggest that the most likely transformation route in this study is microbial oxidative dehalogenation to CO_2 via monooxygenases, which has been identified in a number of α-proteobacteria (Coulter et al. 1999; Schaefer and Oremland 1999; Goodwin et al. 2001).

4.2 Analysis of Water Types and Environmental Characteristics

A comparison of Southern Ocean sample types in this study shows that sea ice and brine are the more active environments for dehalogenation than under-ice seawater. This may relate to the specific bacterial community within each sample type capable of dehalogenation or the environmental conditions within ice that induce dehalogenating activity earlier than in other environmental samples. Castro (2003) suggests that the rate-limiting step in microbial dehalogenation is dependent on the specific organism and its ability to access bioavailable reactive sites in a given media rather than the mechanism of dehalogenation or site characteristics, and the highest dehalogenating rates are found where organisms have been 'primed' with previous bioavailable doses of methyl halides that activate specific enzyme systems. Since this study examined rates after one initial MeBr spike, future research might examine if utilization rates increase after repeated MeBr doses, or if repeated doses can stimulate

under-ice seawater to reach the same microbial respiration rates as sea ice and brine. The freezing of seawater results in the expulsion of dissolved halogens from the ice crystal matrix, leading to increased ionic strength of brine trapped within the ice (Macdonald et al. 2005). The bacteria within sea ice and brine may therefore be better prepared for methyl halide utilization than under-ice seawater due to previous survival and adaptation in these conditions.

Since there are no other known studies analyzing bacterial degradation in Southern Ocean sea ice, it is not surprising that no other correlations between brine salinity or ice depth were found for comparison to this paper. Many soil studies identified sensitive relationships between degradation rates and pH, total alkalinity, and nitrogen (Madsen and Aamand 1992; Rhee et al. 1993; Sun, Cole and Tiedke 2001) none of which were found in this analysis. This is unusual for pH and total alkalinity in particular, since pH and buffering capacity have been found to limit the continued dehalogenation of halocarbons due to proton release and pH shifting (Loffler et al. 2003). However, the results of this analysis suggest that the most indicative environmental characteristics governing degradation potential may be ambient halocarbon levels. While ambient halocarbon concentrations have not yet been analyzed for the Oden 2008-9 research cruise, chloride and bromide levels are inherently related to salinity, and certain biologically produced halocarbons have been found to share this correlation as well (Gribble 1996). This relationship does not suggest that higher salinity would indicate a higher degradation rate (in which case under-ice seawater would have higher degradation rates than ice core melt), but rather that exposure to previous halocarbons *within* a given media may prime bacteria for further halocarbon degradation, as suggested by Miller et al. 1997 and Oremland 2003.

The degradation rates identified in this study are significantly higher than many studies conducted in other environmental media (Miller et al. 1997; Bradley and Chapelle 1998).

However, the largest number of MeBr degradation studies have been examined in soil microcosms, while MeBr is most bioavailable in the aqueous phase (Ogram et al. 1985; Harmansson and Marshall 1985; Rijnaarts et al. 1990; Robinson et al. 1990; Bossert and Compeau 1995; Bosma et al. 1997). While the MeBr used in this study was introduced at the beginning of analysis, the bioavailability of MeBr along with the potential for bacteria in each sample type to have previous exposure to biogenic MeBr from Antarctic ice microalgae (Gribble 2000) both support the suggestion that prior exposure to this halocarbon may influence and increase the capability for marine bacteria to degrade it.

Master and Mohn (1998) suggest that psychrotolerant bacteria may be capable of higher rates of halocarbon utilization due to increased fluidity of the cell membrane and unique adaptations to their environments. In sea ice particularly, flexible cell membranes that resist freezing may provide an advantage for transporting halocarbons within the cell for use in dehalogenation. No relationship was found between incorporation/respiration rates and the bacterial abundance of samples in this study, which agrees with Tokarczyk et al.'s studies of MeBr degradation in Pacific and Southern Ocean surface waters (Tokarczyk et al. 2001). Since only specific bacterial strains are capable of dehalogenation, the species responsible in sea ice, brine, and under-ice seawater may not be proportional to the overall bacterial abundance in each sample type.

4.3 Glucose Amendments

While the addition of glucose did not have a consistent effect throughout all incubations, glucose appeared to eliminate induction yet decrease the overall rate of degradation in respiration studies. This pattern may not necessarily be a rate depression; glucose additions were simply not able to increase rates beyond the potential of unamended incubations after induction. This response is similar to the glucose patterns found by Goodwin et al. 2001 and opposite to those found by Schaefer and Oremland (1999), and may indicate certain features about the environment of each incubation. While alternative glucose responses include decreased degradation rates due to over-competition with glucose-utilizing bacteria (Miller et al. 1997), this does not seem to be the case in this study since glucose encouraged the immediate degradation of MeBr. Adding glucose to 'quick-start' respiration may suggest that certain bacteria need an initial boost to degrade MeBr, but once started, in the presence of glucose there may not have been as much of a need for the energy-creating process of halorespiration. Glucose may also serve to encourage the degradation of MeBr as a cometabolic process. As previously stated, the question of whether or not these bacteria had exposure to previous 'doses' of halocarbons could help to indicate why glucose caused these patterns in the incubations.

4.4 Implications of Nonlinear Models and Degradation Rate Constants

Nonlinear curve fits using Michaelis-Menten first-order saturation kinetics suggests that MeBr degradation rates continue to increase until saturation is achieved in levels >2000-fold above environmental concentrations. While this suggests higher rates of degradation are possible at higher concentrations (exceeding 490nM·day^{-1} in sea ice), such high concentrations of MeBr are not found naturally in any of the sample types studied. The toxicity of MeBr may start to inhibit dehalogenation after a given threshold, since toxic inhibition was found in other bacterial

dehalogenation studies at 0.3-0.5MmM concentrations (Coulter et al. 1999, Hoeft et al. 2000, Goodwin et al. 2001). Nonetheless the identification of degradation rates in each sample may help to explain the under-saturation of MeBr in the Southern Ocean (Tokarczyk et al. 2003a; Yvon-Lewis et al. 2004), and respiration rates normalized against the MeBr concentration introduced reached 0.51 day^{-1} in sea ice samples, 0.23 day^{-1} in brine samples, and 0.15 day^{-1} in under-ice seawater. While no other known studies analyzed degradation within Southern Ocean brine or sea ice, the degradation rates identified in under-ice seawater are similar to those identified by Tokarczyk et al. in their 2003 analysis of Southern Ocean surface water degradation rates, reaching 0.18 day^{-1} using a ^{13}C-MeBr incubation technique. Scaling the highest MeBr degradation rate identified in this study (760pM·hr^{-1}) in 10-cm ice core melt samples against the area of sea ice in the Southern Ocean (18 x $10^{16}km^2$) yields rates exceeding 2.12 x 10^{12} mol MeBr degradation (via respiration)·hr^{-1} for a comparable 10cm-slice throughout all Southern Ocean sea ice; far exceeding the practical estimates for a MeBr sink. While the rates and degradation rate constants identified in this study can describe the breadth and strength of dehalogenation possible in a given sample, the amount of variability from one sample to the next as well as the simulated conditions used in each analysis may limit the applicability of this data in estimating ambient biological degradation. Rather, this study serves to identify environmental media containing dehalogenating communities and promote further research into the dehalogenases used by these bacteria for use in bioremediative applications. Isolating enzymes from the bacteria themselves could remove some of the environmental limitations due to biological dehalogenation (particularly when applying sea ice bacteria to pollution in mesothermic climates) and broaden the breadth of climates in which a specific isolate can be used.

4.5 Adjustments to Methodology

In future studies of methyl halide respiration in sea ice, it may be valuable to narrow the time-course interval to a 1- or 2-hr sequence rather than 6hrs in order to describe the initial patterns that lead to induction and eventual drop-off due to bottle effects. A narrower time interval may also refine data of MeBr saturation kinetics, since the 24-hour interval used for all station 41 studies may have lowered the rates calculated by using a longer time-course during which cells may have died in laboratory conditions. However, the 6-hr measurement interval chosen for stations 16, 21 and 39 was sufficient to demonstrate that induction patterns exist in certain samples within 12 hours of MeBr introduction.

5. CONCLUSIONS

Results from this study are significant in identifying additional environmental media containing dehalogenating communities, as well as determining the ability of marine cold-adapted bacteria to use MeBr in nM day^{-1} quantities. Respiration rates normalized against the MeBr concentration introduced reached 0.51 day^{-1} in sea ice samples, 0.23 day^{-1} in brine samples, and 0.15 day^{-1} in under-ice seawater. Extrapolating the highest respiration rates against the enormity of sea ice in the Southern Ocean yields rates far exceeding practical estimates for a MeBr sink, but may help to explain the undersaturation of MeBr in the Southern Ocean if even a small percentage of this degradation can occur in brine pockets and sea ice. Since the MeBr concentrations used in this study exceed ambient levels and degradation rates varied with environmental conditions, this analysis identifies the *ability* for microbiota within sea ice, brine, and under-ice seawater samples to degrade MeBr, rather than measuring accurate environmental fluxes. Identification and isolation of the dehalogenase enzymes responsible for this utilization may have significant implications in the field of bioremediation, while the results of this study have identified sea ice, brine, and under-ice seawater as containing additional biological sinks for the global methyl bromide cycle.

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APPENDIX A- Liquid Scintillation Counter ^{14}C Output for Stations 16, 21 and 39 (Organized by water type). KC refers to killed controls (using formalin additions).

Brine Data (no additions)

station	date	timepoint (hrs)	water type	wick code	wick DPM	wick pM ^{14}C	filter code	filter DPM	filter pM ^{14}C
16	17-Dec-08	0	brine	1	23514	6712.22	37	37	10.55
16	17-Dec-08	0	brine	2	16524	4716.87	38	30	8.60
16	17-Dec-08	6	brine	7	12728	3633.22	79	75	21.54
16	17-Dec-08	6	brine	8	8352	2384.24	80	96	27.28
16	17-Dec-08	12	brine	13	7685	2193.63	85	71	20.41
16	17-Dec-08	12	brine	14	8472	2418.40	86	104	29.68
16	17-Dec-08	18	brine	19	12360	3528.11	91	82	23.52
16	17-Dec-08	18	brine	20	14933	4262.65	92	82	23.33
16	17-Dec-08	24	brine	25	10763	3072.29	97	98	28.03
16	17-Dec-08	24	brine	26	8125	2319.41	98	111	31.57
21	20-Dec-08	0	brine	147	9437	2693.82	219	114	32.67
21	20-Dec-08	0	brine	148	9633	2749.69	220	88	25.19
21	20-Dec-08	6	brine	153	8925	2547.55	225	108	30.77
21	20-Dec-08	6	brine	154	9322	2660.96	226	92	26.27
21	20-Dec-08	12	brine	159	13860	3956.40	231	93	26.47
21	20-Dec-08	12	brine	160	13632	3891.48	232	105	29.84
21	20-Dec-08	18	brine	165	11273	3217.95	237	68	19.31
21	20-Dec-08	18	brine	166	15474	4417.21	238	115	32.81
21	20-Dec-08	24	brine	171	7939	2266.17	243	94	26.70
21	20-Dec-08	24	brine	172	10753	3069.63	244	119	33.96
39	29-Dec-08	0	brine	291	1814	517.77	363	73	20.92
39	29-Dec-08	0	brine	292	1055	301.26	364	68	19.39
39	29-Dec-08	6	brine	297	1982	565.89	369	93	26.56
39	29-Dec-08	6	brine	298	2897	826.90	370	80	22.96
39	29-Dec-08	12	brine	303	11460	3271.28	375	118	33.74
39	29-Dec-08	12	brine	304	12222	3488.82	376	106	30.16
39	29-Dec-08	18	brine	309	9798	2796.96	381	94	26.84
39	29-Dec-08	18	brine	310	8246	2353.91	382	112	32.07
39	29-Dec-08	24	brine	315	12372	3531.53	387	105	30.05
39	29-Dec-08	24	brine	316	7846	2239.62	388	92	26.13
16	17-Dec-08	24	brine KC	31	6712	1916.07	103	113	32.32
16	17-Dec-08	24	brine KC	32	9769	2788.76	104	107	30.66
21	20-Dec-08	24	brine KC	177	10630	3034.26	249	69	19.65
21	20-Dec-08	24	brine KC	178	6433	1836.25	250	89	25.31
39	29-Dec-08	24	brine KC	321	5410	1544.21	393	58	16.59
39	29-Dec-08	24	brine KC	322	9081	2592.30	394	57	16.19

Brine Data (with 10µM glucose)

station	date	timepoint (hrs)	water type	wick code	wick DPM	wick pM ^{14}C	filter code	filter DPM	filter pM ^{14}C
16	17-Dec-08	0	brine	40	21322	6086.59	109	54	15.38
16	17-Dec-08	0	brine	41	23018	6570.70	110	79	22.41
16	17-Dec-08	6	brine	46	10096	2882.01	115	105	29.99
16	17-Dec-08	6	brine	47	14305	4083.47	116	121	34.43
16	17-Dec-08	12	brine	52	7102	2027.26	121	101	28.76
16	17-Dec-08	12	brine	53	14233	4062.94	122	98	27.99
16	17-Dec-08	18	brine	58	8168	2331.59	127	88	25.17
16	17-Dec-08	18	brine	59	8540	2437.73	128	90	25.69
16	17-Dec-08	24	brine	64	7560	2157.97	133	131	37.51
16	17-Dec-08	24	brine	65	8728	2491.44	134	102	29.14
21	20-Dec-08	0	brine	183	7571	2161.26	255	81	22.99
21	20-Dec-08	0	brine	184	8753	2498.63	256	95	27.14
21	20-Dec-08	6	brine	189	8406	2399.55	261	77	21.95
21	20-Dec-08	6	brine	190	14316	4086.54	262	89	25.43
21	20-Dec-08	12	brine	195	11340	3237.08	267	78	22.31
21	20-Dec-08	12	brine	196	14513	4142.74	268	48	13.58
21	20-Dec-08	18	brine	201	11549	3296.62	273	90	25.59
21	20-Dec-08	18	brine	202	14915	4257.50	274	87	24.79
21	20-Dec-08	24	brine	207	13626	3889.69	279	88	25.13
21	20-Dec-08	24	brine	208	14329	4090.37	280	87	24.75
39	29-Dec-08	0	brine	327	2734	780.51	399	99	28.13
39	29-Dec-08	0	brine	328	3083	880.10	400	85	24.31
39	29-Dec-08	6	brine	333	10950	3125.63	405	75	21.46
39	29-Dec-08	6	brine	334	12171	3474.43	406	98	28.04
39	29-Dec-08	12	brine	339	11327	3233.37	411	113	32.34
39	29-Dec-08	12	brine	340	10929	3119.67	412	154	43.89
39	29-Dec-08	18	brine	345	10609	3028.54	417	83	23.68
39	29-Dec-08	18	brine	346	12415	3544.06	418	75	21.53
39	29-Dec-08	24	brine	351	9413	2687.03	423	123	35.12
39	29-Dec-08	24	brine	352	9210	2628.94	424	95	27.22
16	17-Dec-08	24	brine KC	70	9378	2677.06	139	104	29.67
16	17-Dec-08	24	brine KC	71	8118	2317.32	140	115	32.95
21	20-Dec-08	24	brine KC	213	10960	3128.74	285	77	21.93
21	20-Dec-08	24	brine KC	214	8911	2543.60	286	66	18.83
39	29-Dec-08	24	brine KC	357	9969	2845.63	429	98	28.04
39	29-Dec-08	24	brine KC	358	7790	2223.83	430	86	24.48

Melt Data (no additions)

station	date	timepoint (hrs)	water type	wick code	wick DPM	wick pM ^{14}C	filter code	filter DPM	filter pM ^{14}C
16	17-Dec-08	0	melt	3	9407	2685.19	39	104	29.74
16	17-Dec-08	0	melt	4	4738	1352.41	76	85	24.29
16	17-Dec-08	6	melt	9	6923	1976.25	81	76	21.77
16	17-Dec-08	6	melt	10	10944	3124.12	82	112	31.90
16	17-Dec-08	12	melt	15	13785	3935.10	87	102	29.20
16	17-Dec-08	12	melt	16	10258	2928.12	88	125	35.58
16	17-Dec-08	18	melt	21	10228	2919.60	93	126	36.09
16	17-Dec-08	18	melt	22	11299	3225.30	94	112	31.95
16	17-Dec-08	24	melt	27	8713	2487.26	99	127	36.15
16	17-Dec-08	24	melt	28	6973	1990.38	100	110	31.41
21	20-Dec-08	0	melt	149	3975	1134.55	221	51	14.55
21	20-Dec-08	0	melt	150	3484	994.60	222	91	26.03
21	20-Dec-08	6	melt	155	4658	1329.77	227	85	24.15
21	20-Dec-08	6	melt	156	5119	1461.15	228	100	28.49
21	20-Dec-08	12	melt	161	4480	1278.83	233	115	32.79
21	20-Dec-08	12	melt	162	4564	1302.83	234	153	43.55
21	20-Dec-08	18	melt	167	4190	1196.10	239	98	28.08
21	20-Dec-08	18	melt	168	5572	1590.67	240	151	43.14
21	20-Dec-08	24	melt	173	5541	1581.75	245	138	39.35
21	20-Dec-08	24	melt	174	4562	1302.21	246	132	37.54
39	29-Dec-08	0	melt	293	9435	2693.35	365	120	34.23
39	29-Dec-08	0	melt	294	7039	2009.28	366	113	32.30
39	29-Dec-08	6	melt	299	10242	2923.51	371	65	18.53
39	29-Dec-08	6	melt	300	11318	3230.70	372	56	16.04
39	29-Dec-08	12	melt	305	2572	734.23	377	75	21.31
39	29-Dec-08	12	melt	306	2982	851.22	378	85	24.19
39	29-Dec-08	18	melt	311	2461	702.50	383	146	41.78
39	29-Dec-08	18	melt	312	2168	619.00	384	97	27.74
39	29-Dec-08	24	melt	317	2582	736.97	389	65	18.47
39	29-Dec-08	24	melt	318	3692	1053.76	390	77	21.88
16	17-Dec-08	24	melt KC	33	6552	1870.22	105	69	19.58
16	17-Dec-08	24	melt KC	34	7117	2031.62	106	95	27.08
21	20-Dec-08	24	melt KC	179	3440	982.08	251	49	13.95
21	20-Dec-08	24	melt KC	180	4082	1165.32	252	67	19.23
39	29-Dec-08	24	melt KC	323	2785	794.97	395	89	25.39
39	29-Dec-08	24	melt KC	324	2794	797.48	396	79	22.60

Ice Core Melt Data (with 10µM glucose)

station	date	timepoint (hrs)	water type	wick code	wick DPM	wick pM ^{14}C	filter code	filter DPM	filter pM ^{14}C
16	17-Dec-08	0	melt	42	7583	2164.50	111	116	33.03
16	17-Dec-08	0	melt	43	6952	1984.44	112	103	29.30
16	17-Dec-08	6	melt	48	7247	2068.71	117	112	31.99
16	17-Dec-08	6	melt	49	7560	2158.00	118	132	37.63
16	17-Dec-08	12	melt	54	13638	3892.92	123	99	28.14
16	17-Dec-08	12	melt	55	8587	2451.21	124	108	30.75
16	17-Dec-08	18	melt	60	10112	2886.55	129	134	38.16
16	17-Dec-08	18	melt	61	10568	3016.68	130	138	39.43
16	17-Dec-08	24	melt	66	7410	2115.29	135	141	40.24
16	17-Dec-08	24	melt	67	8587	2451.13	136	108	30.73
21	20-Dec-08	0	melt	185	4198	1198.46	257	90	25.65
21	20-Dec-08	0	melt	186	4269	1218.49	258	102	29.14
21	20-Dec-08	6	melt	191	5244	1497.02	263	89	25.33
21	20-Dec-08	6	melt	192	5575	1591.53	264	83	23.63
21	20-Dec-08	12	melt	197	4980	1421.48	269	115	32.82
21	20-Dec-08	12	melt	198	4516	1289.12	270	99	28.39
21	20-Dec-08	18	melt	203	4880	1392.97	275	129	36.96
21	20-Dec-08	18	melt	204	5875	1677.18	276	107	30.66
21	20-Dec-08	24	melt	209	5921	1690.30	281	147	41.82
21	20-Dec-08	24	melt	210	4137	1180.95	282	136	38.90
39	29-Dec-08	0	melt	329	11033	3149.36	401	52	14.82
39	29-Dec-08	0	melt	330	10633	3035.33	402	87	24.93
39	29-Dec-08	6	melt	335	2295	654.99	407	109	31.14
39	29-Dec-08	6	melt	336	3629	1036.01	408	91	25.86
39	29-Dec-08	12	melt	341	2782	794.14	413	91	25.85
39	29-Dec-08	12	melt	342	3335	952.03	414	71	20.36
39	29-Dec-08	18	melt	347	1667	475.99	419	88	25.03
39	29-Dec-08	18	melt	348	2145	612.26	420	87	24.81
39	29-Dec-08	24	melt	353	3821	1090.71	425	128	36.40
39	29-Dec-08	24	melt	354	3974	1134.29	426	168	48.02
16	17-Dec-08	24	melt KC	72	5953	1699.20	141	75	21.49
16	17-Dec-08	24	melt KC	73	5485	1565.78	142	82	23.37
21	20-Dec-08	24	melt KC	215	4894	1397.05	287	96	27.40
21	20-Dec-08	24	melt KC	216	3225	920.47	288	65	18.62
39	29-Dec-08	24	melt KC	359	2664	760.44	431	83	23.69
39	29-Dec-08	24	melt KC	360	3001	856.76	432	59	16.85

Under-Ice Seawater Data (no additions)

station	date	timepoint (hrs)	water type	wick code	wick DPM	wick pM ^{14}C	filter code	filter DPM	filter pM ^{14}C
16	17-Dec-08	0	under ice	5	14502	4139.65	77	104	29.56
16	17-Dec-08	0	under ice	6	17267	4928.97	78	92	26.29
16	17-Dec-08	6	under ice	11	16115	4600.03	83	114	32.52
16	17-Dec-08	6	under ice	12	7989	2280.46	84	95	27.17
16	17-Dec-08	12	under ice	17	9142	2609.50	89	99	28.22
16	17-Dec-08	12	under ice	18	14233	4062.87	90	110	31.31
16	17-Dec-08	18	under ice	23	12159	3470.75	95	86	24.44
16	17-Dec-08	18	under ice	24	6786	1937.15	96	59	16.90
16	17-Dec-08	24	under ice	29	8684	2478.87	101	84	23.87
16	17-Dec-08	24	under ice	30	7537	2151.52	102	86	24.47
21	20-Dec-08	0	under ice	151	10912	3114.96	223	109	31.17
21	20-Dec-08	0	under ice	152	7785	2222.15	224	84	24.11
21	20-Dec-08	6	under ice	157	11229	3205.28	229	104	29.78
21	20-Dec-08	6	under ice	158	10213	2915.39	230	83	23.59
21	20-Dec-08	12	under ice	163	11292	3223.50	235	116	33.09
21	20-Dec-08	12	under ice	164	9869	2817.21	236	102	29.13
21	20-Dec-08	18	under ice	169	12085	3449.61	241	100	28.43
21	20-Dec-08	18	under ice	170	10155	2898.94	242	101	28.87
21	20-Dec-08	24	under ice	175	10331	2949.02	247	93	26.42
21	20-Dec-08	24	under ice	176	8696	2482.20	248	99	28.33
39	29-Dec-08	0	under ice	295	8185	2336.40	367	137	39.14
39	29-Dec-08	0	under ice	296	6656	1899.98	368	70	19.95
39	29-Dec-08	6	under ice	301	7738	2208.74	373	54	15.28
39	29-Dec-08	6	under ice	302	12351	3525.70	374	62	17.56
39	29-Dec-08	12	under ice	307	11060	3157.11	379	111	31.65
39	29-Dec-08	12	under ice	308	11431	3263.00	380	82	23.38
39	29-Dec-08	18	under ice	313	9557	2728.00	385	69	19.68
39	29-Dec-08	18	under ice	314	10730	3063.02	386	67	19.02
39	29-Dec-08	24	under ice	319	10374	2961.37	391	77	22.10
39	29-Dec-08	24	under ice	320	10782	3077.89	392	80	22.95
16	17-Dec-08	24	under ice KC	35	6435	1837.02	107	81	23.12
16	17-Dec-08	24	under ice KC	36	7408	2114.61	108	86	24.42
21	20-Dec-08	24	under ice KC	181	12016	3430.16	253	82	23.34
21	20-Dec-08	24	under ice KC	182	12508	3570.39	254	80	22.85
39	29-Dec-08	24	under ice KC	325	5739	1638.10	397	65	18.55
39	29-Dec-08	24	under ice KC	326	5298	1512.36	398	49	14.11

Under-Ice Seawater Data (with 10µM glucose)

station	date	timepoint (hrs)	water type	wick code	wick DPM	wick pM ^{14}C	filter code	filter DPM	filter pM ^{14}C
16	17-Dec-08	0	under ice	44	14358	4098.57	113	90	25.59
16	17-Dec-08	0	under ice	45	16438	4692.46	114	106	30.18
16	17-Dec-08	6	under ice	50	8015	2287.89	119	63	18.00
16	17-Dec-08	6	under ice	51	8262	2358.56	120	74	21.19
16	17-Dec-08	12	under ice	56	10440	2980.25	125	98	28.01
16	17-Dec-08	12	under ice	57	8467	2417.00	126	101	28.81
16	17-Dec-08	18	under ice	62	9715	2773.28	131	71	20.17
16	17-Dec-08	18	under ice	63	6627	1891.75	132	81	23.13
16	17-Dec-08	24	under ice	68	7224	2062.21	137	92	26.37
16	17-Dec-08	24	under ice	69	12607	3598.69	138	107	30.48
21	20-Dec-08	0	under ice	187	7375	2105.38	259	103	29.53
21	20-Dec-08	0	under ice	188	11112	3171.87	260	116	32.98
21	20-Dec-08	6	under ice	193	12175	3475.41	265	75	21.51
21	20-Dec-08	6	under ice	194	13361	3814.04	266	71	20.19
21	20-Dec-08	12	under ice	199	7598	2168.92	271	94	26.88
21	20-Dec-08	12	under ice	200	13348	3810.38	272	74	21.25
21	20-Dec-08	18	under ice	205	9004	2570.26	277	107	30.44
21	20-Dec-08	18	under ice	206	12095	3452.52	278	68	19.30
21	20-Dec-08	24	under ice	211	10538	3008.11	283	92	26.38
21	20-Dec-08	24	under ice	212	10203	2912.42	284	93	26.55
39	29-Dec-08	0	under ice	331	10117	2888.02	403	73	20.81
39	29-Dec-08	0	under ice	332	7530	2149.47	404	53	15.11
39	29-Dec-08	6	under ice	337	8813	2515.81	409	76	21.73
39	29-Dec-08	6	under ice	338	11766	3358.64	410	138	39.50
39	29-Dec-08	12	under ice	343	6548	1869.26	415	77	21.85
39	29-Dec-08	12	under ice	344	7426	2119.94	416	74	21.12
39	29-Dec-08	18	under ice	349	8814	2516.03	421	105	30.02
39	29-Dec-08	18	under ice	350	7330	2092.26	422	93	26.45
39	29-Dec-08	24	under ice	355	11084	3163.99	427	163	46.53
39	29-Dec-08	24	under ice	356	10872	3103.44	428	128	36.56
16	17-Dec-08	24	under ice KC	74	8381	2392.49	143	108	30.93
16	17-Dec-08	24	under ice KC	75	10601	3026.04	144	97	27.74
21	20-Dec-08	24	under ice KC	217	9675	2761.80	289	93	26.62
21	20-Dec-08	24	under ice KC	218	12257	3498.90	290	88	25.14
39	29-Dec-08	24	under ice KC	361	4061	1159.13	433	60	17.12
39	29-Dec-08	24	under ice KC	362	4064	1160.09	434	50	14.21

APPENDIX B- Liquid Scintillation Counter ^{14}C Output and Rate Calculations for Station 41 (organized by water type).

Station 41 Brine Data (no additions)

station	date	timepoint (hrs)	water type	pM MeBr added	wick code	wick DPM	pM ^{14}C on wick	filter code	filter DPM	pM ^{14}C on filter
41	1-Jan-09	0	brine	4750	477	1175	335.43	597	75	21.50
41	1-Jan-09	0	brine	4750	478	1053	300.68	598	119	33.98
41	1-Jan-09	0	brine	23750	479	6475	1848.36	599	132	37.59
41	1-Jan-09	0	brine	23750	480	7753	2213.10	600	133	37.85
41	1-Jan-09	0	brine	47500	481	8382	2392.69	601	161	45.83
41	1-Jan-09	0	brine	47500	482	7598	2169.00	602	178	50.87
41	1-Jan-09	0	brine	237500	483	36030	10284.93	603	861	245.70
41	1-Jan-09	0	brine	237500	484	37798	10789.67	604	635	181.39
41	1-Jan-09	0	brine	475000	485	50843	14513.51	605	984	280.95
41	1-Jan-09	0	brine	475000	486	53232	15195.37	606	1091	311.48
41	1-Jan-09	24	brine	4750	487	1350	385.43	607	59	16.96
41	1-Jan-09	24	brine	4750	488	1003	286.21	608	65	18.53
41	1-Jan-09	24	brine	23750	489	5633	1607.88	609	152	43.43
41	1-Jan-09	24	brine	23750	490	8030	2292.23	610	148	42.31
41	1-Jan-09	24	brine	47500	491	11262	3214.75	611	209	59.74
41	1-Jan-09	24	brine	47500	492	11883	3392.03	612	197	56.18
41	1-Jan-09	24	brine	237500	493	67905	19383.96	613	981	280.10
41	1-Jan-09	24	brine	237500	494	53890	15383.14	614	916	261.34
41	1-Jan-09	24	brine	475000	495	80830	23073.48	615	1185	338.28
41	1-Jan-09	24	brine	475000	496	85604	24436.24	616	1280	365.44

Station 41 Brine Rate Calculations (no additions)

water type	pM added	average of wick t0s (pM)	wick pM/day	wick pM/hr	average of filter t0s (pM)	filter pM/day	filter pM/hr
brine	4750	318.05	67.37	2.81	27.74	-10.78	-0.449
brine	4750	318.05	-31.84	-1.33	27.74	-9.21	-0.384
brine	23750	2030.73	-422.85	-17.62	37.72	5.71	0.238
brine	23750	2030.73	261.50	10.90	37.72	4.59	0.191
brine	47500	2280.85	933.91	38.91	48.35	11.39	0.474
brine	47500	2280.85	1111.19	46.30	48.35	7.83	0.326
brine	237500	10537.30	8846.66	368.61	213.54	66.56	2.773
brine	237500	10537.30	4845.84	201.91	213.54	47.80	1.992
brine	475000	14854.44	8219.04	342.46	296.21	42.07	1.753
brine	475000	14854.44	9581.81	399.24	296.21	69.23	2.884

Station 41 Brine Data (with 10µM glucose)

station	date	timepoint (hrs)	water type	pM MeBr added	wick code	wick DPM	pM ^{14}C on wick	filter code	filter DPM	pM ^{14}C on filter
41	1-Jan-09	0	brine	4750	537	1131	322.88	657	60	17.15
41	1-Jan-09	0	brine	4750	538	1039	296.60	658	73	20.95
41	1-Jan-09	0	brine	23750	539	7430	2120.80	659	102	28.99
41	1-Jan-09	0	brine	23750	540	6063	1730.61	660	99	28.23
41	1-Jan-09	0	brine	47500	541	8357	2385.58	661	164	46.87
41	1-Jan-09	0	brine	47500	542	6953	1984.80	662	178	50.77
41	1-Jan-09	0	brine	237500	543	30210	8623.68	663	1021	291.53
41	1-Jan-09	0	brine	237500	544	32938	9402.37	664	699	199.55
41	1-Jan-09	0	brine	475000	545	52674	15036.04	665	1061	302.89
41	1-Jan-09	0	brine	475000	546	58359	16658.87	666	1392	397.46
41	1-Jan-09	24	brine	4750	547	1285	366.85	667	49	14.01
41	1-Jan-09	24	brine	4750	548	1285	366.88	668	93	26.60
41	1-Jan-09	24	brine	23750	549	7897	2254.13	669	163	46.53
41	1-Jan-09	24	brine	23750	550	8212	2344.21	670	151	43.04
41	1-Jan-09	24	brine	47500	551	11157	3184.84	671	196	55.84
41	1-Jan-09	24	brine	47500	552	11414	3258.19	672	262	74.77
41	1-Jan-09	24	brine	237500	553	58781	16779.34	673	999	285.16
41	1-Jan-09	24	brine	237500	554	42457	12119.67	674	972	277.60
41	1-Jan-09	24	brine	475000	555	78127	22301.73	675	1290	368.28
41	1-Jan-09	24	brine	475000	556	74493	21264.48	676	1396	398.61

Station 41 Brine Rate Calculations (with 10µM glucose)

water type	pM added	average of wick t0s (pM)	wick pM/day	wick pM/hr	average of filter t0s (pM)	filter pM/day	filter pM/hr
brine	4750	309.74	57.11	2.38	19.05	-5.04	-0.210
brine	4750	309.74	57.14	2.38	19.05	7.55	0.314
brine	23750	1925.71	328.43	13.68	28.61	17.92	0.747
brine	23750	1925.71	418.50	17.44	28.61	14.44	0.601
brine	47500	2185.19	999.65	41.65	48.82	7.02	0.292
brine	47500	2185.19	1073.00	44.71	48.82	25.95	1.081
brine	237500	9013.03	7766.31	323.60	245.54	39.62	1.651
brine	237500	9013.03	3106.64	129.44	245.54	32.06	1.336
brine	475000	15847.45	6454.28	268.93	350.17	18.11	0.754
brine	475000	15847.45	5417.03	225.71	350.17	48.43	2.018

Station 41 Ice Core Melt Data (no additions)

station	date	timepoint (hrs)	water type	pM MeBr added	wick code	wick DPM	pM ^{14}C on wick	filter code	filter DPM	pM ^{14}C on filter
41	1-Jan-09	0	melt	4750	497	808	230.77	617	42	12.10
41	1-Jan-09	0	melt	4750	498	938	267.87	618	50	14.31
41	1-Jan-09	0	melt	23750	499	5087	1452.12	619	135	38.51
41	1-Jan-09	0	melt	23750	500	4093	1168.50	620	121	34.56
41	1-Jan-09	0	melt	47500	501	4782	1364.98	621	157	44.77
41	1-Jan-09	0	melt	47500	502	6253	1784.85	622	155	44.13
41	1-Jan-09	0	melt	237500	503	255154	72835.22	623	1431	408.58
41	1-Jan-09	0	melt	237500	504	285410	81471.93	624	1209	345.15
41	1-Jan-09	0	melt	475000	505	347629	99232.96	625	1700	485.14
41	1-Jan-09	0	melt	475000	506	394518	112617.61	626	1885	538.03
41	1-Jan-09	24	melt	4750	507	745	212.70	627	82	23.46
41	1-Jan-09	24	melt	4750	508	818	233.62	628	79	22.48
41	1-Jan-09	24	melt	23750	509	3730	1064.80	629	135	38.61
41	1-Jan-09	24	melt	23750	510	3433	980.09	630	131	37.41
41	1-Jan-09	24	melt	47500	511	6273	1790.67	631	173	49.40
41	1-Jan-09	24	melt	47500	512	6843	1953.48	632	249	71.04
41	1-Jan-09	24	melt	237500	513	288451	82340.12	633	1410	402.60
41	1-Jan-09	24	melt	237500	514	270373	77179.53	634	1488	424.63
41	1-Jan-09	24	melt	475000	515	369166	105380.75	635	1963	560.28
41	1-Jan-09	24	melt	475000	516	421307	120264.81	636	1496	427.04

Station 41 Ice Core Melt Rate Calculations (no additions)

water type	pM added	average of wick t0s (pM)	wick pM/day	wick pM/hr	average of filter t0s (pM)	filter pM/day	filter pM/hr
melt	4750	249.32	176.07	7.34	13.21	33.71	1.405
melt	4750	249.32	217.93	9.08	13.21	31.75	1.323
melt	23750	1310.31	819.28	34.14	36.54	40.68	1.695
melt	23750	1310.31	649.88	27.08	36.54	38.28	1.595
melt	47500	1574.91	2006.42	83.60	44.45	54.35	2.265
melt	47500	1574.91	2332.05	97.17	44.45	97.62	4.067
melt	237500	77153.58	87526.66	3646.94	376.86	428.34	17.848
melt	237500	77153.58	77205.47	3216.89	376.86	472.41	19.684
melt	475000	105925.29	104836.21	4368.18	511.58	608.97	25.374
melt	475000	105925.29	134604.34	5608.51	511.58	342.50	14.271

*Melt rates were doubled to adjust for the 1:1 seawater dilution of ice samples

Station 41 Ice Core Melt Data (with 10µM glucose)

station	date	timepoint (hrs)	water type	pM MeBr added	wick code	wick DPM	pM ^{14}C on wick	filter code	filter DPM	pM ^{14}C on filter
41	1-Jan-09	0	melt	4750	557	871	248.49	677	46	13.21
41	1-Jan-09	0	melt	4750	558	833	237.68	678	54	15.45
41	1-Jan-09	0	melt	23750	559	4801	1370.48	679	97	27.82
41	1-Jan-09	0	melt	23750	560	4343	1239.76	680	124	35.30
41	1-Jan-09	0	melt	47500	561	4470	1276.04	681	130	36.99
41	1-Jan-09	0	melt	47500	562	5346	1526.15	682	130	37.07
41	1-Jan-09	0	melt	237500	563	220723	63006.85	683	1611	459.89
41	1-Jan-09	0	melt	237500	564	229928	65634.42	684	1045	298.17
41	1-Jan-09	0	melt	475000	565	302124	86243.05	685	2240	639.36
41	1-Jan-09	0	melt	475000	566	310795	88718.41	686	1953	557.60
41	1-Jan-09	24	melt	4750	567	994	283.86	687	69	19.69
41	1-Jan-09	24	melt	4750	568	984	280.87	688	70	20.00
41	1-Jan-09	24	melt	23750	569	4064	1159.97	689	149	42.47
41	1-Jan-09	24	melt	23750	570	3465	989.07	690	112	31.87
41	1-Jan-09	24	melt	47500	571	8287	2365.59	691	159	45.49
41	1-Jan-09	24	melt	47500	572	5889	1680.99	692	161	45.87
41	1-Jan-09	24	melt	237500	573	323235	92269.43	693	1126	321.55
41	1-Jan-09	24	melt	237500	574	302044	86220.41	694	1609	459.17
41	1-Jan-09	24	melt	475000	575	424787	121258.03	695	2276	649.81
41	1-Jan-09	24	melt	475000	576	447515	127745.88	696	1835	523.69

Station 41 Ice Core Melt Rate Calculations (with 10µM glucose)

water type	pM added	average of wick t0s (pM)	wick pM/day	wick pM/hr	average of filter t0s (pM)	filter pM/day	filter pM/hr
melt	4750	243.09	324.64	13.53	14.33	25.05	1.044
melt	4750	243.09	318.65	13.28	14.33	25.68	1.070
melt	23750	1305.12	1014.83	42.28	31.56	53.37	2.224
melt	23750	1305.12	673.02	28.04	31.56	32.18	1.341
melt	47500	1401.10	3330.08	138.75	37.03	53.95	2.248
melt	47500	1401.10	1960.88	81.70	37.03	54.72	2.280
melt	237500	64320.63	120218.23	5009.09	379.03	264.07	11.003
melt	237500	64320.63	108120.19	4505.01	379.03	539.32	22.471
melt	475000	87480.73	155035.33	6459.81	598.48	701.14	29.214
melt	475000	87480.73	168011.03	7000.46	598.48	448.90	18.704

*Melt rates were doubled to adjust for the 1:1 seawater dilution of ice samples

Station 41 Under-Ice Seawater Data (no additions)

station	date	timepoint (hrs)	water type	pM MeBr added	wick code	wick DPM	pM ^{14}C on wick	filter code	filter DPM	pM ^{14}C on filter
41	1-Jan-09	0	under ice	4750	517	1512	431.57	637	48	13.70
41	1-Jan-09	0	under ice	4750	518	1472	420.29	638	56	16.09
41	1-Jan-09	0	under ice	23750	519	13590	3879.23	639	90	25.63
41	1-Jan-09	0	under ice	23750	520	12926	3689.74	640	109	31.17
41	1-Jan-09	0	under ice	47500	521	14270	4073.40	641	144	41.19
41	1-Jan-09	0	under ice	47500	522	17363	4956.43	642	165	47.15
41	1-Jan-09	0	under ice	237500	523	105770	30192.60	643	652	186.17
41	1-Jan-09	0	under ice	237500	524	103241	29470.65	644	823	234.89
41	1-Jan-09	0	under ice	475000	525	174271	49746.78	645	907	258.81
41	1-Jan-09	0	under ice	475000	526	180199	51439.02	646	846	241.37
41	1-Jan-09	24	under ice	4750	527	1583	451.88	647	51	14.69
41	1-Jan-09	24	under ice	4750	528	1707	487.35	648	57	16.33
41	1-Jan-09	24	under ice	23750	529	9904	2827.28	649	151	43.20
41	1-Jan-09	24	under ice	23750	530	9028	2577.09	650	120	34.12
41	1-Jan-09	24	under ice	47500	531	18086	5162.63	651	136	38.85
41	1-Jan-09	24	under ice	47500	532	18026	5145.63	652	134	38.31
41	1-Jan-09	24	under ice	237500	533	95128	27154.86	653	688	196.37
41	1-Jan-09	24	under ice	237500	534	98390	28086.03	654	870	248.39
41	1-Jan-09	24	under ice	475000	535	128778	36760.49	655	945	269.65
41	1-Jan-09	24	under ice	475000	536	175003	49955.73	656	912	260.30

Station 41 Under-Ice Seawater Rate Calculations (no additions)

water type	pM added	average of wick t0s (pM)	wick pM/day	wick pM/hr	average of filter t0s (pM)	filter pM/day	filter pM/hr
under ice	4750	425.93	25.95	1.08	14.90	-0.20	-0.009
under ice	4750	425.93	61.42	2.56	14.90	1.44	0.060
under ice	23750	3784.49	-957.20	-39.88	28.40	14.80	0.617
under ice	23750	3784.49	-1207.40	-50.31	28.40	5.72	0.238
under ice	47500	4514.92	647.71	26.99	44.17	-5.31	-0.221
under ice	47500	4514.92	630.72	26.28	44.17	-5.85	-0.244
under ice	237500	29831.62	-2676.76	-111.53	210.53	-14.16	-0.590
under ice	237500	29831.62	-1745.59	-72.73	210.53	37.86	1.578
under ice	475000	50592.90	-13832.41	-576.35	250.09	19.56	0.815
under ice	475000	50592.90	-637.17	-26.55	250.09	10.21	0.425

Station 41 Under-Ice Seawater Data (with 10µM glucose)

station	date	timepoint (hrs)	water type	pM MeBr added	wick code	wick DPM	pM ^{14}C on wick	filter code	filter DPM	pM ^{14}C on filter
41	1-Jan-09	0	under ice	4750	577	1550	442.34	697	56	16.05
41	1-Jan-09	0	under ice	4750	578	1643	469.14	698	45	12.90
41	1-Jan-09	0	under ice	23750	579	8989	2565.96	699	137	39.22
41	1-Jan-09	0	under ice	23750	580	10223	2918.31	700	107	30.42
41	1-Jan-09	0	under ice	47500	581	12099	3453.73	701	114	32.40
41	1-Jan-09	0	under ice	47500	582	12301	3511.52	702	131	37.25
41	1-Jan-09	0	under ice	237500	583	84705	24179.52	703	718	204.92
41	1-Jan-09	0	under ice	237500	584	111612	31860.20	704	942	268.91
41	1-Jan-09	0	under ice	475000	585	190972	54514.13	705	941	268.61
41	1-Jan-09	0	under ice	475000	586	161768	46177.63	706	1052	300.37
41	1-Jan-09	24	under ice	4750	587	2126	606.79	707	58	16.60
41	1-Jan-09	24	under ice	4750	588	1802	514.28	708	47	13.29
41	1-Jan-09	24	under ice	23750	589	11286	3221.68	709	107	30.52
41	1-Jan-09	24	under ice	23750	590	10732	3063.63	710	107	30.46
41	1-Jan-09	24	under ice	47500	591	16280	4647.33	711	167	47.78
41	1-Jan-09	24	under ice	47500	592	17196	4908.60	712	197	56.36
41	1-Jan-09	24	under ice	237500	593	111374	31792.26	713	633	180.66
41	1-Jan-09	24	under ice	237500	594	93756	26763.25	714	528	150.76
41	1-Jan-09	24	under ice	475000	595	155102	44274.90	715	1167	333.24
41	1-Jan-09	24	under ice	475000	596	159810	45618.85	716	1033	294.79

Station 41 Under-Ice Seawater Rate Calculations (with 10µM glucose)

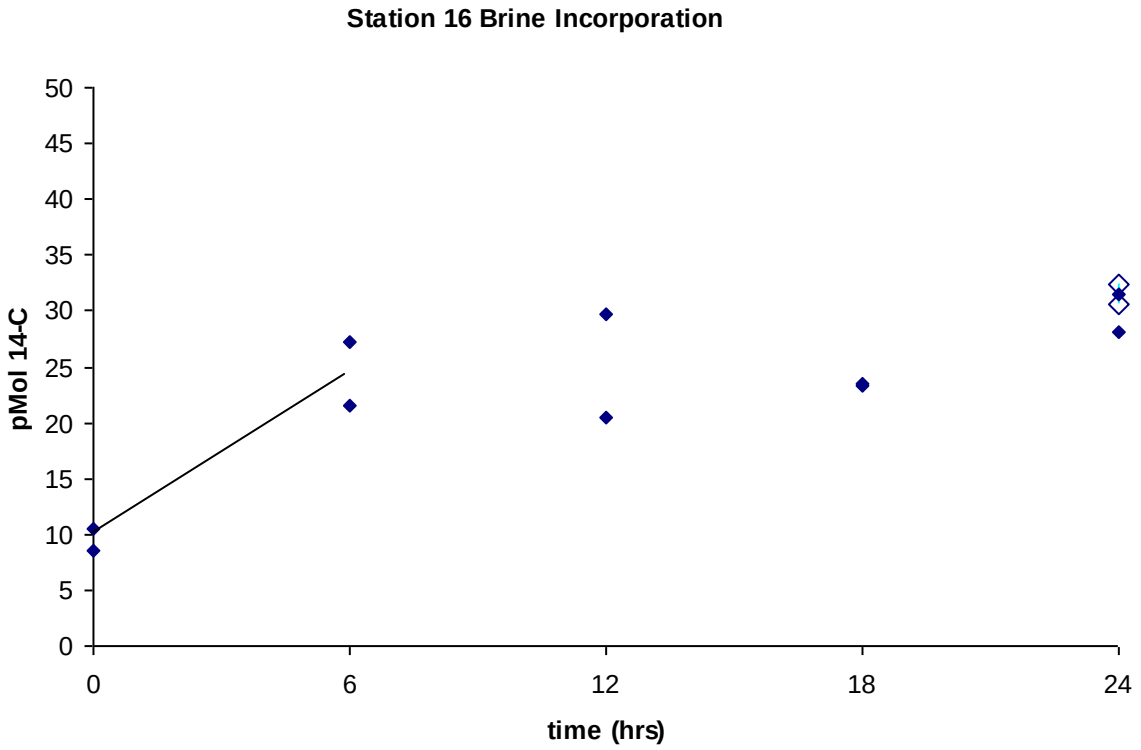
water type	pM added	average of wick t0s (pM)	wick pM/day	wick pM/hr	average of filter t0s (pM)	filter pM/day	filter pM/hr
under ice	4750	455.74	151.06	6.29	14.48	2.13	0.089
under ice	4750	455.74	58.54	2.44	14.48	-1.19	-0.050
under ice	23750	2742.14	479.54	19.98	34.82	-4.30	-0.179
under ice	23750	2742.14	321.50	13.40	34.82	-4.36	-0.182
under ice	47500	3482.62	1164.71	48.53	34.83	12.95	0.540
under ice	47500	3482.62	1425.98	59.42	34.83	21.54	0.897
under ice	237500	28019.86	3772.40	157.18	236.91	-56.25	-2.344
under ice	237500	28019.86	-1256.61	-52.36	236.91	-86.16	-3.590
under ice	475000	50345.88	-6070.98	-252.96	284.49	48.75	2.031
under ice	475000	50345.88	-4727.03	-196.96	284.49	10.30	0.429

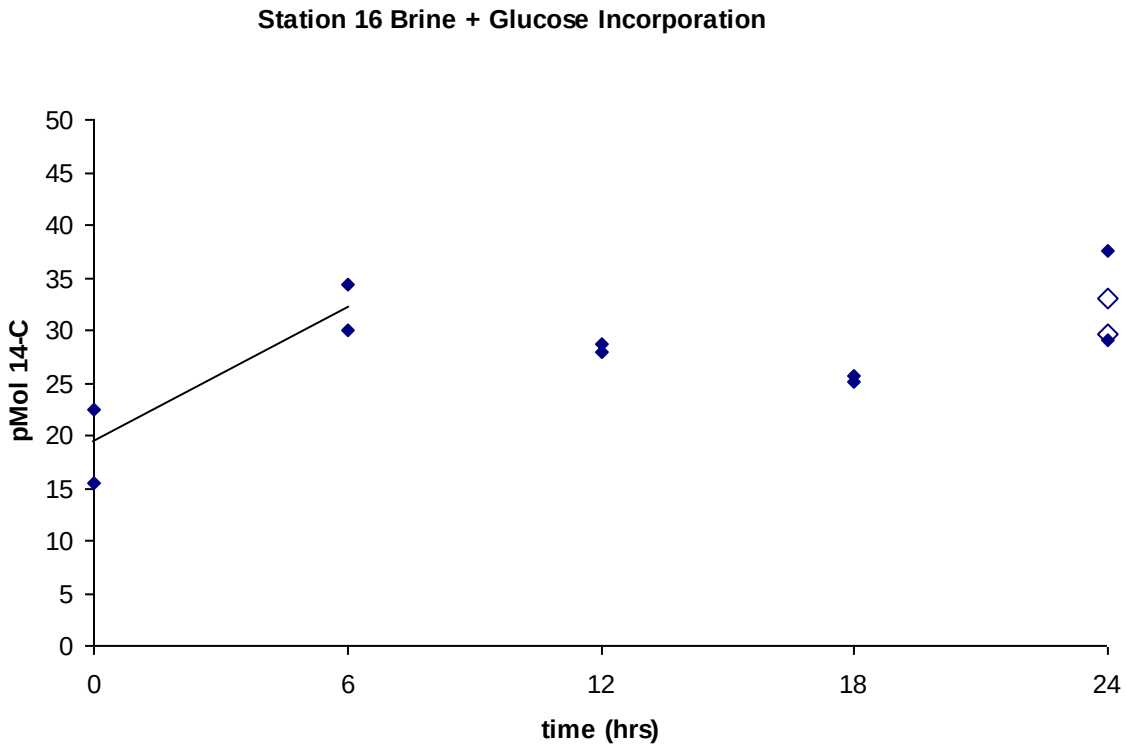
APPENDIX C- Comparative Rate Data for Changing MeBr Concentrations (Station 41 samples)

water type	pM added	Respiration pM·day^{-1}	Respiration rate per conc. day^{-1}	Incorporation pM·day^{-1}	Incorporation rate per conc. day^{-1}
brine	4750	67.37	0.014	no observable rate	no observable rate
brine	4750	no observable rate	no observable rate	no observable rate	no observable rate
brine	23750	no observable rate	no observable rate	5.71	0.00024
brine	23750	261.50	0.011	4.59	0.00019
brine	47500	933.91	0.020	11.39	0.00024
brine	47500	1111.19	0.023	7.83	0.00016
brine	237500	8846.66	0.037	66.56	0.00028
brine	237500	4845.84	0.020	47.80	0.00020
brine	475000	8219.04	0.017	42.07	0.00009
brine	475000	9581.81	0.020	69.23	0.00015
melt	4750	176.07	0.037	33.71	0.00710
melt	4750	217.93	0.046	31.75	0.00668
melt	23750	819.28	0.034	40.68	0.00171
melt	23750	649.88	0.027	38.28	0.00161
melt	47500	2006.42	0.042	54.35	0.00114
melt	47500	2332.05	0.049	97.62	0.00206
melt	237500	87526.66	0.369	428.34	0.00180
melt	237500	77205.47	0.325	472.41	0.00199
melt	475000	104836.21	0.221	608.97	0.00128
melt	475000	134604.34	0.283	342.50	0.00072
under ice	4750	25.95	0.005	0.00	no observable rate
under ice	4750	61.42	0.013	1.44	0.00030
under ice	23750	no observable rate	no observable rate	14.80	0.00062
under ice	23750	no observable rate	no observable rate	5.72	0.00024
under ice	47500	647.71	0.014	0.00	no observable rate
under ice	47500	630.72	0.013	0.00	no observable rate
under ice	237500	no observable rate	no observable rate	0.00	no observable rate
under ice	237500	no observable rate	no observable rate	37.86	0.00016
under ice	475000	no observable rate	no observable rate	19.56	0.00004
under ice	475000	no observable rate	no observable rate	10.21	0.00002

water type	pM added	Respiration pM·day^{-1}	Respiration rate per conc. day^{-1}	Incorporation pM·day^{-1}	Incorporation rate per conc. day^{-1}
brine + glucose	4750	57.11	0.012	no observable rate	no observable rate
brine + glucose	4750	57.14	0.012	7.55	0.00159
brine + glucose	23750	328.43	0.014	17.92	0.00075
brine + glucose	23750	418.50	0.018	14.44	0.00061
brine + glucose	47500	999.65	0.021	7.02	0.00015
brine + glucose	47500	1073.00	0.023	25.95	0.00055
brine + glucose	237500	7766.31	0.033	39.62	0.00017
brine + glucose	237500	3106.64	0.013	32.06	0.00013
brine + glucose	475000	6454.28	0.014	18.11	0.00004
brine + glucose	475000	5417.03	0.011	48.43	0.00010
melt + glucose	4750	324.64	0.068	25.05	0.00527
melt + glucose	4750	318.65	0.067	25.68	0.00541
melt + glucose	23750	1014.83	0.043	53.37	0.00225
melt + glucose	23750	673.02	0.028	32.18	0.00135
melt + glucose	47500	3330.08	0.070	53.95	0.00114
melt + glucose	47500	1960.88	0.041	54.72	0.00115
melt + glucose	237500	120218.23	0.506	264.07	0.00111
melt + glucose	237500	108120.19	0.455	539.32	0.00227
melt + glucose	475000	155035.33	0.326	701.14	0.00148
melt + glucose	475000	168011.03	0.354	448.90	0.00095
under ice + glucose	4750	151.06	0.032	2.13	0.00045
under ice + glucose	4750	58.54	0.012	no observable rate	no observable rate
under ice + glucose	23750	479.54	0.020	no observable rate	no observable rate
under ice + glucose	23750	321.50	0.014	no observable rate	no observable rate
under ice + glucose	47500	1164.71	0.025	12.95	0.00027
under ice + glucose	47500	1425.98	0.030	21.54	0.00045
under ice + glucose	237500	3772.40	0.016	no observable rate	no observable rate
under ice + glucose	237500	no observable rate	no observable rate	no observable rate	no observable rate
under ice + glucose	475000	no observable rate	no observable rate	48.75	0.00010
under ice + glucose	475000	no observable rate	no observable rate	10.30	0.00002

APPENDIX D- Time-course Analysis Graphs for Stations 16, 21 and 39 (organized by water and rate type). Solid and open markers represent live samples and killed controls, respectively. A regression line spans the interval identified for each rate calculation. Straight regression lines represent rates calculated including each intervening data point, while capped (arrow) regression lines represent rates more statistically significant when killed controls were used in place of 0-hr data, with this data reported as the final calculated rate. Graphs without regression lines represent data where no observable, consistent increase (rate) was observed over time. The calculated rates and statistical data for each graph are included in Table 4 of this text.


Station 16 Brine Incorporation
pMol 14-C
50
45
40
35
30
25
20
15
10
5
0
0
6
12
18
24
time (hrs)


Station 16 Brine + Glucose Incorporation
pMol 14-C
50
45
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15
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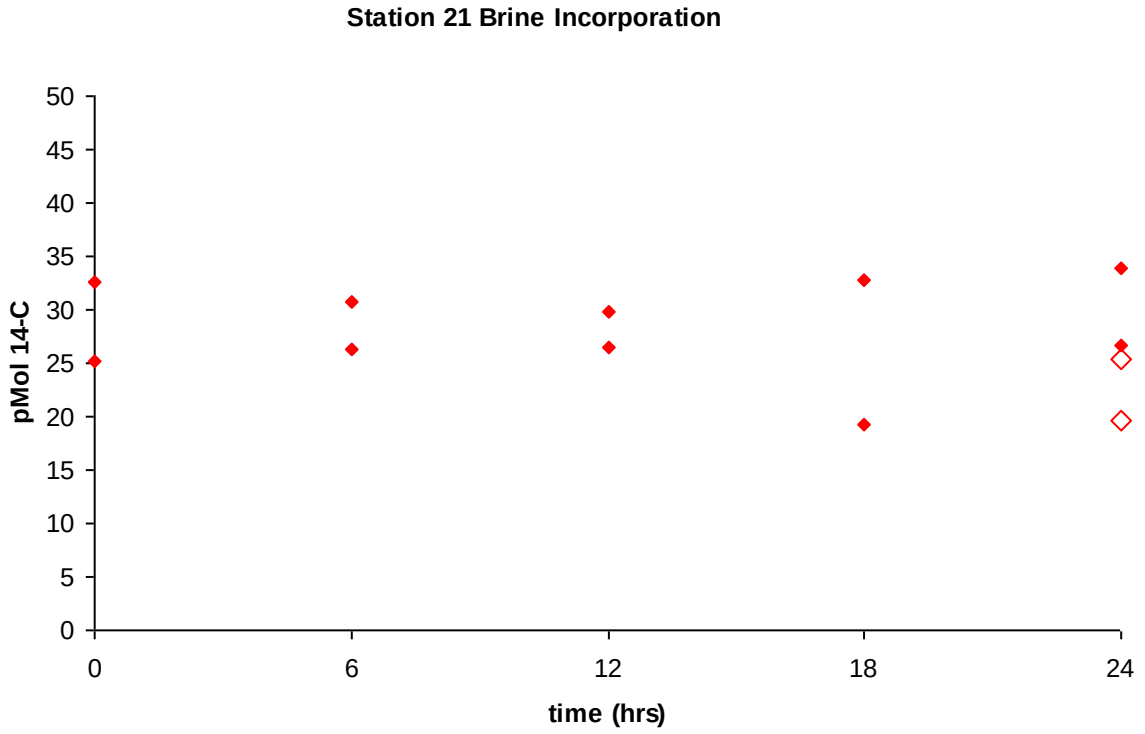
12
18
24
time (hrs)


Station 21 Brine Incorporation
pMol 14-C
50
45
40
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30
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20
15
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0
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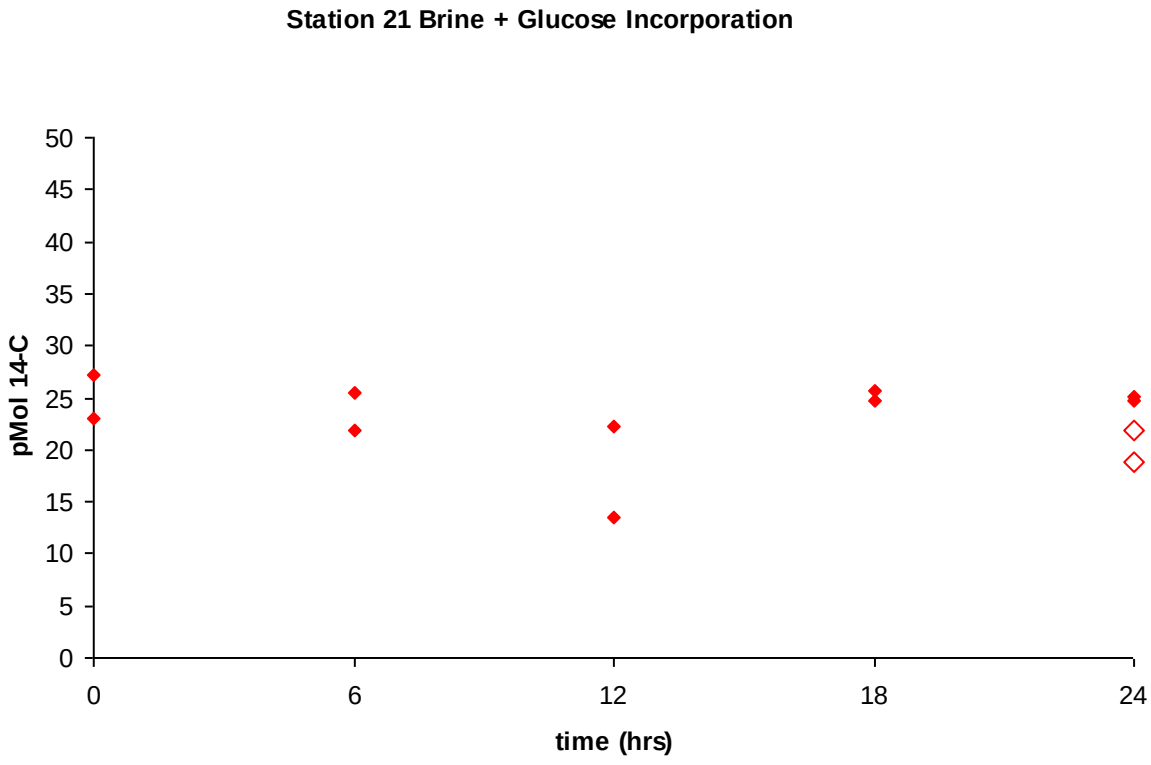
12
18
24
time (hrs)


Station 21 Brine + Glucose Incorporation
pMol 14-C
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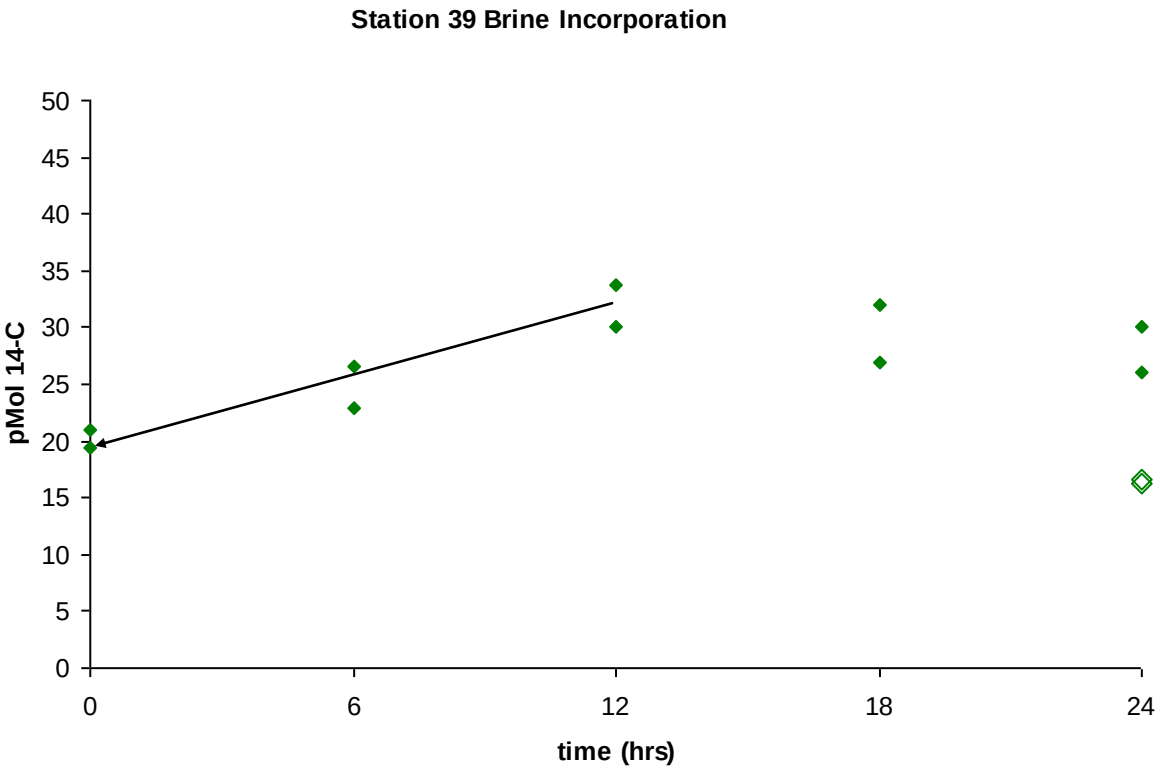
18
24
time (hrs)


Station 39 Brine Incorporation
pMol 14-C
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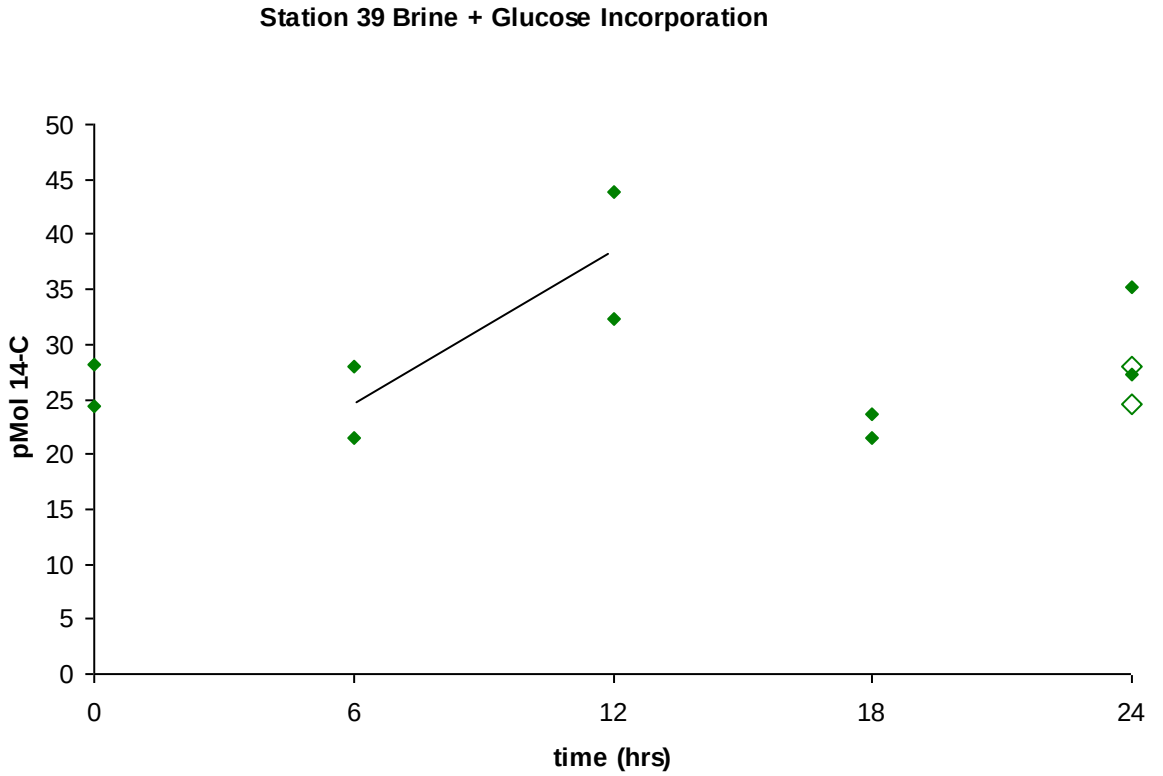
12
18
24
time (hrs)


Station 39 Brine + Glucose Incorporation
pMol 14-C
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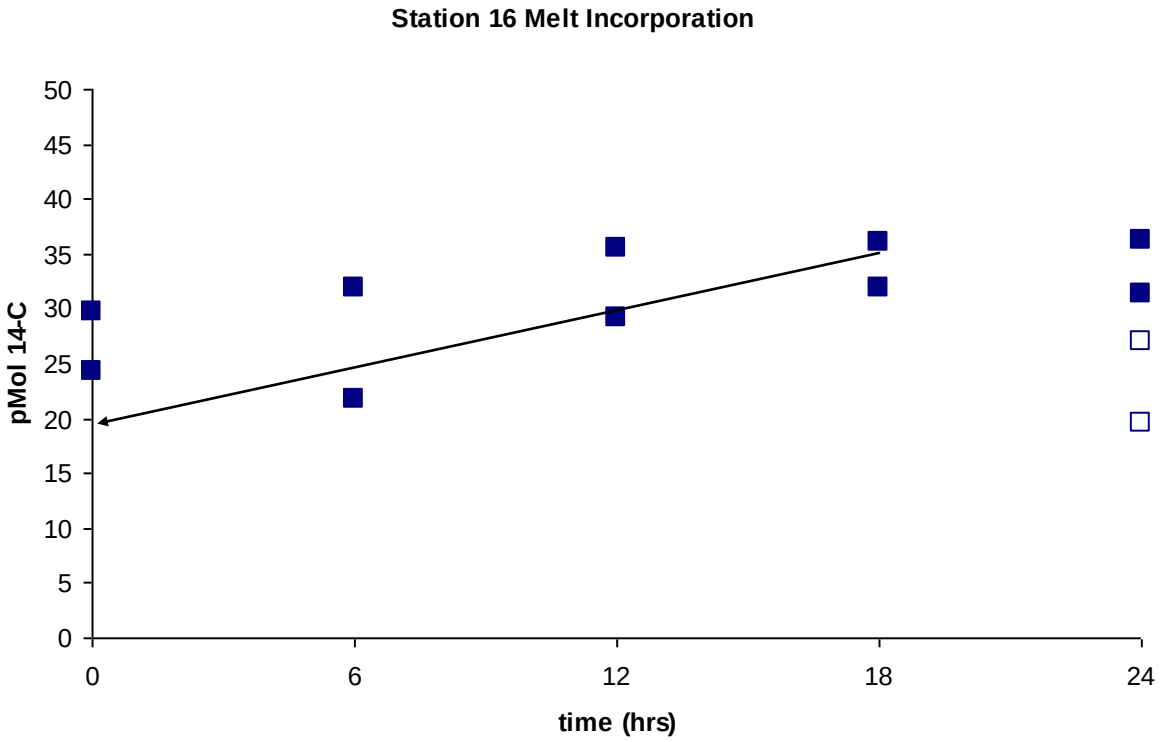
6
12
18
24
time (hrs)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pMol 14-C
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45
40
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30
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12
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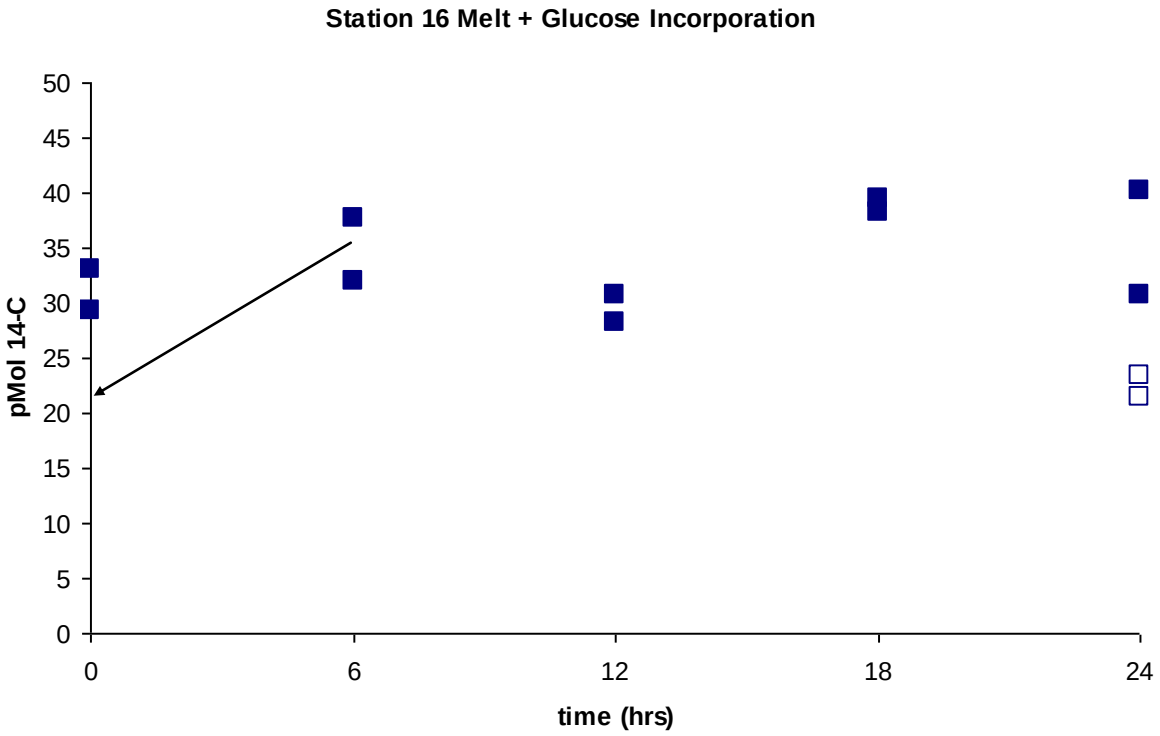
24
time (hrs)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pMol 14-C
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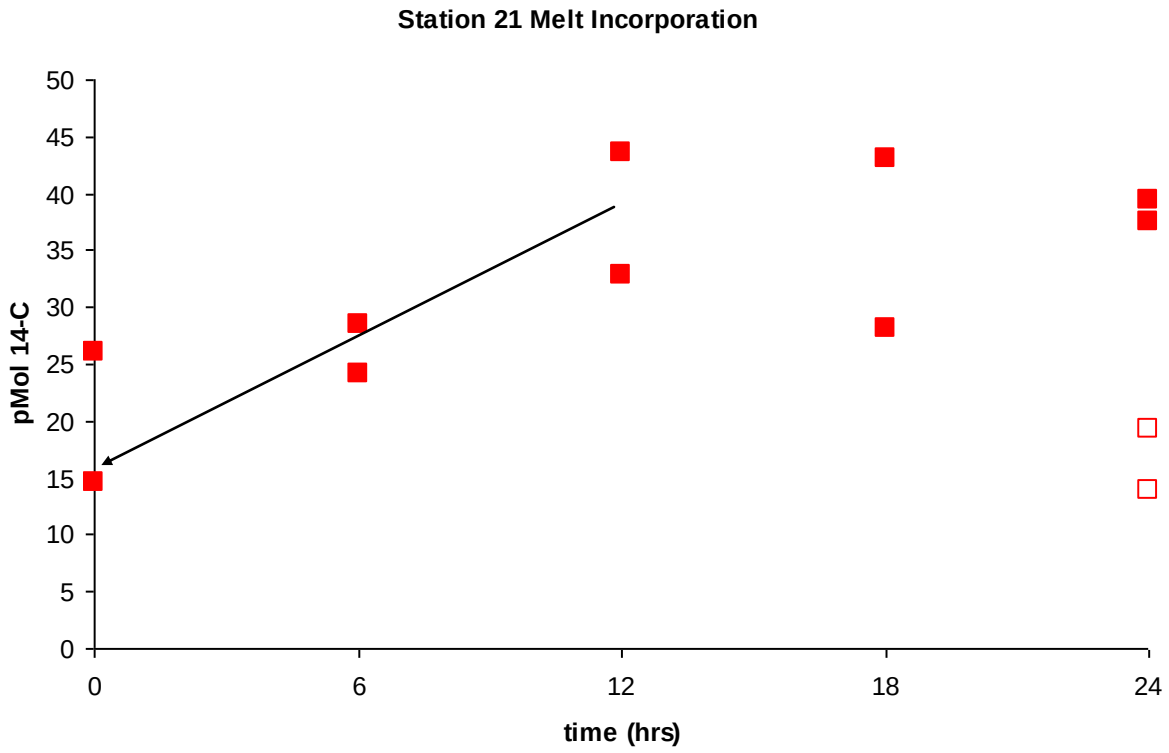
6
12
18
24
time (hrs)


Station 21 Melt Incorporation
pMol 14-C
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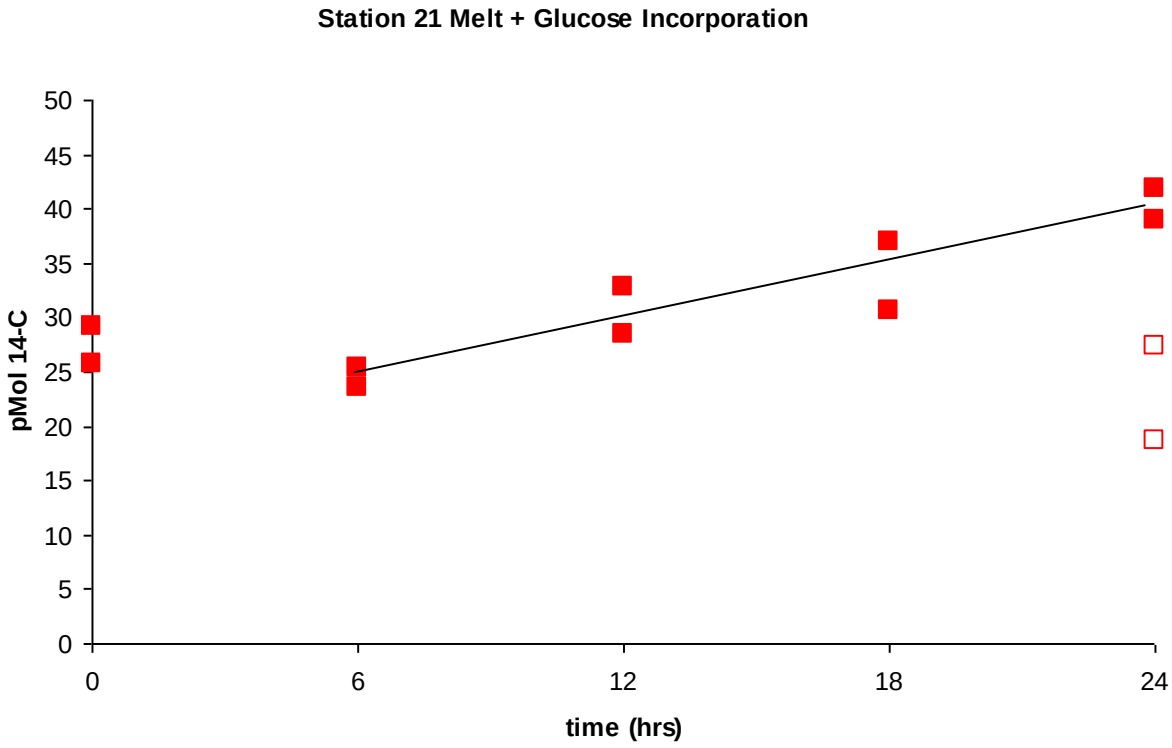
24
time (hrs)


Station 21 Melt + Glucose Incorporation
pMol 14-C
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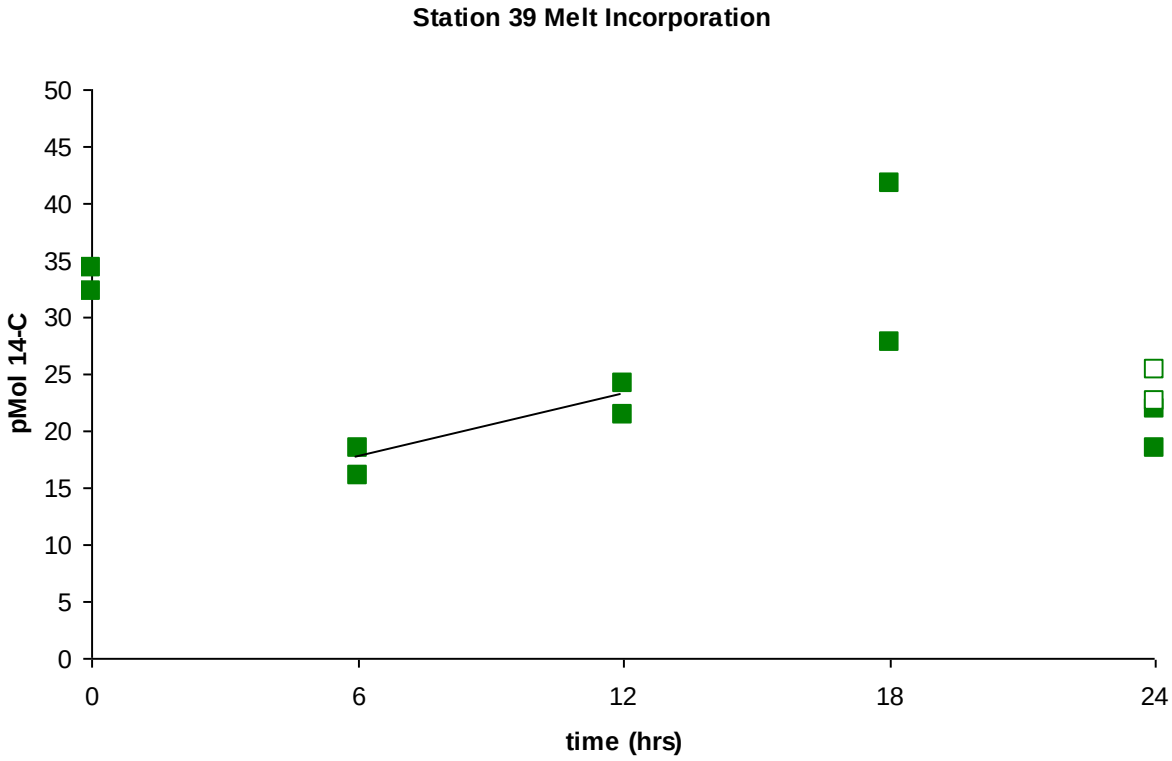
time (hrs)


Station 39 Melt Incorporation
pMol 14-C
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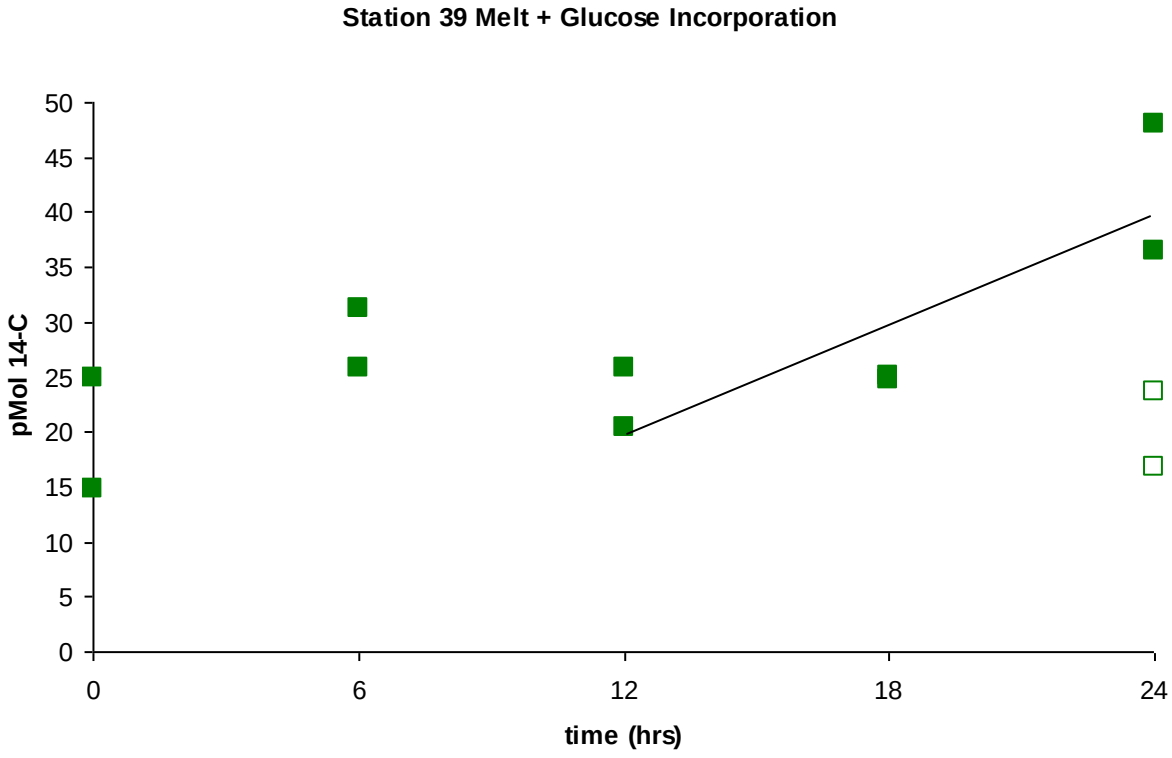
24
time (hrs)


Station 39 Melt + Glucose Incorporation
pMol 14-C
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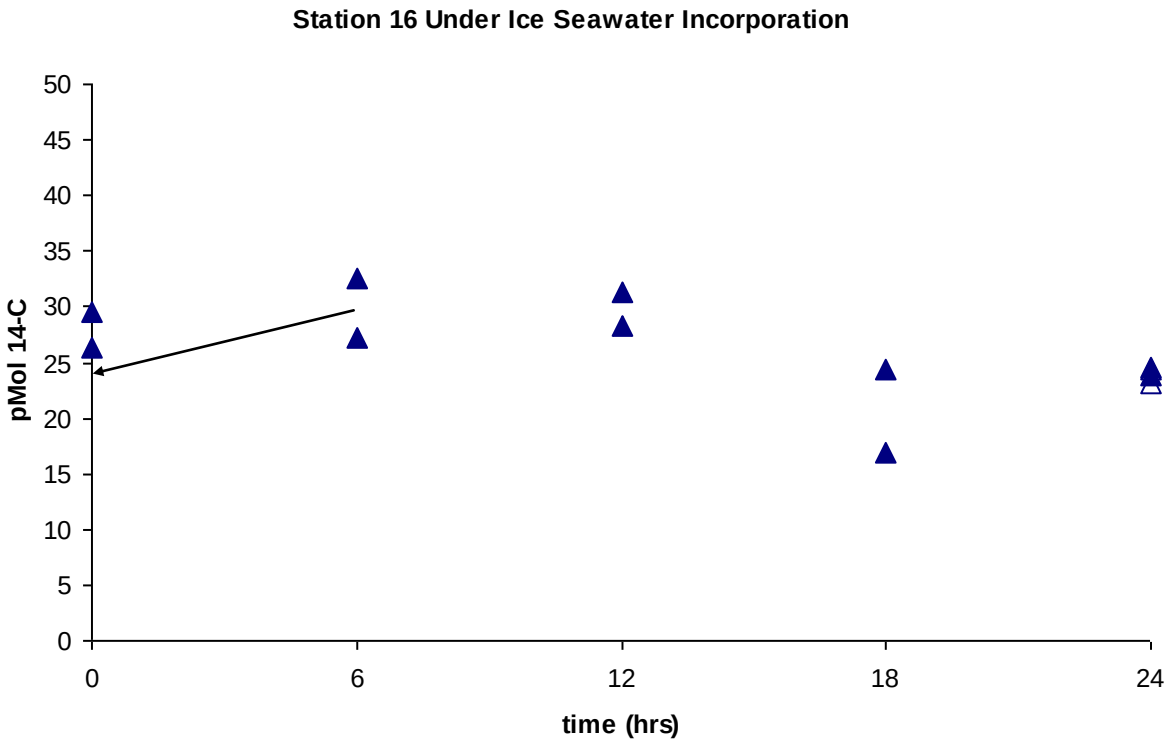
24
time (hrs)


Station 16 Under Ice Seawater Incorporation
pMol 14-C
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45
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30
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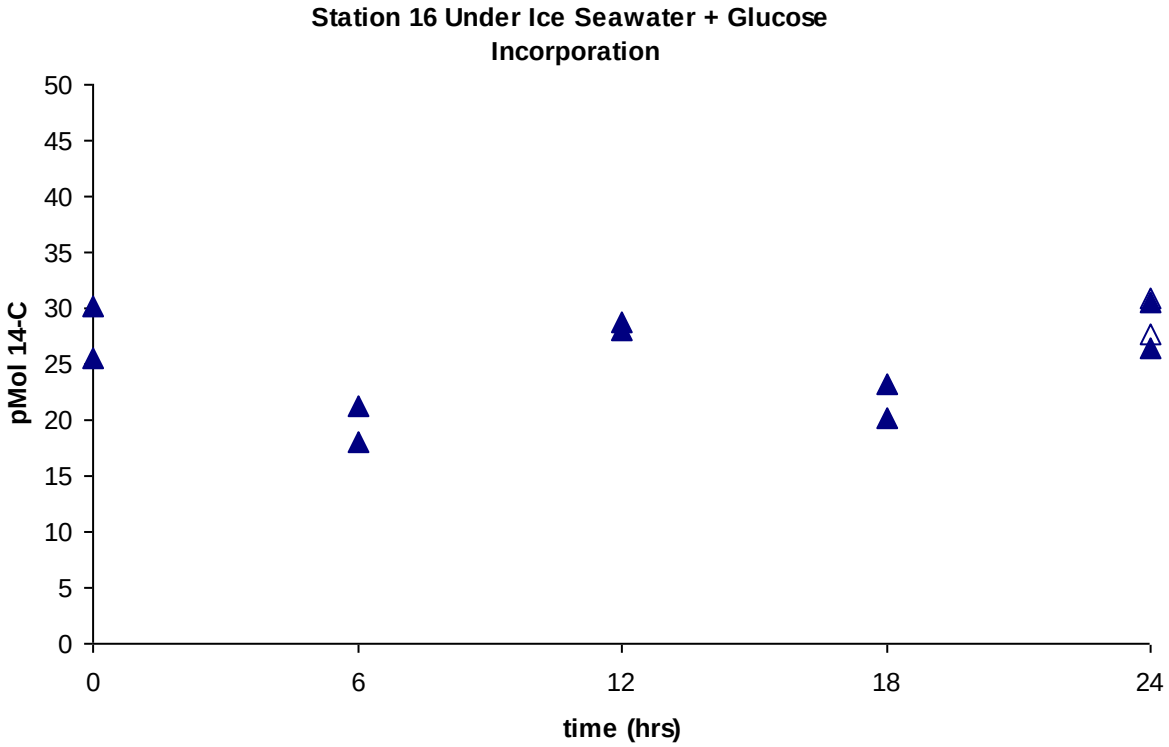
6
12
18
24
time (hrs)


Station 16 Under Ice Seawater + Glucose Incorporation
pMol 14-C
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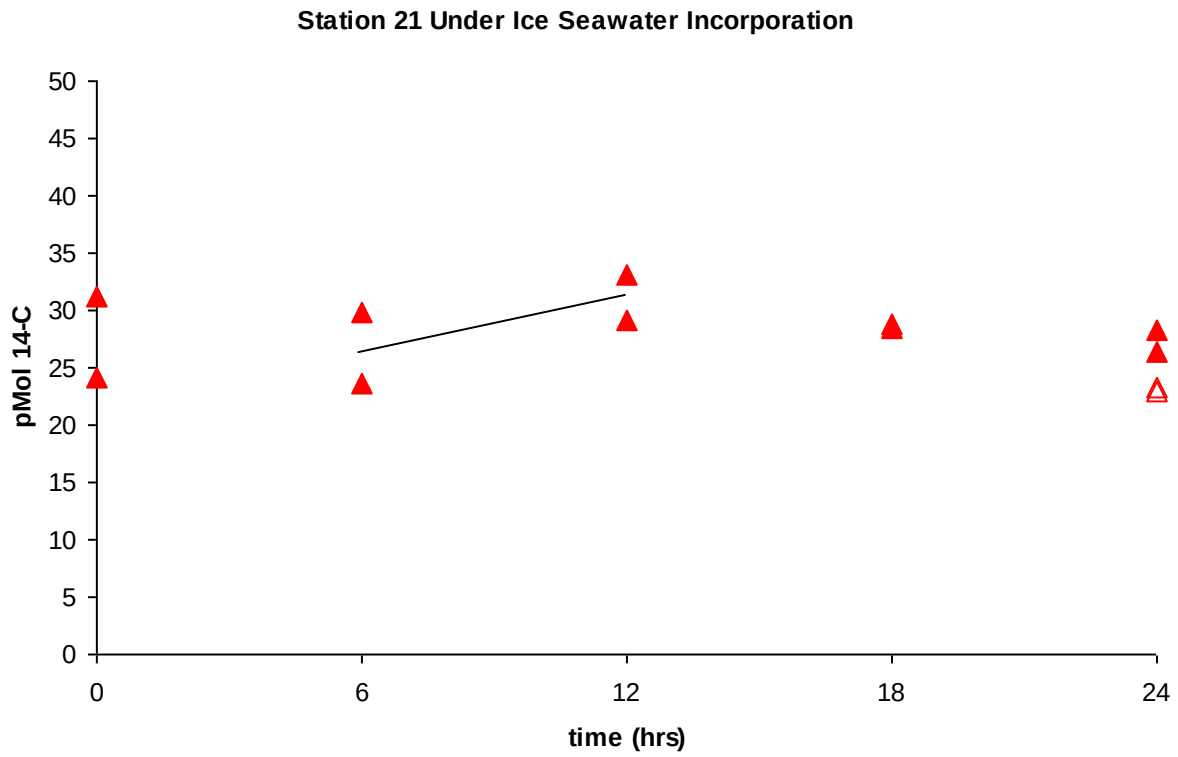
18
24
time (hrs)


Station 21 Under Ice Seawater Incorporation
pMol 14-C
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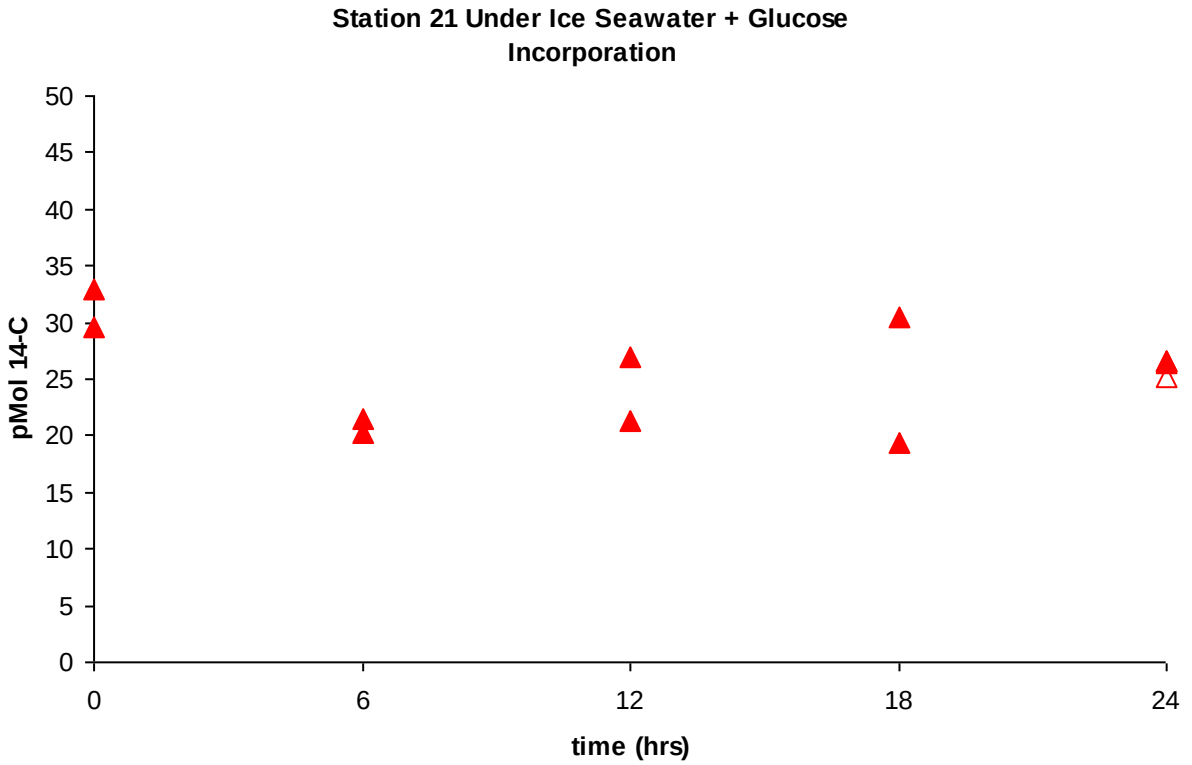
time (hrs)


Station 21 Under Ice Seawater + Glucose Incorporation
pMol 14-C
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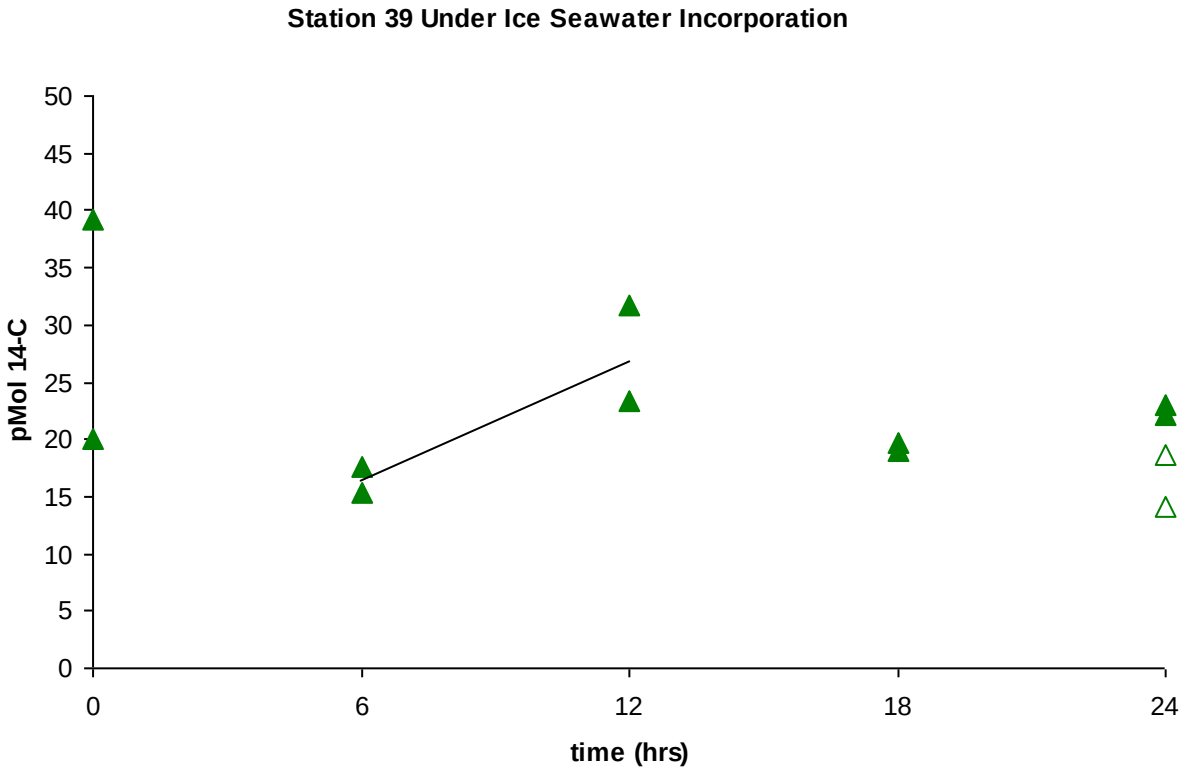
time (hrs)


Station 39 Under Ice Seawater Incorporation
pMol 14-C
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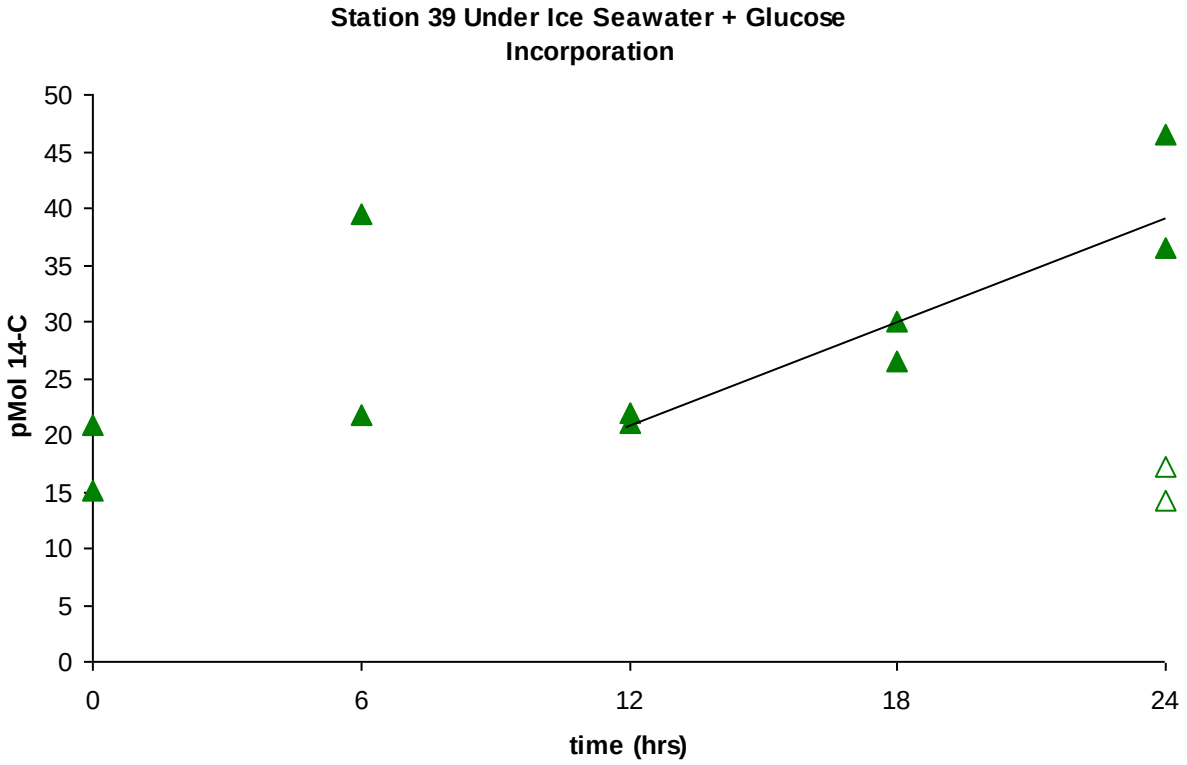
time (hrs)


Station 39 Under Ice Seawater + Glucose Incorporation
pMol 14-C
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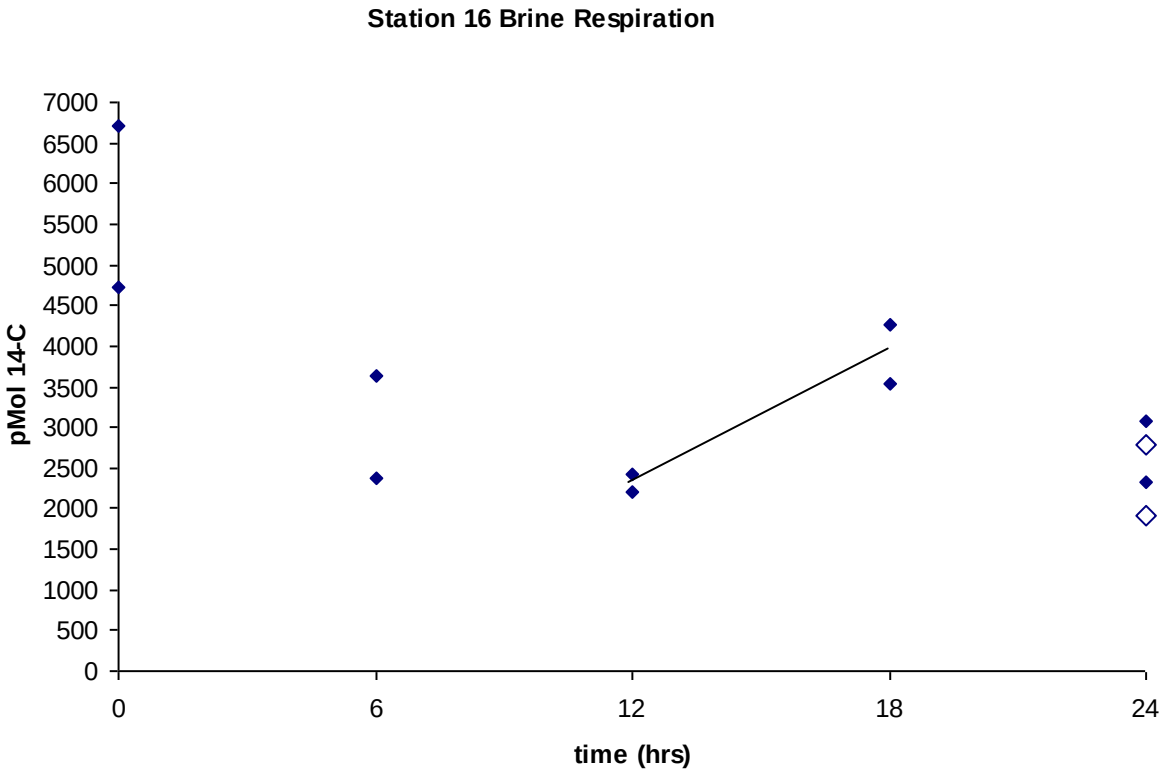
18
24
time (hrs)


Station 16 Brine Respiration
pMol 14-C
7000
6500
6000
5500
5000
4500
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3000
2500
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1500
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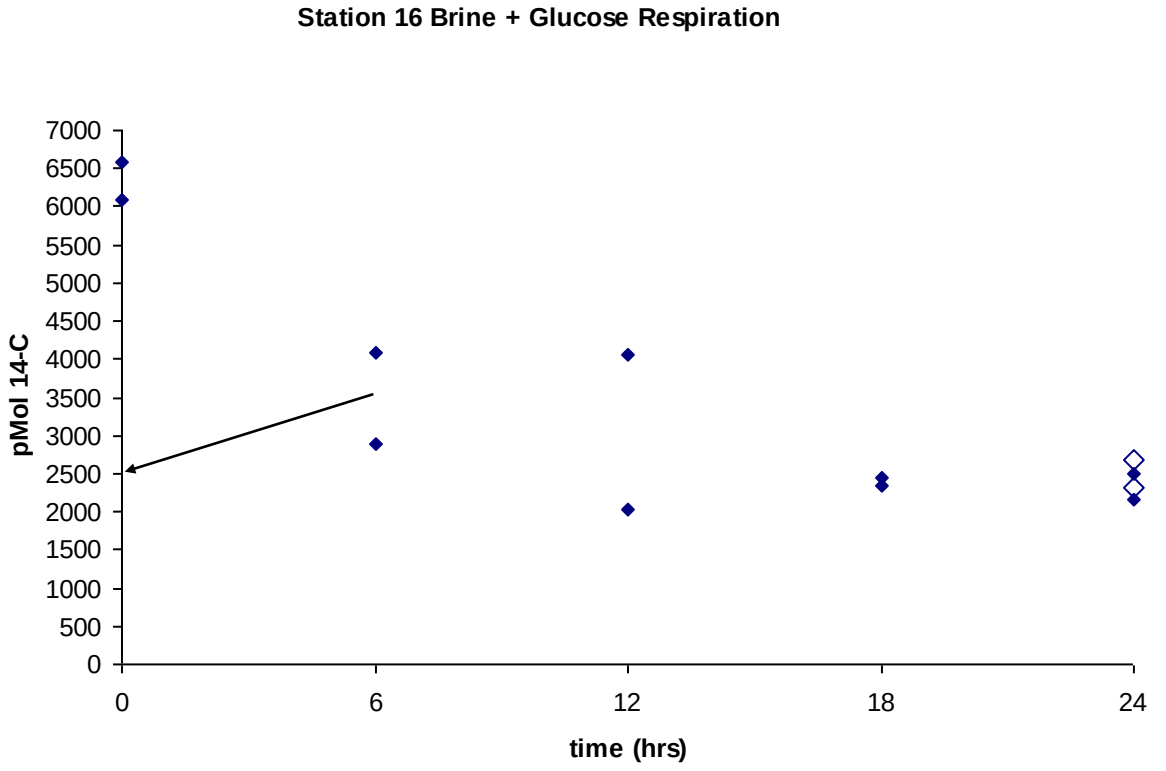
500
0
0
6
12
18
24
time (hrs)


Station 16 Brine + Glucose Respiration
pMol 14-C
7000
6500
6000
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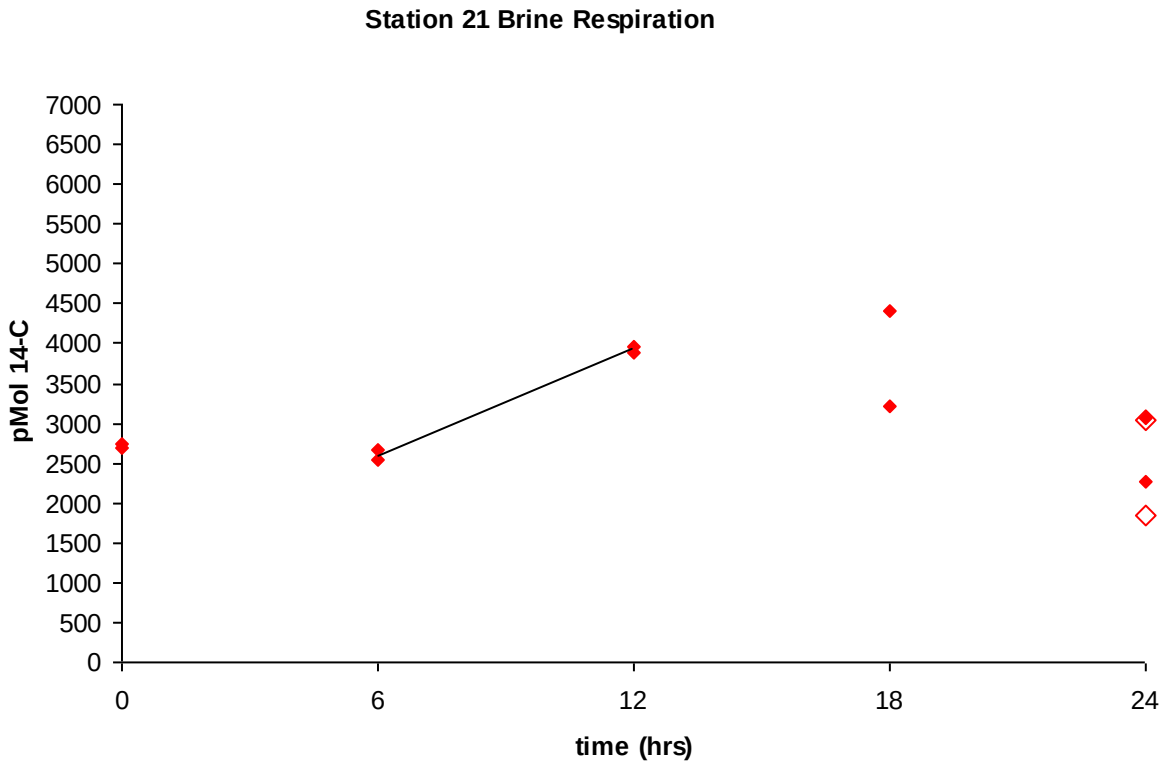
18
24
time (hrs)


Station 21 Brine Respiration
pMol 14-C
7000
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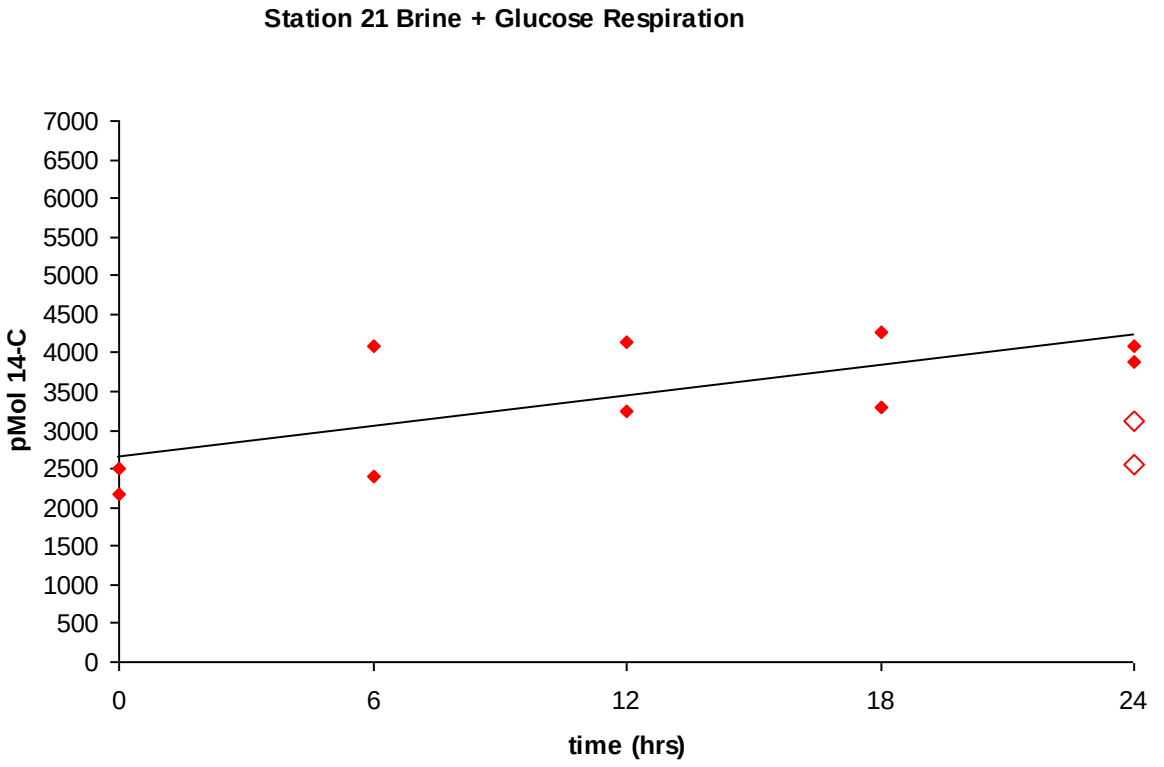
time (hrs)


Station 21 Brine + Glucose Respiration
pMol 14-C
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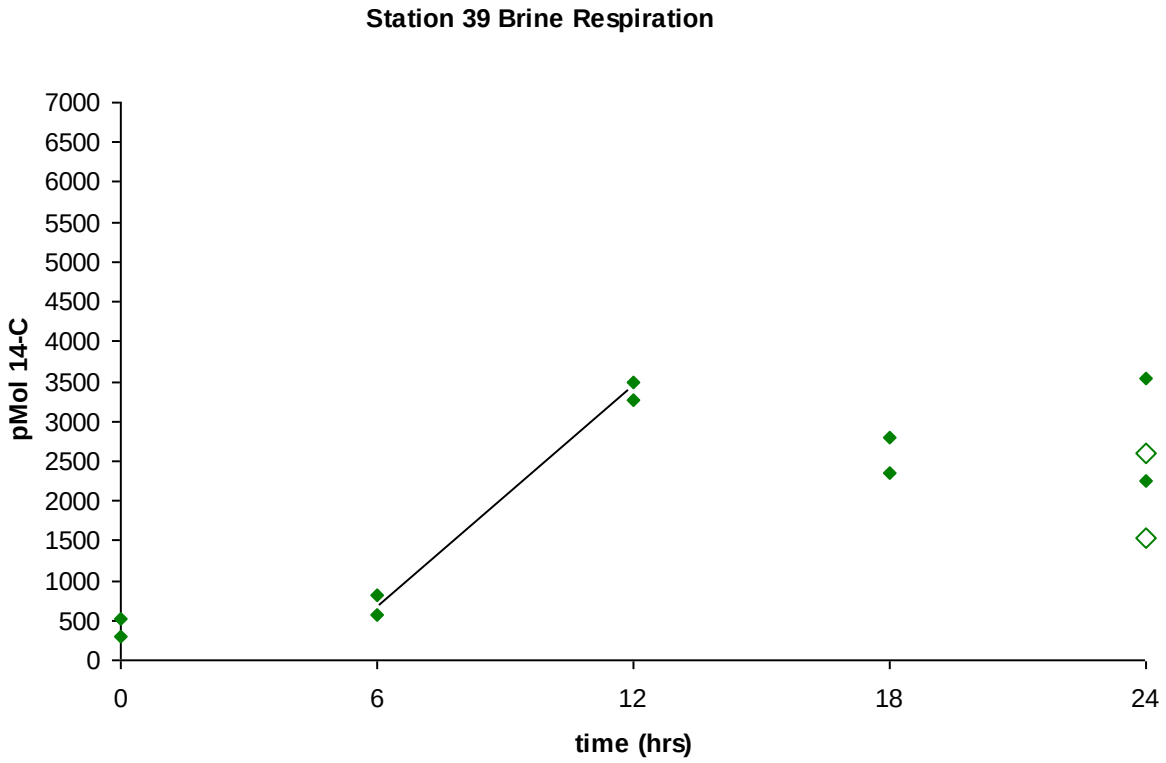
time (hrs)


Station 39 Brine Respiration
pMol 14-C
7000
6500
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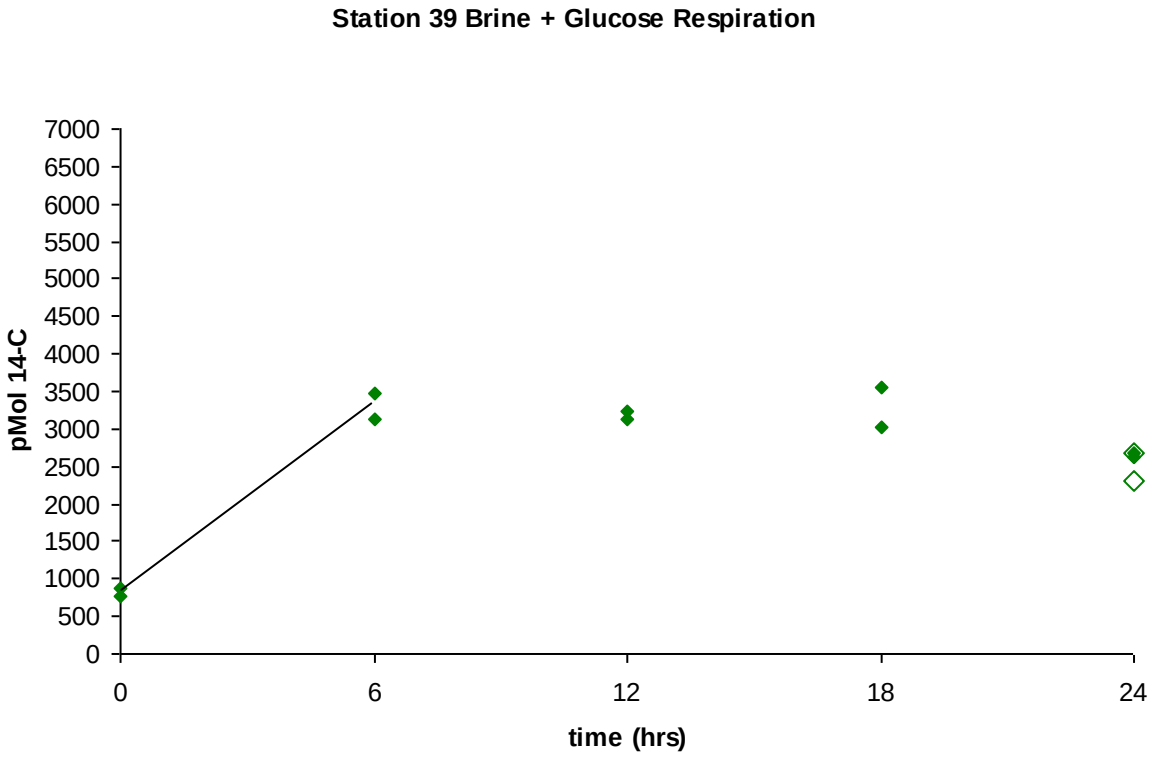
time (hrs)


Station 39 Brine + Glucose Respiration
pMol 14-C
7000
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500
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0
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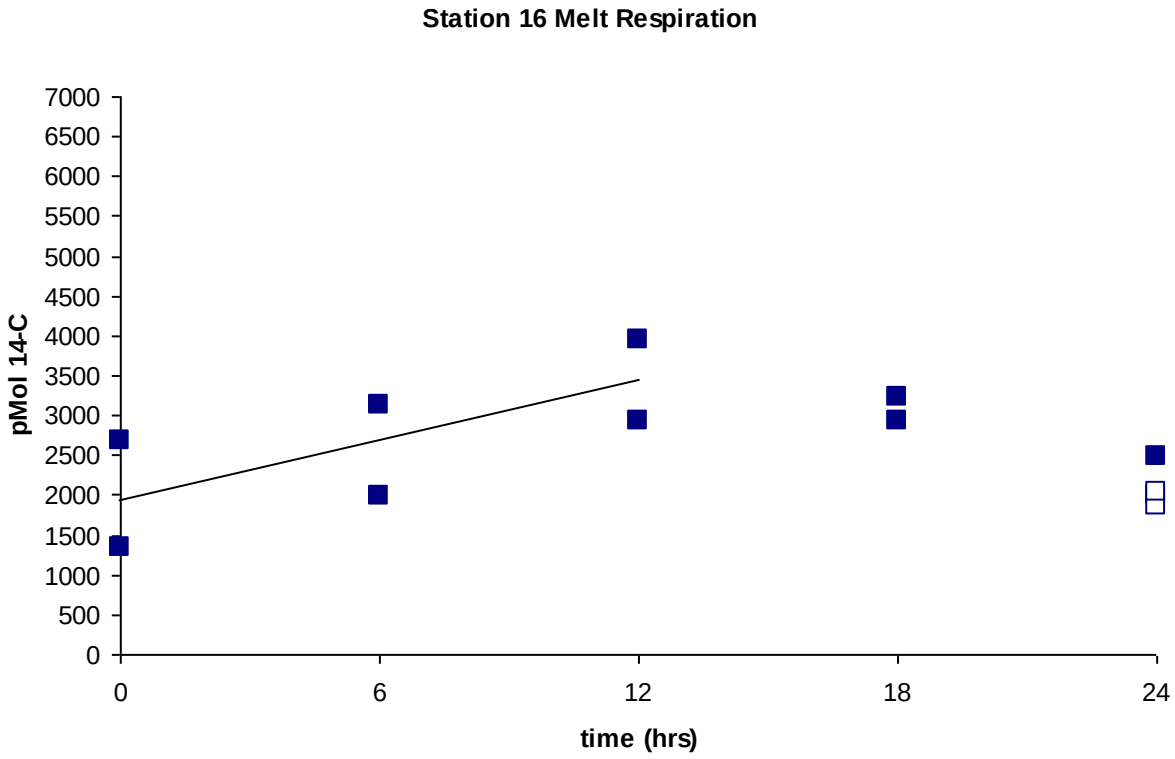
18
24
time (hrs)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pMol 14-C
7000
6500
6000
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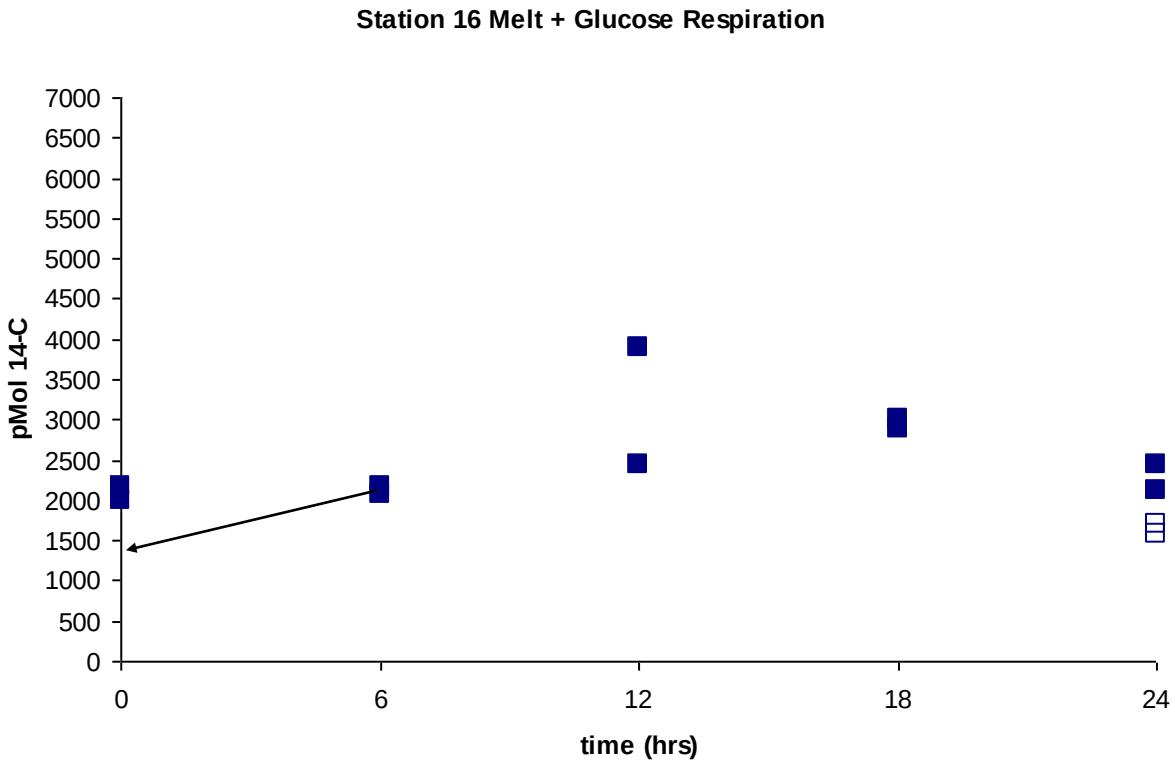
time (hrs)


Station 16 Melt + Glucose Respiration
pMol 14-C
7000
6500
6000
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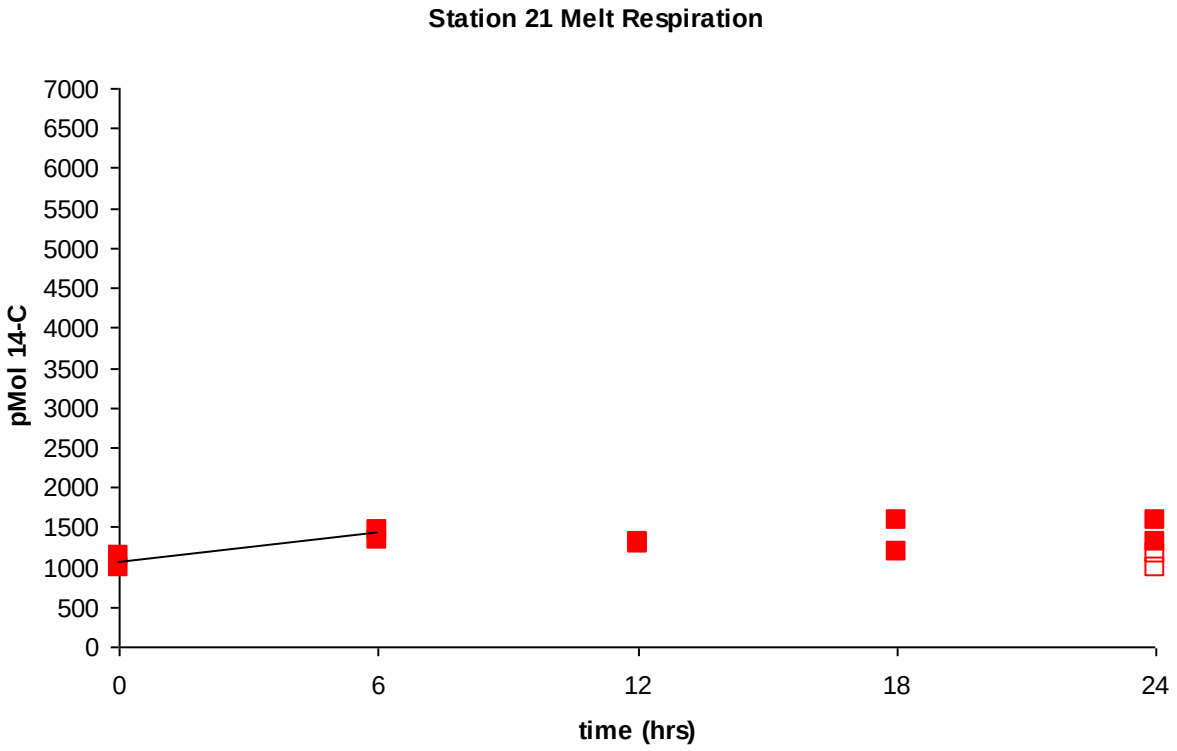
time (hrs)


Station 21 Melt Respiration
pMol 14-C
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
6
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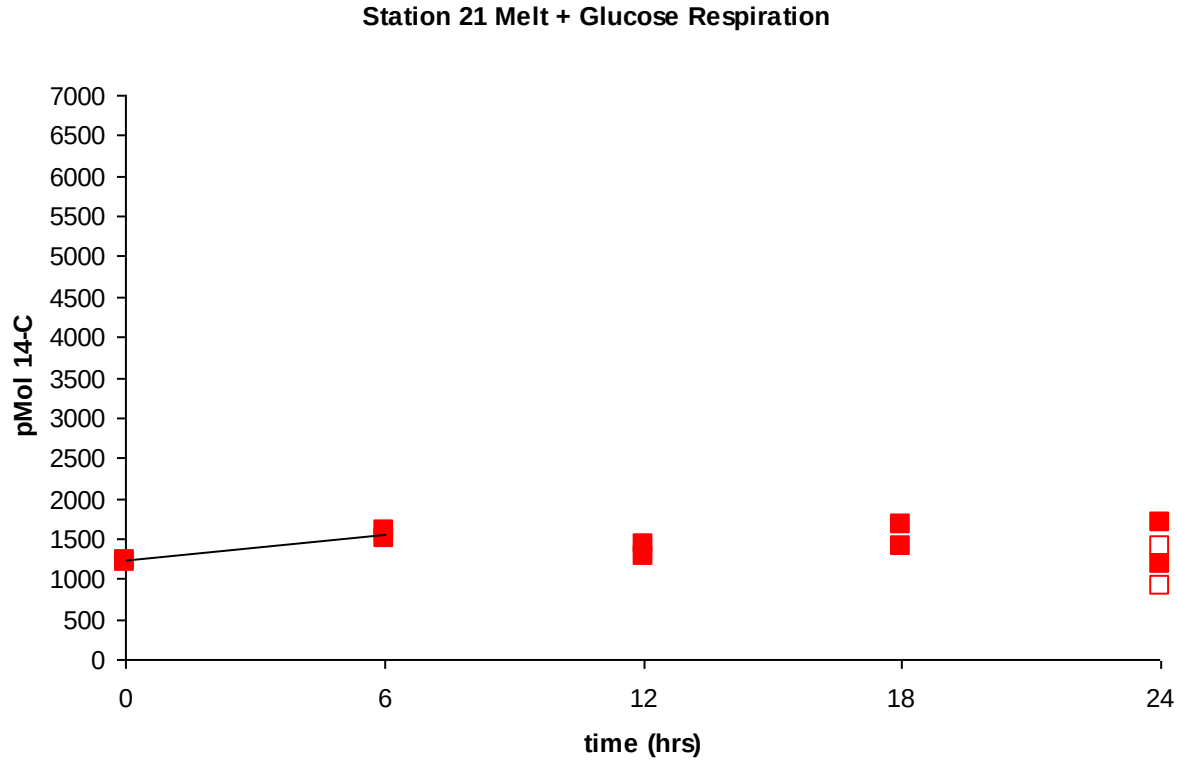
18
24
time (hrs)


Station 21 Melt + Glucose Respiration
pMol 14-C
7000
6500
6000
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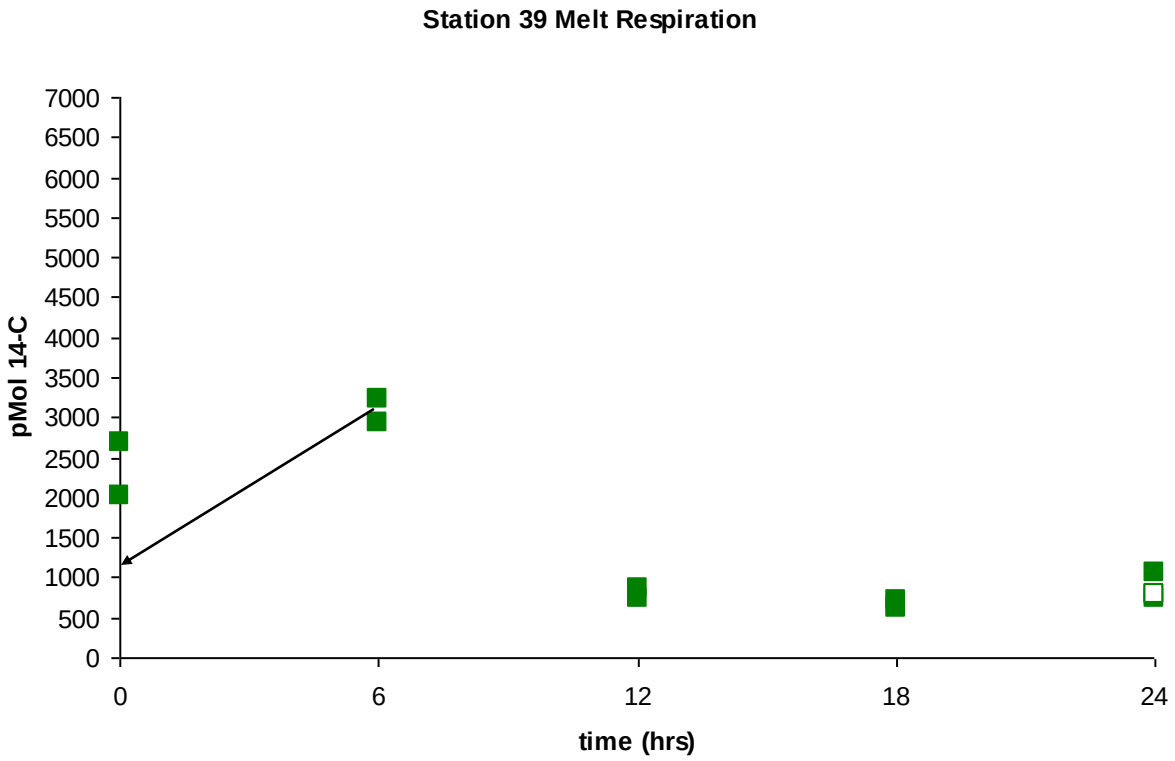
time (hrs)


Station 39 Melt Respiration
pMol 14-C
7000
6500
6000
5500
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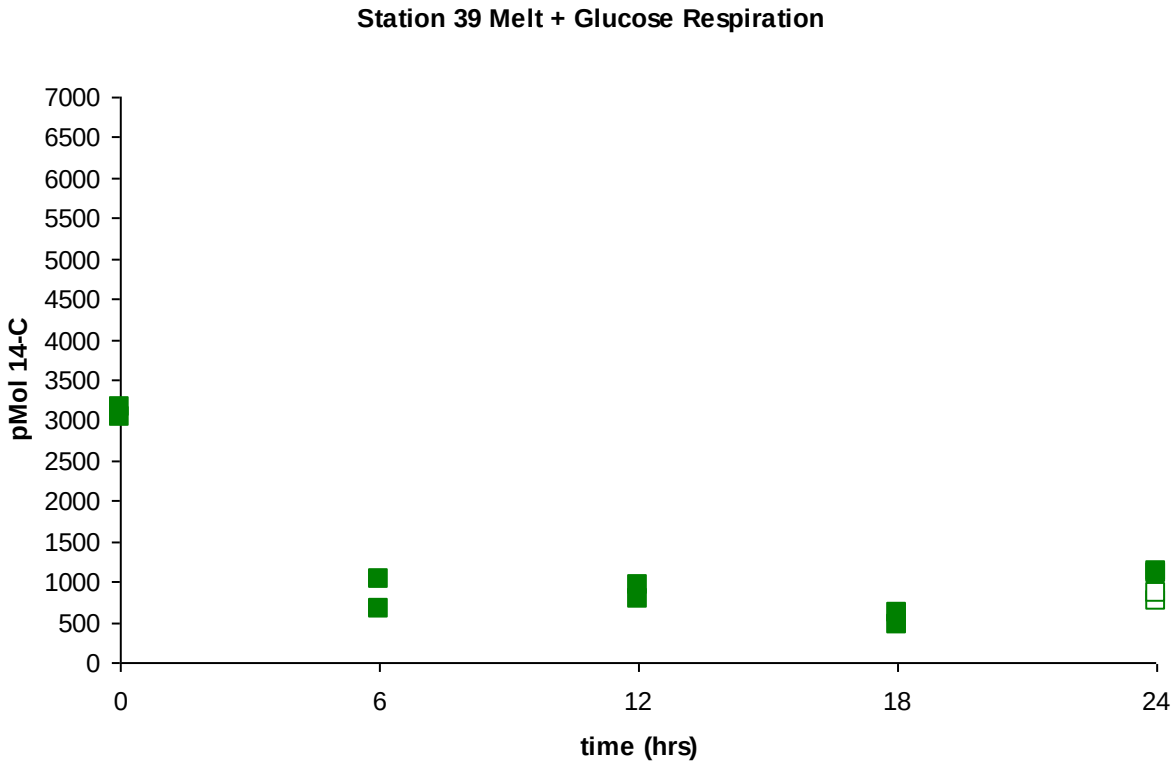
0
0
6
12
18
24
time (hrs)


Station 39 Melt + Glucose Respiration
pMol 14-C
7000
6500
6000
5500
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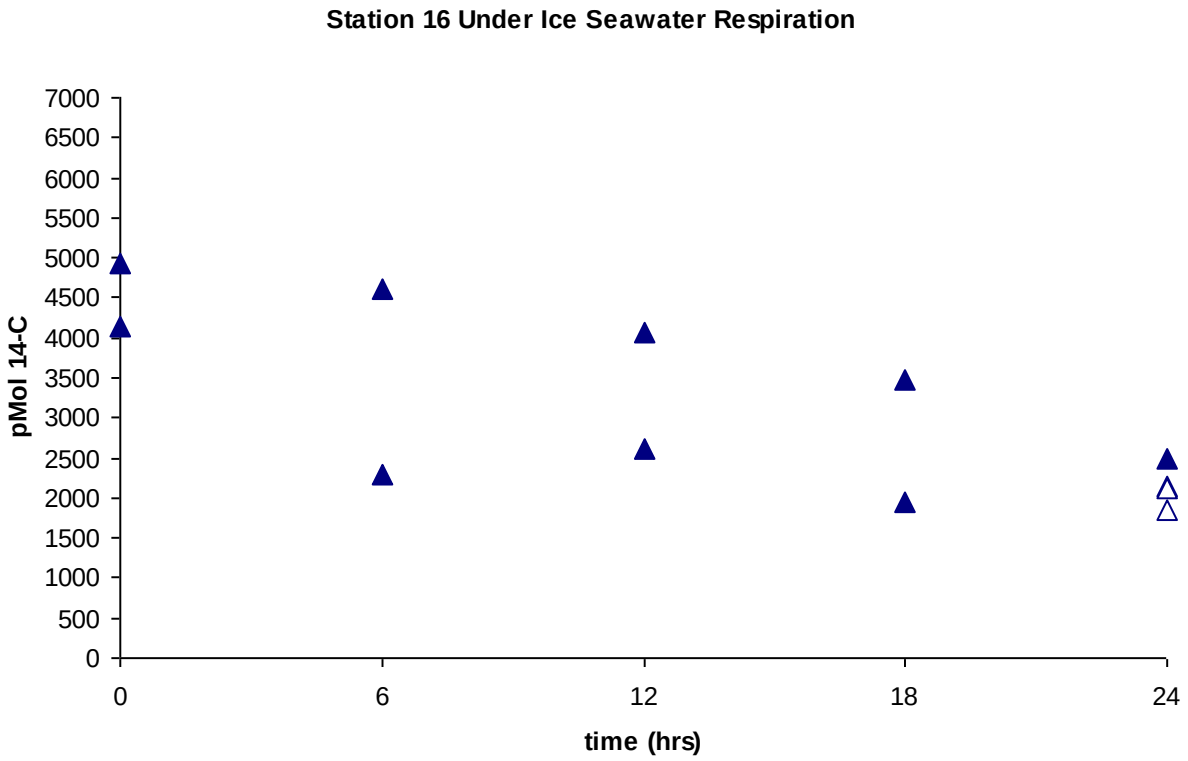
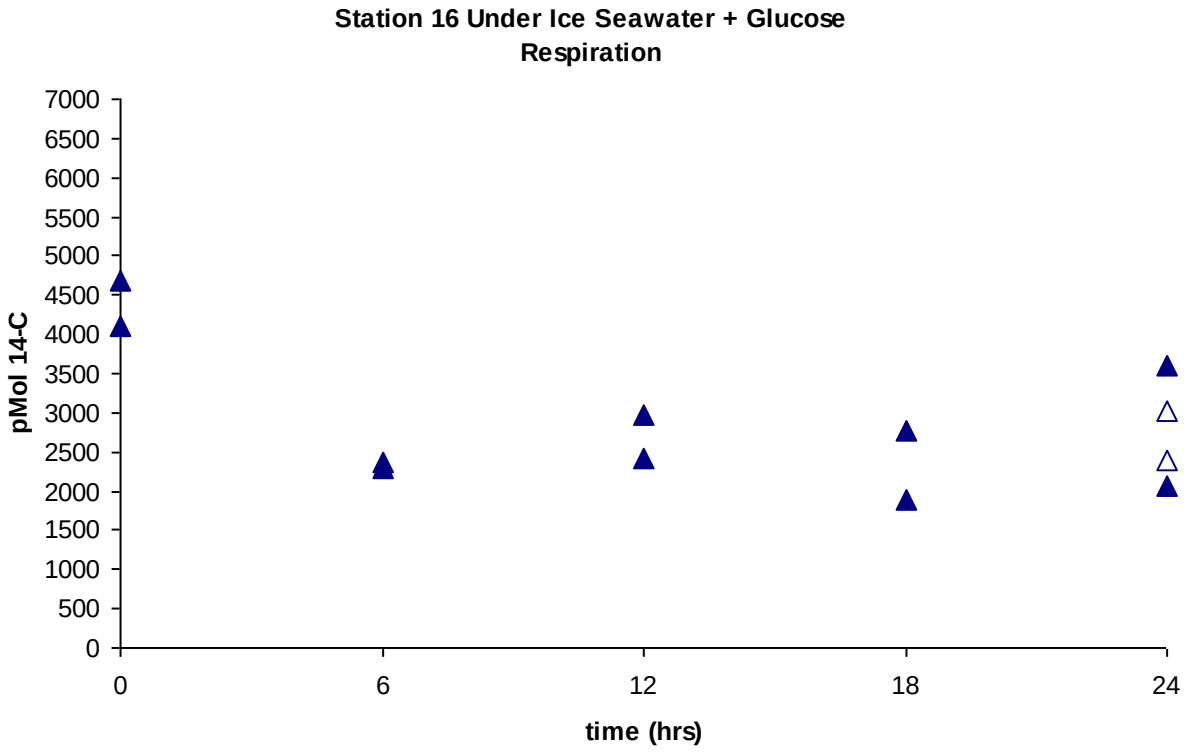
time (hrs)


Station 16 Under Ice Seawater Respiration
pMol 14-C
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
6
12
18
24
time (hrs)


Station 16 Under Ice Seawater + Glucose Respiration
pMol 14-C
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
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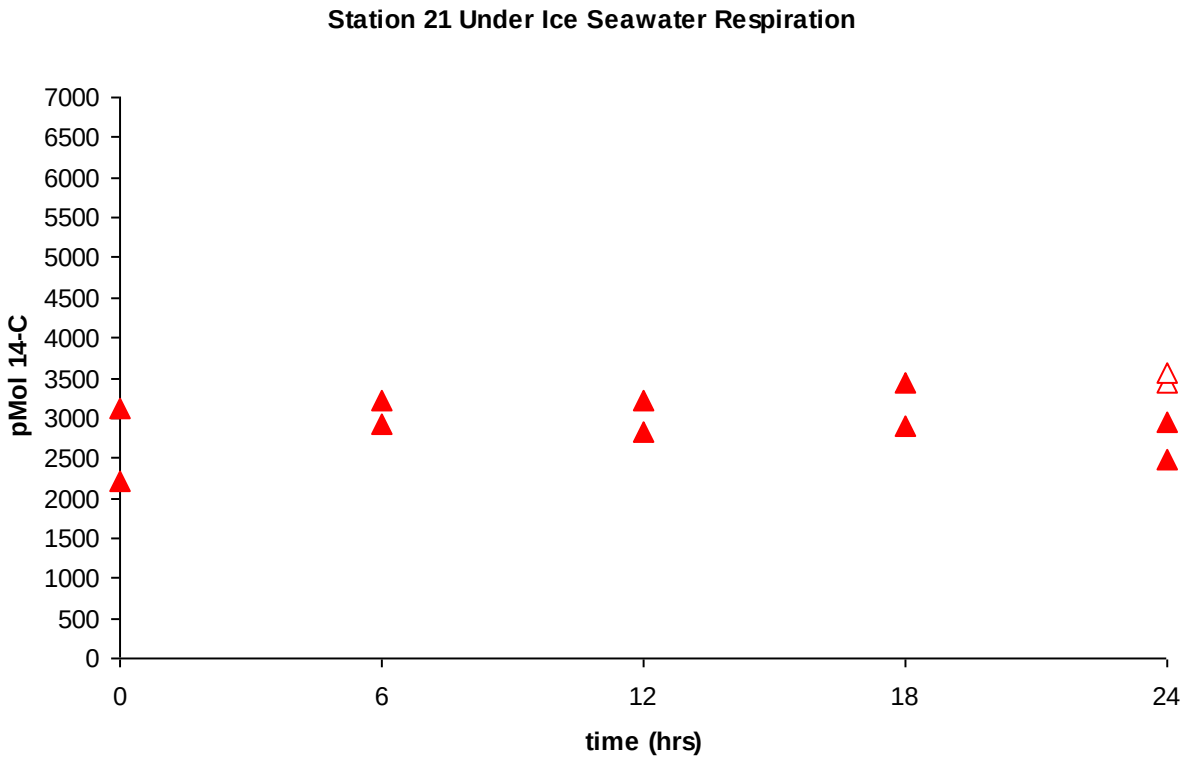
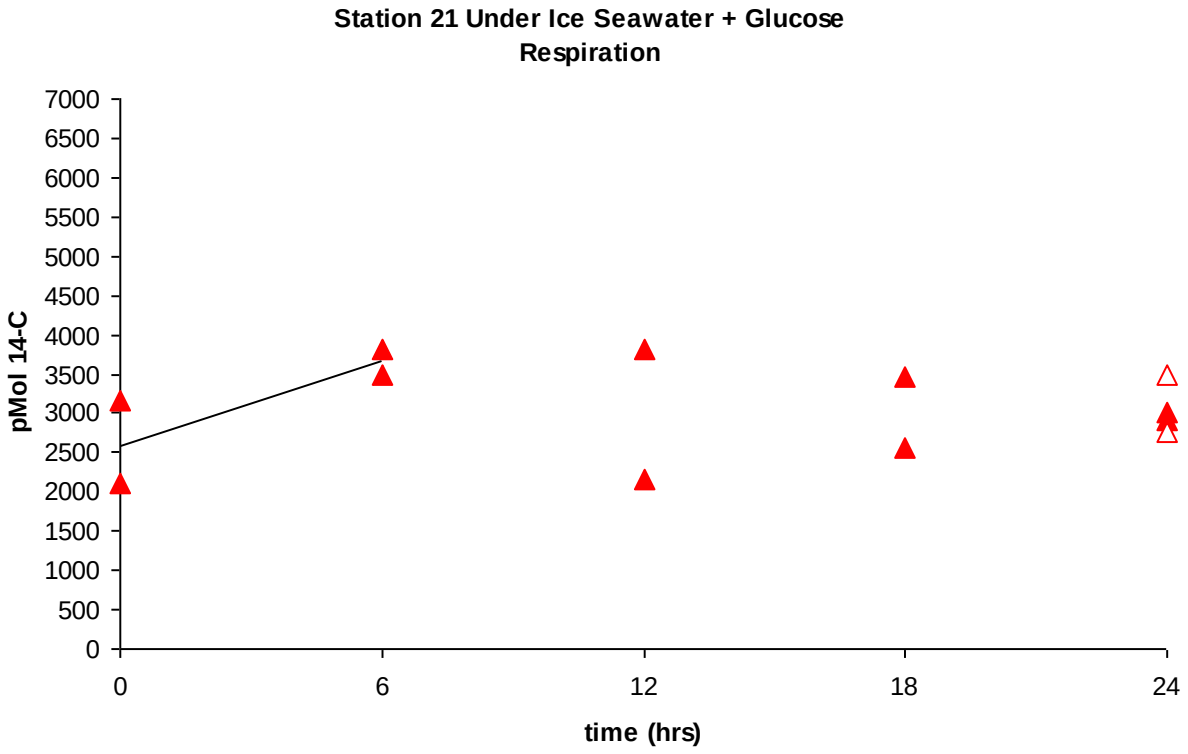
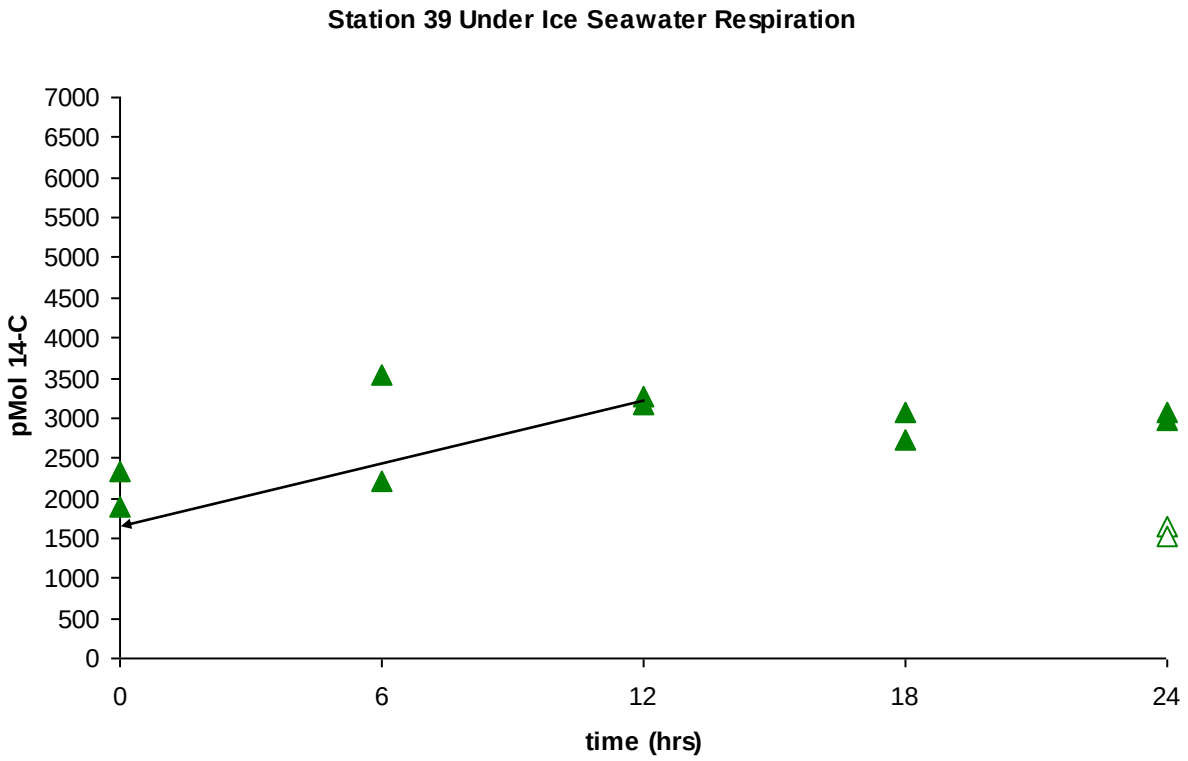
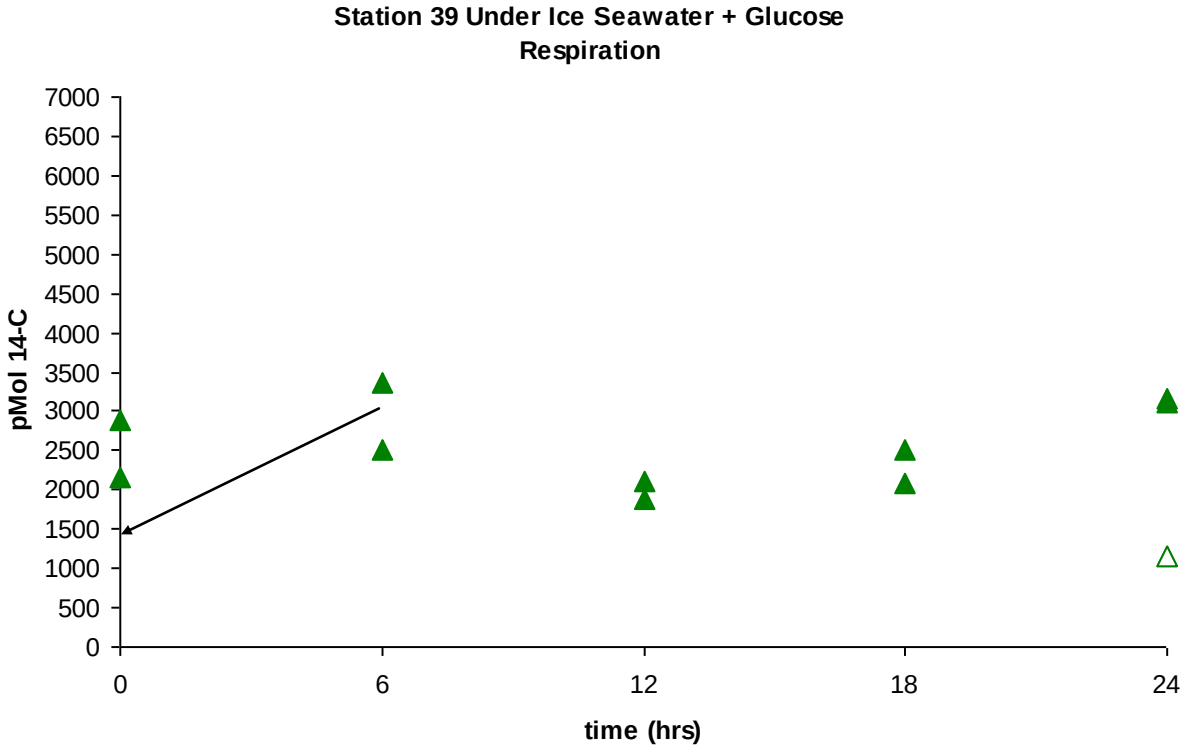
12
18
24
time (hrs)

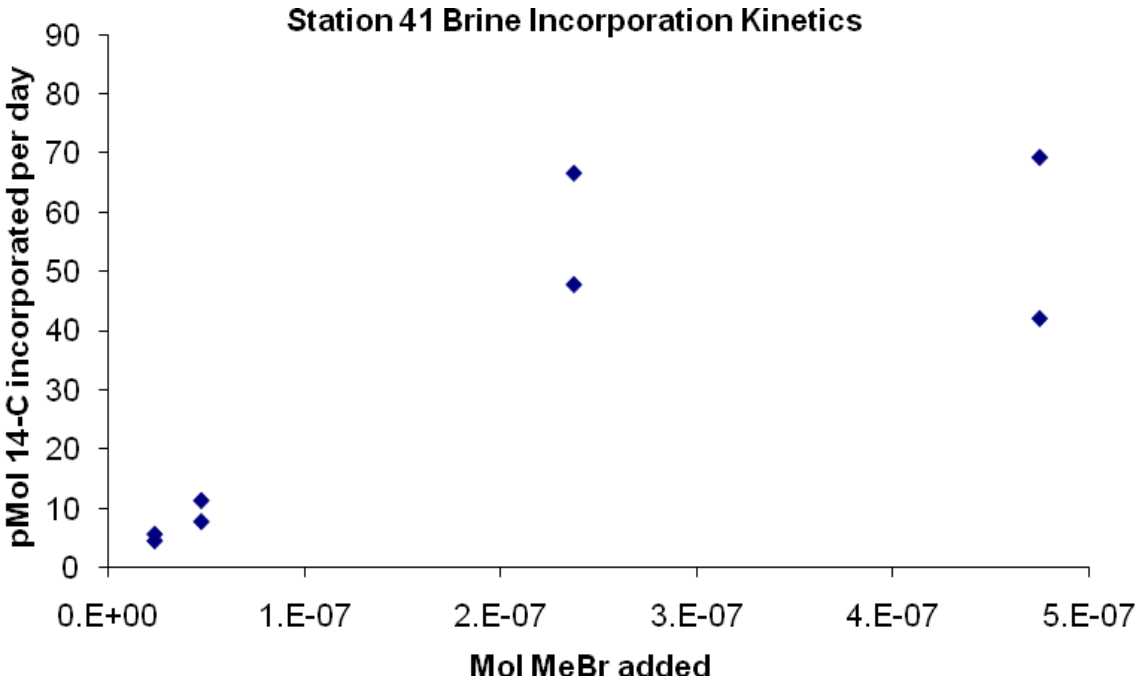

Station 21 Under Ice Seawater Respiration
pMol 14-C
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
6
12
18
24
time (hrs)

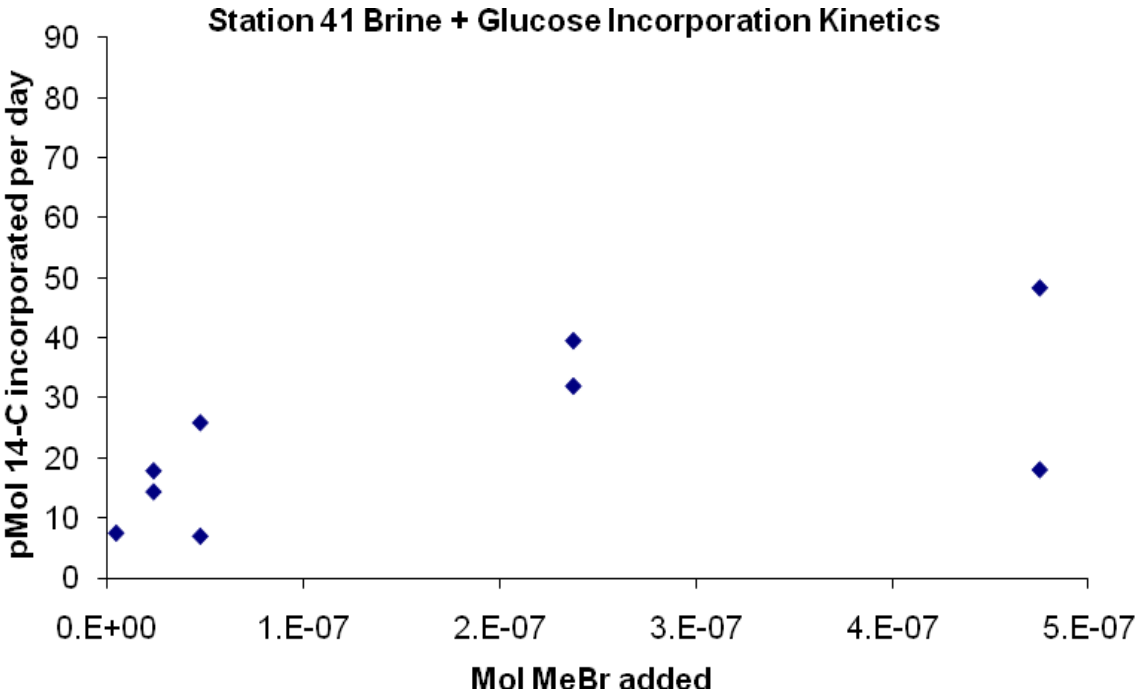

Station 21 Under Ice Seawater + Glucose Respiration
pMol 14-C
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
6
12
18
24
time (hrs)

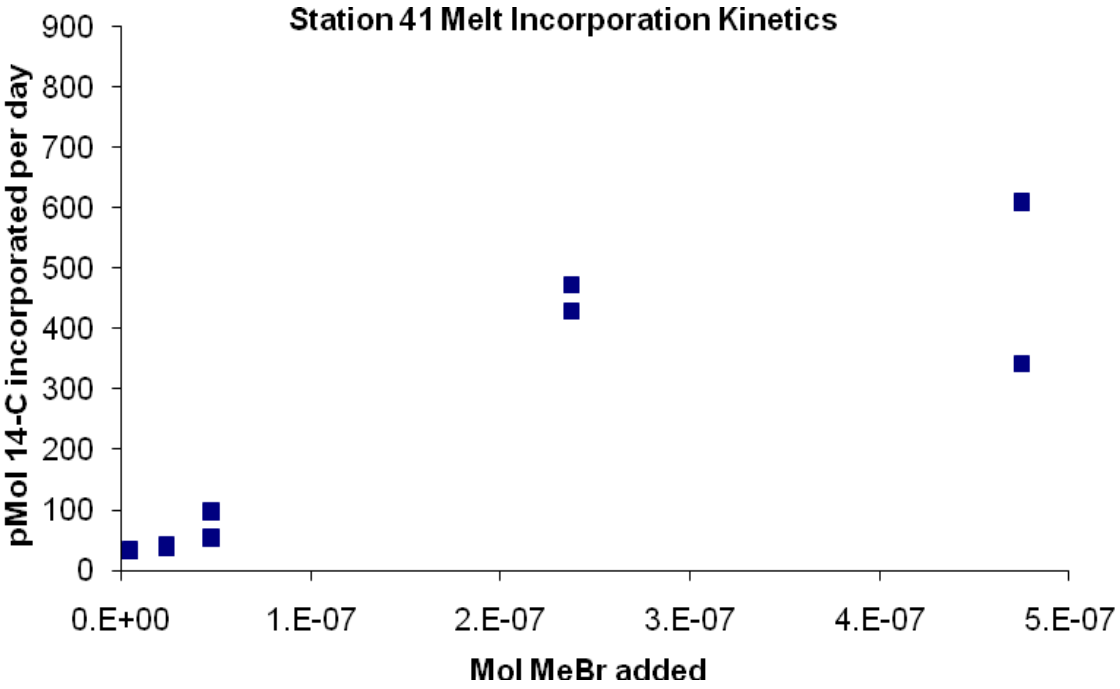

Station 39 Under Ice Seawater Respiration
pMol 14-C
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
6
12
18
24
time (hrs)

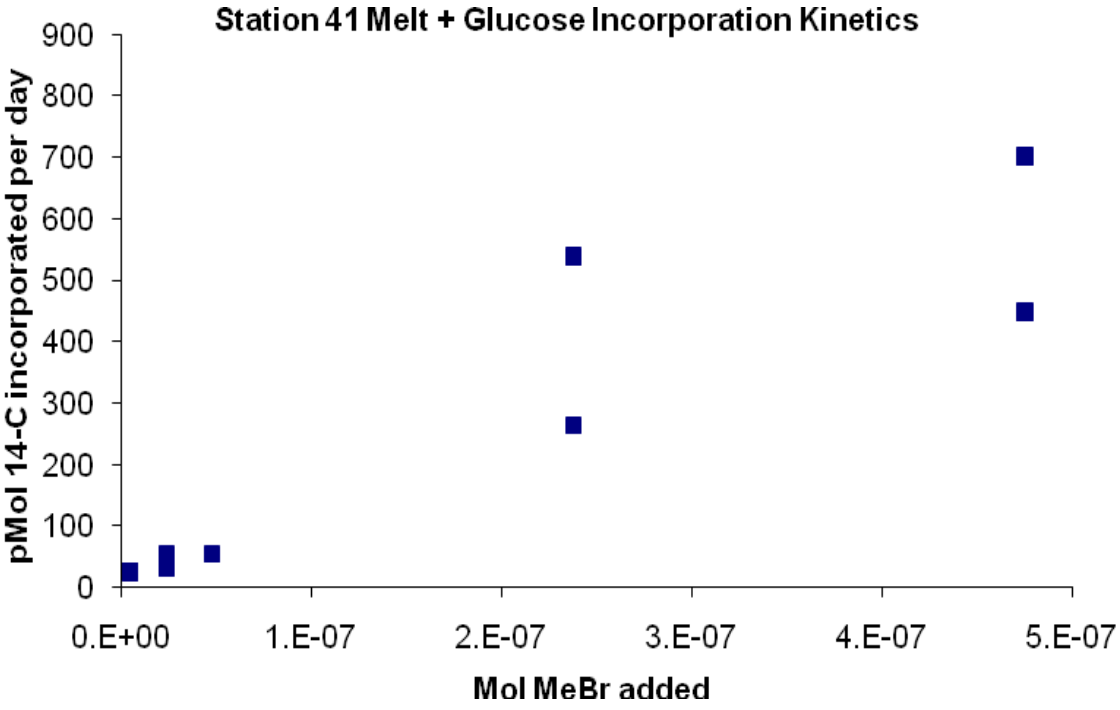

Station 39 Under Ice Seawater + Glucose Respiration
pMol 14-C
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
6
12
18
24
time (hrs)

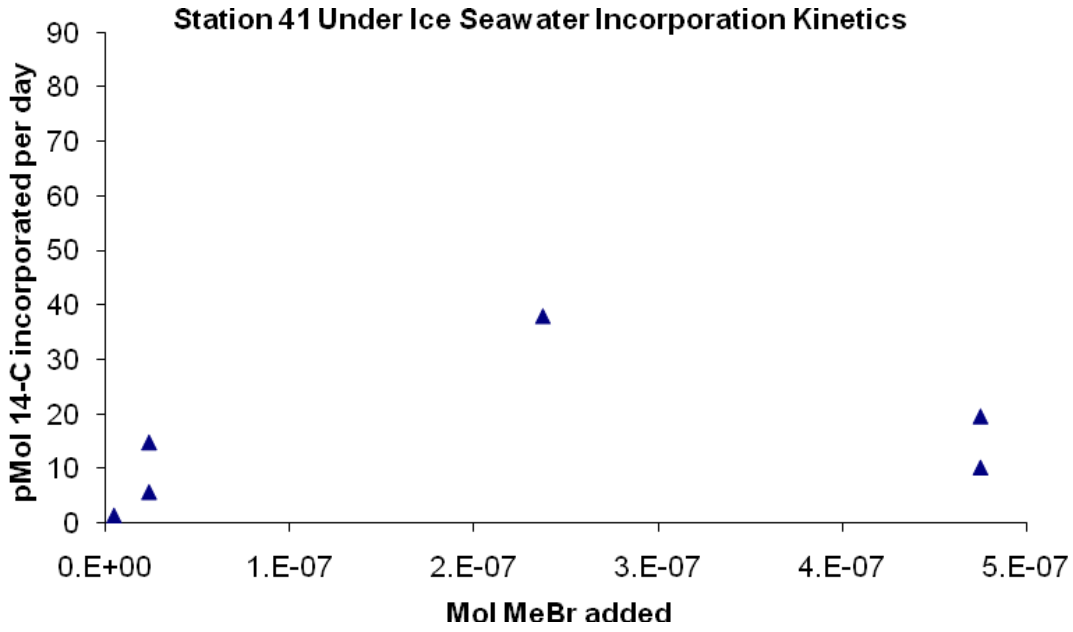
APPENDIX E- Kinetic Analysis Graphs for Station 41 (organized by water and rate type).

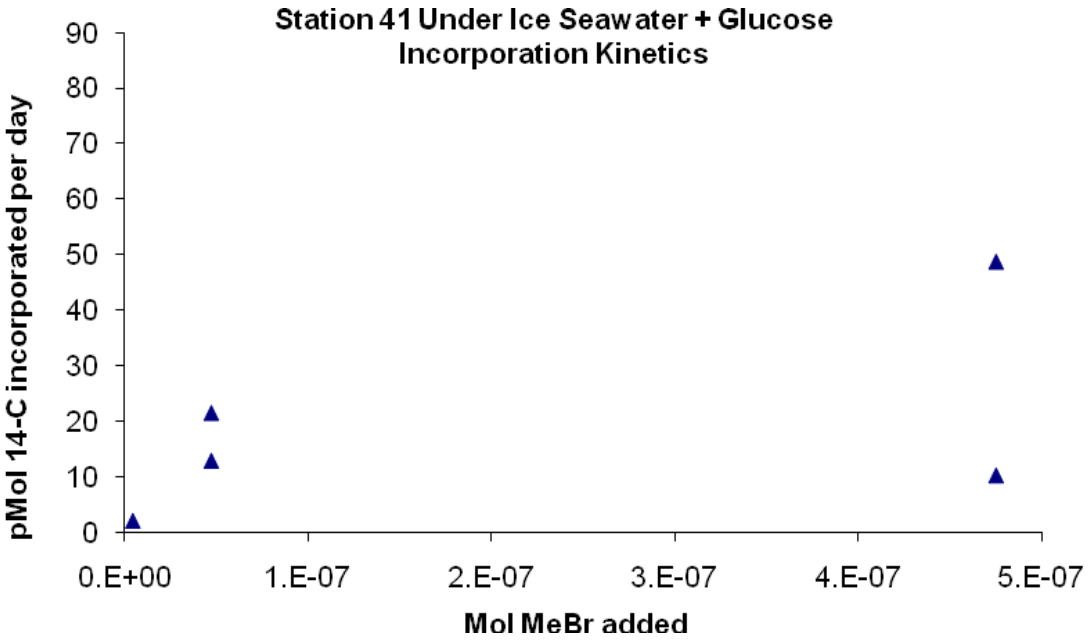


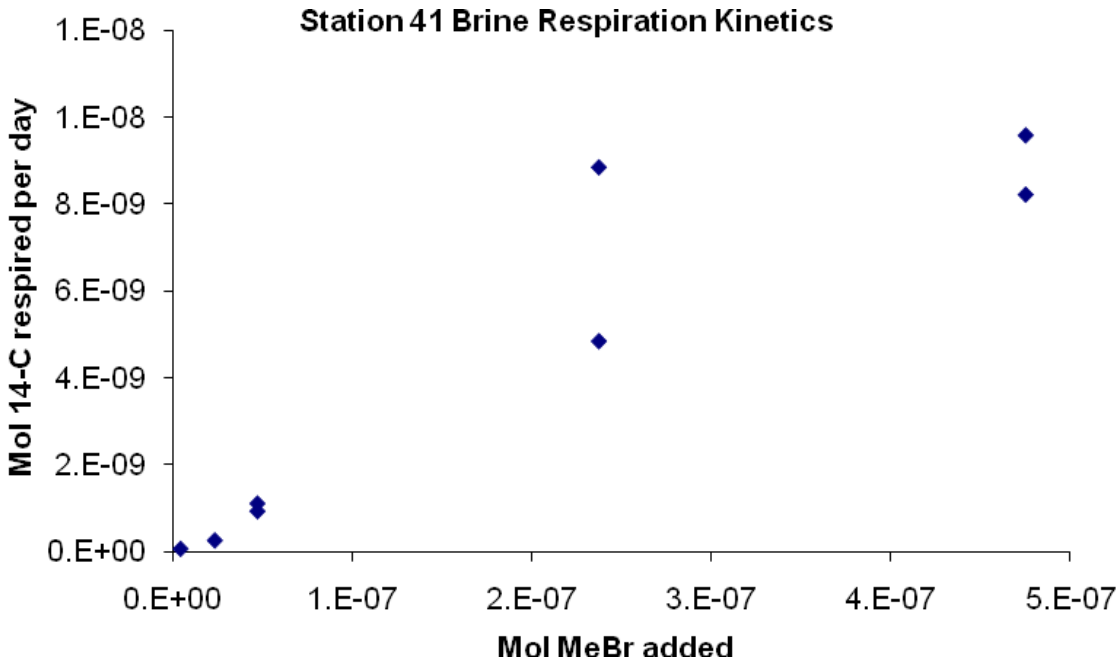


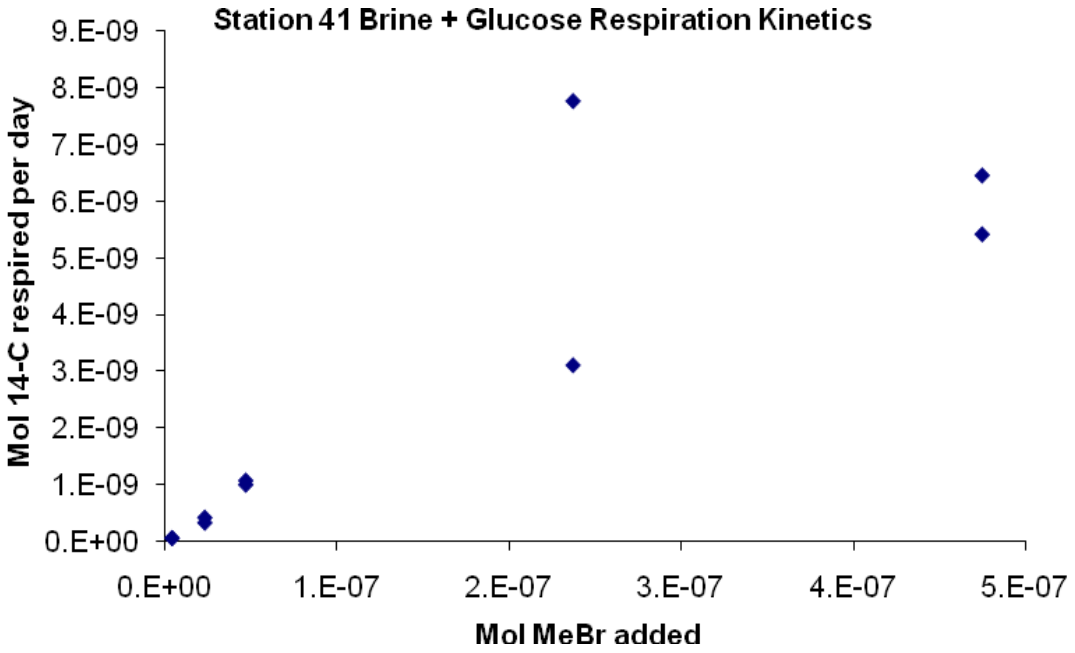

Station 41 Melt Incorporation Kinetics
pMol 14-C incorporated per day
900
800
700
600
500
400
300
200
100
0
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added

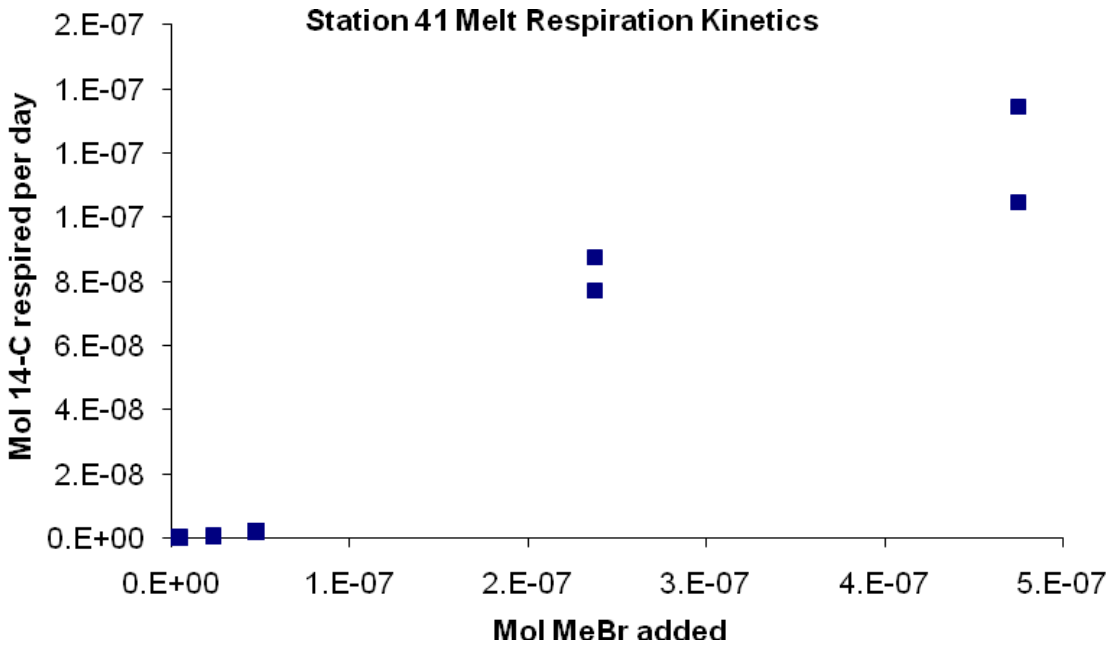

Station 41 Melt + Glucose Incorporation Kinetics
pMol 14-C incorporated per day
900
800
700
600
500
400
300
200
100
0
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added

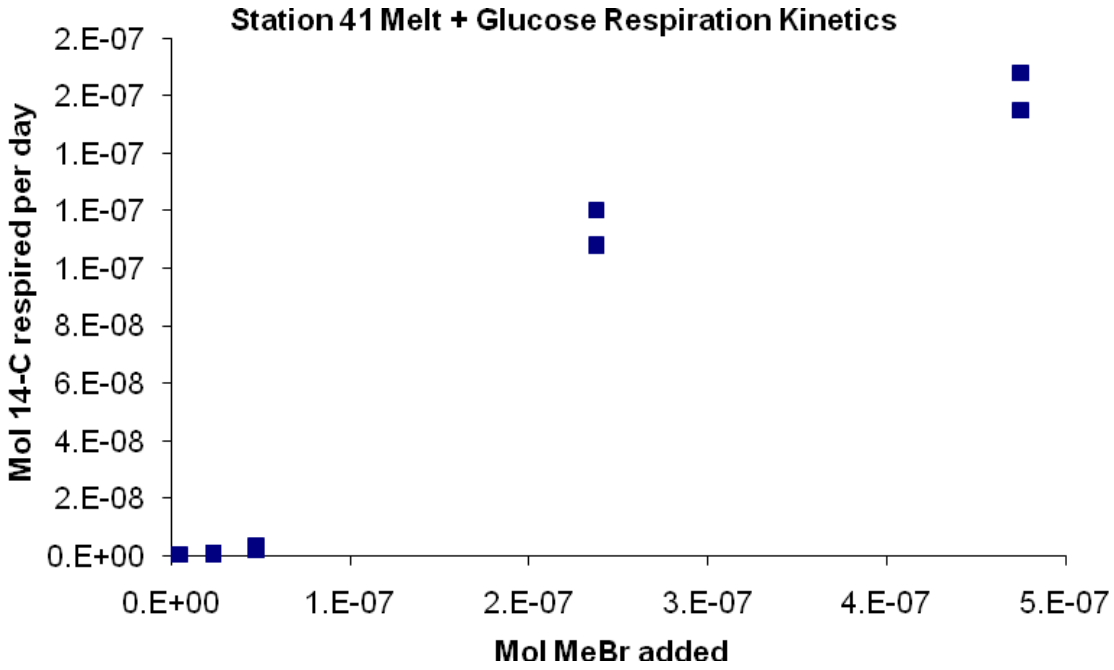

Station 41 Under Ice Seawater Incorporation Kinetics
pMol 14-C incorporated per day
90
80
70
60
50
40
30
20
10
0
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added

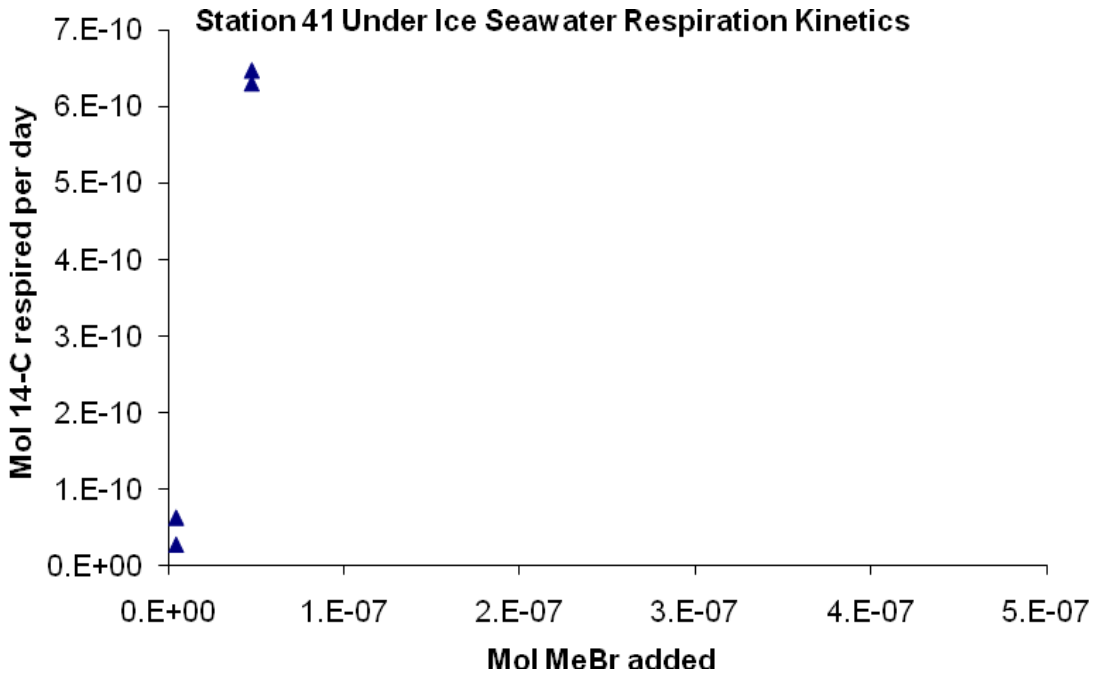

Station 41 Under Ice Seawater + Glucose
Incorporation Kinetics
pMol 14-C incorporated per day
90
80
70
60
50
40
30
20
10
0
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added

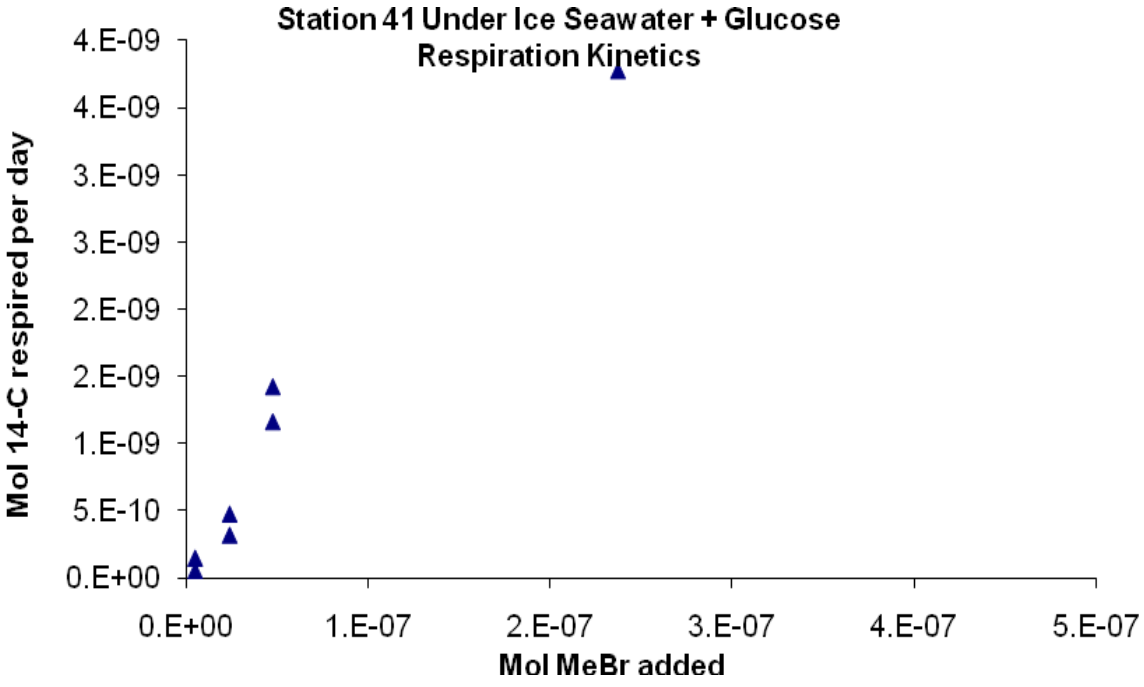

Station 41 Brine Respiration Kinetics
Mol 14-C respired per day
1.E-08
1.E-08
8.E-09
6.E-09
4.E-09
2.E-09
0.E+00
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added


Station 41 Brine + Glucose Respiration Kinetics
Mol 14-C respired per day
9.E-09
8.E-09
7.E-09
6.E-09
5.E-09
4.E-09
3.E-09
2.E-09
1.E-09
0.E+00
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added


Station 41 Melt Respiration Kinetics
Mol 14-C respired per day
2.E-07
1.E-07
1.E-07
1.E-07
8.E-08
6.E-08
4.E-08
2.E-08
0.E+00
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added


Station 41 Melt + Glucose Respiration Kinetics
Mol 14-C respired per day
2.E-07
2.E-07
1.E-07
1.E-07
1.E-07
8.E-08
6.E-08
4.E-08
2.E-08
0.E+00
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added


Station 41 Under Ice Seawater Respiration Kinetics
Mol 14-C respired per day
7.E-10
6.E-10
5.E-10
4.E-10
3.E-10
2.E-10
1.E-10
0.E+00
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added


Station 41 Under Ice Seawater + Glucose Respiration Kinetics
Mol 14-C respired per day
4.E-09
4.E-09
3.E-09
3.E-09
2.E-09
2.E-09
1.E-09
5.E-10
0.E+00
0.E+00
1.E-07
2.E-07
3.E-07
4.E-07
5.E-07
Mol MeBr added

APPENDIX F- SAS Parameter Estimates for Nonlinear Modeling.

		Parameter Estimates		**Model Results**				
Station 41 Nonlinear Modeling	**# of 24>0hr data**	**alpha (v_{max})**	**beta (K_m)**	**alpha (v_{max})**	**beta (k_m)**	**R^2 of model fit**	**nlin error**	**linear corrected total sum of squares**
Brine incorporation	8	70	150000	88	206110	0.82	945.2	5382.86
Brine + glucose incorporation	9	60	200000	38	41572	0.54	756.4	1628.88
Melt incorporation	10	700	200000	765	237422	0.87	56721.5	450893
Melt + glucose incorporation	10	1000	250000	1330	605337	0.87	75720.9	581496
UI Seawater incorporation	6	40	100000	23	25780	0.43	479.1	836.32
UI Seawater + glucose incorporation	5	60	250000	32	42454	0.40	777.4	1288.31
Brine respiration	8	9000	120000	17498	431923	0.91	11351465	119914691
Brine + glucose respiration	10	8000	100000	9696	254366	0.82	13748515	77472461
Melt respiration	10	170000	240000	394161	1049922	0.95	1277400000	25900488888
Melt + glucose respiration	10	190000	240000	493060	934383	0.96	1775200000	47173813119
UI Seawater respiration	4	900	50000	*not enough data to fit models				
UI Seawater + glucose respiration	7	4200	150000	8842	316949	0.98	186499	10213124

APPENDIX G- Chemical Characteristics of All Water Types, with degradation rates represented in $pM \cdot hr^{-1} \cdot 10^9$ cells^{-1}

Station	Water type or Correlation	Resp. Rate (pmol·hr^{-1} ·10^9 cells^{-1})	(+Glu) Resp. Rate	Incorp. Rate (pmol·hr^{-1} ·10^9 cells^{-1})	(+Glu) Incorp. Rate	Chl a (mg·L^{-1}) (A)	DMSP (nM) (A)	PO_4 (µM) (B)	N+N (µM) (B)	DON (µM)	TDN (µM)	DOC (µM)	DIC (µM) (B)	pH (B)	Total Alkalinity (µmol·kg^{-1}) (B)	Salinity (B)
16	Melt	467	304	2.38	7.82	34.94	227.5	1.49	5.13				273.6	8.0	270	8.6
21	Melt	115	117	3.75	1.77	13.53	208.1	0.35	-0.09				262.2	8.9	160	6.3
39	Melt	1966	nd	4.71	8.22	8.6	110.0	0.06	1.40				191.5	8.4	210	4.4
41	Melt	379	462	13.28	9.47	1.72	175.2	0.00	3.43				521.2	8.1	510	5.9
	Melt Respiration					-0.21	-0.89	-0.31	-0.14				-0.50	-0.06	-0.23	-0.65
	Melt + glu Respiration					-0.30	-0.58	-0.18	0.70				0.86	-0.85	**0.97**	-0.09
	Melt Incorporation					-0.74	**0.99**	-0.62	0.13				**0.91**	-0.33	**0.90**	-0.34
	Melt + glu Incorporation					-0.11	**-0.99**	-0.03	0.70				0.40	-0.88	0.69	-0.08
16	Brine	1213	752	11.32	10.16	0.02	14.5	0.56	0.84	8.3	9.3	87.5	2151.1			42.0
21	Brine	310	90	nd	nd	0.46	29.3	1.33	22.63	9.0	9.8	86.3	1407.3			34.6
39	Brine	1352	1244	3.92	6.74	0.11	26.5	0.00	0.00	3.4	3.4	65.7	1917.5			37.9
41	Brine	183	185	1.72	2.95	0.13	74.1	0.00	0.00	6.3	6.3	74.2	1811.1			31.1
	Brine Respiration					-0.61	-0.73	-0.31	-0.49	-0.45	-0.36	-0.24	0.71			0.87
	Brine + glu Respiration					-0.62	-0.52	-0.52	-0.59	-0.71	-0.64	-0.54	0.65			0.66
	Brine Incorporation					**-0.99**	-0.80	**0.98**	**0.98**	0.66	0.74	0.82	**0.99**			**0.90**
	Brine + glu Incorporation					**-0.93**	**-0.95**	0.85	0.85	0.38	0.48	0.58	**0.97**			**0.99**
16	UI Seawater	nd	nd	6.27	nd	0.26	5.3	1.92	27.96	0.0	25.0	45.0	2194.9			33.6
21	UI Seawater	nd	368	1.47	nd	6.05	70.5	1.38	15.66	3.7	21.3	60.5	2109.2			33.4
39	UI Seawater	526	1145	7.15	6.45	0.14	11.2	1.76	30.96	8.4	39.7	38.4	2170.7			33.5
41	UI Seawater	76	154	nd	2.05	0.41	13.8	1.80	29.77	11.6	41.7	34.6	2165.5			33.3
	UI-SW Respiration					*not enough rates for any analyses										
	UI-SW + glu Respiration					-0.35	-0.35	0.23	0.38	-0.10	0.23	-0.18	0.38			**0.97**
	UI-SW Incorporation					**-0.99**	**-0.97**	**0.91**	**0.99**	0.21	0.76	**-0.99**	**0.91**			0.79
	UI-SW + glu Incorporation					*not enough rates for any analyses										

Environmental characteristics were measured from different sources of ice core melt depending on availability. (A) represents characteristics measured from ice core melt 1:1 diluent, (B) represents characteristics measured directly from a 10cm slice of ice core corresponding to the depth used in each analysis, and for bacterial abundance (C), the cell counts from 1:1 diluent were subsequently doubled to represent an estimate of cell counts in the original undiluted core. Dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), and dissolved organic carbon (DOC) were not measured in ice core samples, while pH and total alkalinity were only measured in ice cores. Rates represented in pM·hr are in Table 9.