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Sampling techniques for sediment pore water in evaluation of reactive capping efficacy

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SAMPLING TECHNIQUES FOR SEDIMENT PORE WATER IN EVALUATION OF REACTIVE CAPPING EFFICACY

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THESIS

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Date

DEDICATION

This thesis is dedicated to the women of my life. To my granddaughters, Makayla, Marissa and Skyla, who think Grampa is the greatest. To my daughters, Keri and Cindy, who think Dad is the smartest but stills needs their guidance. To my mother who feels her son may finally be meeting his potential. Most importantly it is dedicated to my wife, Sandy, who has shared all the ups and downs of my journey. It is tough being married to Peter Pan.

ACKNOWLEDGEMENTS

Ending retirement and going back to school has been a tremendous adventure. I met some great people who helped me reach my goals. I would like to thank Dr. Kevin Gardner for making this journey possible. His patience allowed me the time to enjoy the whole process. I wish to thank Dr. Jeff Melton for his support. His input in the peeper designs was very helpful. I would also like to thank my other committee member, Dr. M. Robin Collins. Doc Collins had to put up with me every semester in his classes and I will never look at water the same way again.

Attending the University of New Hampshire, and being a member of the ERG community in particular, was very fulfilling. Every member of the Environmental Research Group from Maddy to Geri and Ron to Kelly did everything they could to help me succeed. My fellow students were terrific and we bonded in the team projects and study groups. I especially enjoyed the football and whiffleball games beside Gregg Hall. The professors at UNH, like Doc Collins, Dr. Malley and Dr. Kenner made challenging classes fun and spent an enormous amount of extra time with us.

I would like to give special thanks to Deana Aulisio and Scott Greenwood. Their help in the lab and on field projects was invaluable. Scott was a terrific mentor. He patiently answered questions, sometimes over and over.

Go Wildcats!

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ABSTRACT

SAMPLING TECHNIQUES FOR SEDIMENT PORE WATER USEFULNESS IN EVALUATION OF REACTIVE CAPPING EFFICACY

By

Donald E. Wise

University of New Hampshire, September, 2009

Contaminated sediments are a significant problem that has adverse effects on human, animal and plant health. Heavy metal contamination, with dissolved metals being the most bioavailable form, has been occurring since man first started living in communities around water bodies. Pore water provides contaminated metals a medium for transport from the sediment to the water body. Determining the toxic metal concentration in pore water is essential to any remediation plan. In-situ dialysis samplers or peepers were investigated in this thesis as a tool for evaluating metal contamination in sediments. Peeper performance was compared to direct suction samplers. Both samplers were evaluated for effectiveness in determining geotextile reactive cap efficacy.

The industry standard, as defined by Richard Carignan from the University of Quebec at Montréal, is to eliminate oxygen in peeper material, preparation and sample removal. Studies preformed by Carignan indicated oxygen caused redox

sensitive metals to precipitate, resulting in lower concentrations. Oxygen in peeper material resulted in an orange tint on the peeper and membrane. It should be noted that the majority of his studies were performed at the bottom of freshwater lakes. Deoxygenating peepers is a time consuming and complicated operation. The theory evaluated in this thesis is that oxygen effects are mitigated during peeper equilibration. Equilibration time allows oxygen to be dissipated into the surrounding sediment or consumed by microbial activity.

The effects of oxygen introduced during preparation were evaluated by comparing peepers assembled with makeup water purged with air and nitrogen. These effects were examined in field studies in the intertidal zone and in tub in laboratory studies. Sample removal compared filtering with unfiltered samples to evaluate whether colloidal phases could form in the chambers and affect measured concentrations. Samples removed with the use of a nitrogen purged glove box were compared with the standard removal procedure. Analysis of redox sensitive metals, anions and the selected heavy metals indicated oxygen was not a problem in the preparation or sample removal. Results indicated orange tint was dependent on sediment type and not peeper material.

The push point sampling device yields a sample with a minimum of effort and training but it is only effective in loose, sandy sediment. The prevailing evidence is that push point yields a higher concentration than those obtained with peepers. The difference is not so great that it does not preclude using the devices together as part of the overall sampling plan.

CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Contaminated sediments are a significant problem that has adverse affects on human, animal and plant health. They have been identified as one of the main reasons for over 3,200 fish consumption advisories sited by the USEPA (2008). Heavy metal contamination of sediment has been occurring since man first started living in communities around water bodies (Stanley et al., 2007).

Methods for remediating contaminated sediment include natural recovery, dredging and capping. Dredging is used extensively to maintain navigable water ways and for removing contamination hot spots. Dredging is the most expensive option. There are also problems associated with how to treat and where to put the dredged material. Another difficulty with dredging is that a considerable amount of contaminated sediments are re-deposited down stream. Unless there are significant environmental health issues, natural recovery can be done (Bokuniewicz et al., 1997). Capping is becoming more of a choice to contain contaminated hot spots. New capping technologies, such as the geotextile reactive cap, are being investigated. Both natural recovery and capping require long-term monitoring.

One of the problems with capping with sand is the cap is usually thick. This thick cap can affect the water body depth and, thus, navigation. Geotextile reactive caps are very thin in comparison. The reactive cap contains layers with material such as phosphate to sequester metals and granular activated carbon that adsorbs organics. The geotextile cap presents a monitoring challenge. The geotextile material is tough and difficult to penetrate. Any device that punctures the cap will also provide a route for the pore water to channel through it, which reduces the caps efficiency.

Dissolved heavy metals are the most bioavailable form of metal contamination and, therefore, have the most adverse biological effect (Bufflap and Allen, 1995). Pore water provides heavy metals and other contaminants a medium for transport from the sediment to the water body. Determining the toxic metal concentration in pore water is essential to any remediation plan. Pore water can be analyzed ex-situ by *grabbing* a section of sediment then removing the pore water from it. A pore water sample may also be obtained in-situ by a device that only collects the pore water. Collecting only the pore water reduces artifacts from the sampling process.

Examining in-situ pore water sampling methods is the primary purpose of this thesis. Determining a device and method that can be used to evaluate the effectiveness of geotextile reactive caps is also a major goal.

1.2 Oxygen Affects on Sediment Sampling

Below the sediment water interface, pore water is usually anoxic. Any oxygen introduced into a pore water sample becomes a primary source of analysis error (Bufflap and Allen, 1995). The effects of oxidation are particularly seen in redox sensitive metals, like iron and manganese. Oxidation can lead to both increased and decreased levels of dissolved metals subject to sediment characteristics.

Anoxic pore water generally has a high concentration of sulfide. The low soluble metal sulfide complexes are not considered bioavailable or toxic. Introducing oxygen into the sediment with a high sulfide level will cause the metal speciation to change, thus becoming more soluble. Chapman et al. (2002) stated this will lead to a sample that appears to have more bioavailable metals. Their study noted that the release of iron and manganese was faster than that of other heavy metal sulfides such as cadmium and lead. In highly sulfidic sediment, oxidation can lead to samples that show higher metal concentrations.

Richard Carignan, from the University of Quebec at Montréal, performed studies on in-situ dialysis sampling device preparation, material and sample removal. The field portions of Carignan's studies were performed mostly at the bottom of lakes in Canada and northeastern United States. Peepers were inserted and retrieved by divers or power insertion devices. These studies showed the introduction of oxygen caused redox sensitive metals to precipitate. The resulting samples had lower concentrations of metals then were actually in the sediment. His study on device material found that oxygen leaching out of plastic caused the redox sensitive metal, iron, to precipitate within the device. He found that atmospheric oxygen introduce during sample removal has the same affect. In Carignan's preparation experiment, he determined that oxygen in the makeup water showed lowered metal concentrations. He stated that the oxygen migrating from the device cause metals in its vicinity to precipitate. Carignan's work has been cited in many papers and books as the preferred method for deploying in-situ dialysis sampling devices regardless of the type of sediment being tested.

The Carignan and Chapman studies showed that oxygenation during the sampling process can result in differing levels of metal concentration. Both studies cited the effects were greater on redox sensitive metals. Whether oxygen introduction caused more or less metals in the sediment, it must be taken into consideration during the sampling process.

1.3 Thesis Objectives & Experimental Approach

Preliminary research determined that the in-situ dialysis sampler, or peeper, was an effective method for in-situ sampling. Peepers have been used since the 70s for sediment sampling. The main objective of this thesis is to evaluate the performance of the peepers in the top one foot of sediment. Studying the affects of oxygen will be a significant portion of the evaluation. Deoxygenating peepers is a time consuming and complicated operation. It is made more difficult when preparing peepers for sites that are a long distance from the laboratory. If oxygen affects are proven not to be a problem, then peeper preparation can be reduced by 48 hours. Not worrying about oxygen will also make transportation, insertion and sample removal much less complicated.

The theory put forth by this thesis is that oxygen effects will be mitigated the longer the peepers are left in the sediment. The extended time will allow oxygen to be dissipated into the surrounding sediment. Microbial activity will reduce oxygen effects by consuming any available oxygen as a terminal electron acceptor. The elimination of oxygen in the sediment adjacent to or in the peepers will also alleviate any indirect effects, such as adsorption to iron oxide precipitate surfaces, to heavy metal concentration analysis.

Experiments in this thesis will evaluate the oxygen affects by looking at equilibration and post equilibration peeper samples in a variety of sediments. The redox sensitive metals, Fe and Mn, plus selected heavy metals will be examined to determine oxygenation effects. The peeper's performance will be compared to the push point direct suction sampler. Sample removal techniques for both devices will also be evaluated. The information obtained will allow a method to be developed to evaluate the performance of geotextile reactive caps.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

2.1.1 Sediment Pore Water

Sediments are an important aspect of aquatic ecosystems. They provide an essential habitat for aquatic species' growth and reproduction (EPA, 2006). One of the earliest people to write about the properties of sediment was a Greek geographer named Strabo (64BC – 24AD). He described, "The soil is not only friable and crumbly but it is also full of salts and easy to burn out" (Mudroch et.al., 1995).

Sediments are composed of organic and inorganic particulate that have deposited on the bottom of water bodies (EPA, 2008). The organic particles consist of algal material, vegetation debris, organism secretions and remains (EPA, 2003). Gravel, sand, silt and chemical precipitates are the inorganic components of sediment. The material collects through deposition from current and tidal effects, storm water runoff, erosion, atmospheric deposition, chemical precipitation and organism excretions.

Interstitial or pore water is the fluid between the solid particles of the sediment. Pore water is comprised of dissolved sediment constituents, material from the water body above and the ground water that has flowed into it. Sandy sediments generally contain around 30% pore water. Although, different mixtures of sand and silt can contain as much as 99% pore water (Mudroc and Azcue, 1995). Movement of pore water through sediments is regulated by porosity and permeability (Chapman et al., 2002). Additional properties that affect the direction and velocity of interstitial water movement include sediment pore size, hydraulic pressure, ground water and tidal influences.

2.1.2 Contaminated Sediment

The EPA defines contaminated sediment as "soil, sand, organic matter, or minerals that accumulate on the bottom of water bodies and contain toxic or hazardous materials at concentrations that may adversely affect human health or the environment" (EPA, 2008). Contamination occurs when pollutants are added through natural means like storm water runoff, erosion, or wind deposition. They can also be added by anthropogenic means, which can accelerate the rate of accumulation, from sources like waste treatment plants. A "natural" contaminant is one that occurs without human introduction, whereas "anthropogenic" contaminants are produced through human activity. It should be noted that natural contaminants can also have anthropogenic origins (Adolphson, 1995).

Anthropogenic sediment contamination started when man first began living in communities. These early civilizations always grew up around water bodies. The water bodies provided needed resources to sustain life but were also used as waste deposits. Sediment cores taken from the Nile's delta indicated that a coastal population flourished in this area during Egypt's Intermediate (ca. B.C. 1000) and Late Dynastic (pre-Ptolemaic) periods. The cores from this period, that pre-dates Alexander the Great, showed elevated lead concentrations (Stanley et al., 2007). The advent of the industrial revolution is responsible for a significant increase in sediment contamination. For example, steel plants have flourished for more than a century and are responsible for elevated levels of organic compounds and heavy metals (Romano et al., 2004). The early electronic and metal plating industries also contributed metal and organic pollutants to sediments by discharging their toxic wastes and by-products. Contaminated sediments have been identified as the major reservoir for trace metals in coastal ecosystems. Redox conditions of sediment can be evaluated by the distribution of redox sensitive metals (Huerta-Diaz et al., 2007).

Through microbial activity, redox reactions, sorption processes and compound solubility, sediments are a “biogeochemical reactor. Pore water is the solvent for many of these activities. Therefore, understanding pore water chemistry will lead to a better understanding of contamination in sediments (Allen, 1995). More specifically, Carignan et al. (1985) noted the key to aquatic systems is a firm knowledge of trace metal dynamics near the surface of sediments. He also noted that trace metal concentrations in sediment pore water are usually no more than 10^{-7} mol/L. Metals are a conservative contaminant, they do not biodegrade, and their redox characteristics have been identified as one the major factors influencing their speciation and mobility.

Pore water is the main component of sediment capable of movement. The dissolved constituents in pore water can be actively transported to and from the sediment and water body above it. Pore water and solid sediment constituents can be stirred up by a storm or boat's propeller. They are then re-suspended in another area (EPA, 2008). Movement of the dissolved constituents through pore water can be caused not only by sediment movement or hydraulic gradients but by also by benthic, or bottom living, organisms. Worms and larva can cause these constituents to travel by bioturbation or bioirrigation (Chapman et al., 2002). Some organisms construct a "U-tube" in the sediment with their burrowing. These U-tubes will cause the overlying water to penetrate the sediment. Thus, allowing an exchange of dissolved constituents between the sediment and water column.

2.2 Regulatory Considerations

2.2.1 Introduction

Most laws governing contaminated sediments were not written specifically for them. Although, there are federal, state or local laws that pertain to the handling, treatment, disposal, and containment of contaminated sediment. There are also numerous organizations with responsibility for particular aspects of marine sediment. These include the U.S. Environmental Protection Agency (USEPA), National Oceanic and Atmospheric Administration (NOAA), US Army Corp of Engineers (USACE), US Geological Survey, Coast Guard and individual local and states agencies. The number of organizations dealing with contaminated sediments results in an inconsistent regulatory approach with no single authority geared specifically to the management of contaminated sediments (Bokuniewicz et al., 1997). Liu et al., noted in 1999 that a majority of sediment quality criteria was determined for a specific location. This inconsistent approach to remediation decision making can cause the implementation phase to take 3-15 yrs to start.

2.2.2 Regulations

One of the main driving forces for sediment management is maintaining navigable waterways. The Rivers and Harbors Acts (RHA) of 1890 and 1899 were the first regulations dealing with the area in and around a navigation channel. The legislation required the Department of the Army to remove obstructions or make alterations for any navigable water of the United States. Work such as dredging and disposal of dredged material, excavation, filling or other modifications are included in the regulations (FEMA, 2006).

The Clean Water Act (CWA) directs the EPA "to identify the location of in-place pollutants with emphasis on toxic pollutants in harbors and navigable waterways." It also authorizes the EPA, in conjunction with USACE, "to make contracts for the removal and appropriate disposal of such materials from critical port and harbor areas" (EPA, 2008). Although the CWA does not specifically regulate sediments, it controls point source discharges, toxics spills and regulates discharge of dredged material.

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), or Superfund, was created to protect communities from contaminated abandoned toxic waste sites. The EPA is responsible for conducting removal actions, identifying responsible parties, generating community involvement, and involving individual states to guarantee long-term corrective action of hazardous substances. The National Priority List (NPL) is used to prioritize the hazardous waste sites (EPA, 2008). As of 2001, there were 350 contaminated sediment sites identified. The sites in current remediation are using technologies such as dredging, in-situ capping and monitored natural recovery (EPA, 2003).

Marine Protection, Research, and Sanctuaries (MPRSA) act deals with unregulated dumping of material into ocean waters. The law was designed to protect human health, marine ecological systems, and economic potentialities (U.S. Senate, 1972). Under authority of MPRSA Section 102, the EPA and USACE are charged with developing discharge criteria for the dumping of dredged material in ocean waters. An ocean dumping manual or "Green Book" is used to determine the contaminant status of dredged material (EPA, 2008).

The Water Resources Development Act of 2007 was written to "provide for the conservation and development of water and related resources, to authorize the Secretary of the Army to construct various projects for improvements to rivers and harbors of the United States, and for other purposes" (H.R.1495). Some of the provisions of this law deal with projects for navigation, ecosystem restoration, and hurricane, flood, or storm damage reduction. It also authorizes projects associated with aquatic nuisance plants.

2.2.3 Agencies

Among the agencies concerned with contaminated sediment, the EPA is most concerned with public health. One of their main objectives is to reduce the risks posed by contaminated sediments. They published the "Framework for

Developing Suspended and Bedded Sediments (SABS) Water Quality Criteria" in May 2006. The primary purpose of this document is to provide guidelines for affected state and local authorities in "adopting consistent scientifically defensible SABS criteria". The document is a result of the CWA (EPA, 2008). The EPA also works with other federal agencies to implement the regulations.

NOAA has developed guidelines for screening concentrations of contaminants in a multitude of environmental media. The guidelines provide an informal, non-regulatory standard for analyzing chemical data and sediments. They can be found in NOAA "Screening Quick Reference Tables" or SQuiRTs.

Table 2.1: NOAA Sediment Inorganic Compound Concentration Guidelines

	Guidelines (ppm, dry wt.)		
Chemical	TEL	ERL	ERM
Arsenic	7.24	8.2	70
Cadmium	0.68	1.2	9.6
Chromium	52.3	81	370
Copper	18.7	34	270
Lead	30.2	46.7	218
Mercury	0.13	0.15	0.71
Nickel	15.9	20.3	51.6
Silver	0.73	1.0	3.7
Zinc	124	150	410

Table 2.1 shows NOAA's guidelines for inorganic compounds. Threshold effective level (TEL), effects range low (ERL) and effects range medium (ERM) values were calculated for trace metals, individual PAHs and PAH classes and several classes of chlorinated organic hydrocarbons. TEL defines the concentration level at which biological effects can be expected. ERL is intended

to represent concentrations below which effects are rarely observed. ERM values define concentration where adverse effects increase from 60% to 90% for trace metals and 80% to 100% for most organics (NOAA, 2006).

The mission statement of the USACE reads in part: "Planning, designing, building and operating water resources and other civil works projects (Navigation, Flood Control, Environmental Protection, Disaster Response, etc.)". Restoration and stewardship are the two major focus areas of the U.S. Army Corps of Engineers environmental mission. Every year the USACE oversees the dredging of approximately 300 million cubic yards of sediment. The dredging is done to deepen harbors and clear shipping lanes. Approximately 3 to12 million cubic yards of these sediments are so contaminated they require special handling (USACE, 2008).

Table 2.2: Washington Department of Ecology Sediment Quality Standards

	Sediment Quality Standards	Sediment Impact Zone Maximum Level
CHEMICAL	MG/KG DRY WEIGHT (PPM, DRY)	MG/KG DRY WEIGHT (PPM, DRY)
ARSENIC	57	93
CADMIUM	5.1	6.7
CHROMIUM	260	270
COPPER	390	390
LEAD	450	530
MERCURY	0.41	0.59
SILVER	6.1	6.1
ZINC	410	960

In conjunction with federal authorities, individual states have adopted guidelines for contaminated sediment. For example, Florida's guidelines are based on NOAA's standards and Washington State's department of Ecology has implemented "The Sediment Management Standards". Washington State's document contains two sets of numeric chemical criteria (WAC-173-204-320). These criteria, seen in Table 2.2, differ slightly from those of NOAA. They are based on amount of contaminant in a kilogram of sediment on dry mass basis.

2.3 Toxicity

Sediments act like a sponge removing contamination from the surface water. This reduces the direct toxicity to aquatic organisms in the water column (Bufflap and Allen, 1995). As the toxic material leaches back into the water column, it makes sediments an ongoing source of toxic substances even as the water meets quality standards (EPA, 1992). Anthropogenic actions that increase the naturally occurring concentrations of elements can make the contaminated sediment toxic and detrimental to the marine organisms (Adolphson, 1995).

Creatures in the benthic environment are most affected by contaminated sediment. These organisms include insect larvae, worms and crustaceans. Toxic substances can kill these organisms reducing their availability as a food source and the biodiversity of the benthic environment. Organisms that survive the toxins can cause adverse effects to the predators higher up on the food chain. The contaminant concentration can increase in these animal's systems through the process of "biomagnification". The toxins in the sediment then can cause harm, with chronic heath problems, or death to marine mammals, water fowl and fish (EPA. 2008).

Heavy metals can be a toxin to marine organisms. Copper, for example, is used as an herbicide in vessel bottom paint. Pore water is a key exposure route for heavy metals in sediment. The dissolved metals, the most "bioavailable" fraction of metals in sediment, can produce a significant amount of biological damage to benthic organisms. Although humic acid, sulfide and polysulfide complexes can be soluble, they are not considered bioavailable compounds. As a result, these complexes can cause an overestimation of their toxicity in pore water (Bufflap and Allen, 1995) (Chapman et al., 2002).

Toxicity of contaminated sediment is a significant problem for marine organisms. Since pore water is a primary exposure route, it is important to develop a credible method of sampling and analyzing contamination in sediment.

2.4 Pore Water Sampling

2.4.1 Introduction

The first sediment sampling was actually done as prospecting. As early as 1500 B.C., ancient civilizations used wooden shovels to look for gold, iron or copper in streams or at the edges of larger water bodies. Today's environmental studies require a wide variety of sophisticated sampling equipment. Each of these sophisticated devices and techniques comes with both benefits and drawbacks.

Although pore water sampling dates back to 1930 (Chapman et al., 2002), it is considered a relatively new technology. In 1976, Hesslein was one of the first to develop an in-situ pore water sampler. Pore water sampling is being used to evaluate the impact and transport of dissolved sediment components, equilibrium reactions, and chemical changes (Mudroch & Azcue, 1995). Howes et al. (1984) pointed out that there is a better understanding of analyzing methods for pore water than extraction techniques. Pore water extracted deeper than a few centimeters is usually anoxic, although, "surifcial" sediment shows signs of being aerobic (Liu et al., 1999). Bufflap and Allen (1995) found that the primary source of error in pore water sampling was oxidation of anoxic pore water. Therefore, care must be taken during extraction or the sampling method can change the chemical speciation and, therefore, its bioavailability (Chapman et al., 2002).

2.4.2 Sampling Devices

With any sampling technique, the purpose is to obtain an undisturbed sample of sediment or its pore water (Mudroch & Azcue, 1995). Carignan et al. (1985) indicated that trace metal concentrations in pore water rarely surpass 10^{-7} mol/L. Pore water sampling methods can be divided into two basic categories. Grabbers and cores are examples of devices that remove both sediment solids and pore water. Membrane dialysis and direct suction samplers are examples of devices that are intended to just remove pore water.

One of the advantages of ponar grab sampler and cores is they are effective in obtaining samples of benthic organisms along with the other sediment components. Like it sounds, the grabber uses a shovel like device to obtain a sample. Since pore water drains out of the apparatus upon removal from the sediment, it is ineffective in obtaining a pore water sample. The corer is a cylinder of varying length and diameter. The device is pushed into the sediment. Upon removal, a flapper valve causes a vacuum, allowing sediment to be collected. A high speed centrifugation, which may change some of the pore water characteristics, must be used to extract pore water from the sample.

Membrane dialysis and direct suction samplers will be discussed at length later in this chapter. Another device in this category is the "diffusive gradients in thin film" (DGT) sampler. It is a relatively new device that was invented by Davison and Zhang in 1994. Metals transfer through a diffusive gel at a rate controlled by the gel composition and thickness. The metals are absorbed onto the resin beads on the other side of the gel, providing an infinite sink (maintaining a zero concentration condition on that side of the gel). The device requires an average equilibration time of one day and yields a sample of the sediment's metal constituent concentration.

2.5 Peeper Samplers

2.5.1 Background

Membrane dialysis samplers or "peepers" were developed by Hesslein for sampling in the Florida Everglades. The Hesslein peeper and its modifications are extensively used for in-situ pore water sampling (Mudroc and Azcue, 1995). The sampler is inserted into sediment, allowed to reach equilibration with the pore water then removed. The device collects a sample that is an average of the pore water constituent concentration over the equilibration time. The peeper sample is an exact representation of sediment pore water. The device is used to determine concentrations of dissolved metals and organics as well as other pertinent chemical properties such as pH, conductivity or alkalinity.

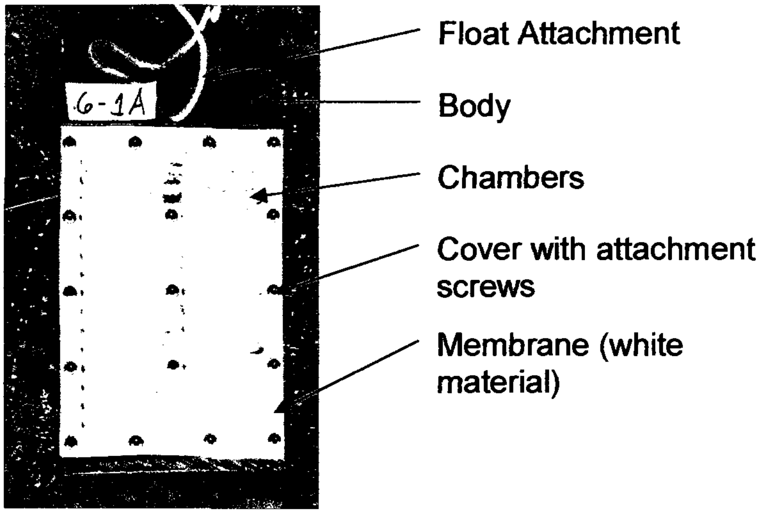


Figure 2.1: Modified Vertical Peeper

The peeper, also called a dialyzer, is made up of three parts. The body contains the chambers for sample collection. A porous membrane covers the chambers and is held in place by a cover. The discrete chambers are filled with distilled, deoxygenated water. The individual peeper parts are depicted in figure 2.1: Modified Vertical Peeper. A critical auxiliary component is the “peeper keeper”. The peeper keeper is used to prepare the deoxygenated water, store and transport the peeper to the sampling site. The keeper’s main purpose is to keep the peeper in a moist, clean, anaerobic environment prior to insertion.

The flexibility of the peeper makes it a useful sampling device for almost any sediment conditions. The chamber size, sediment contact area and membrane can be modified to maximize collection of the pore water constituent in question. For example the chamber volume can be increased for analysis of the same sample for heavy metals in an ICP mass spectrometer and anions in a colorimeter. Most designs feature a rectangular configuration, cylindrically arrangements are also common. Peeper designs vary from project to project based on the researchers needs.

2.5.2 Equilibration

Pore water constituents diffuse across the peeper membrane following Fick's laws of diffusion. The driving force of the flux, according to Fick's first law, is from areas of high concentration to low concentration. Following Brownian motion concepts, the constituents cross back and forth across the membrane until the pore water and fluid in the peeper are the same concentration. The equilibration time is reached based on Fick's second law. Pressure differential across the peeper membrane will also affect the rate the pore water constituents cross the membrane. Carignan confirmed, in his 1984 paper, that the most important factors affecting equilibration time are the diffusion coefficient, temperature and porosity of the sediment. He stated that, in general, the equilibration time for cold conditions is 20 days while for warm temperatures it is 15 days. Carignan stated in a 1985 paper that equilibration time will be different for different metals. The current industry standard is 3 to 4 weeks. This was confirmed by interviews with Michelle Lorah of USGS, Ryan Barth of Anchor Environmental and Jerry Morrison from the Rickley Hydrological Company.

Another factor affecting equilibration is the chamber design. The significant design features are chamber volume and contact area. The type and pore size of the membrane, a filtering device, is also a factor in determining equilibration time (Carignan et al., 1994). Reduction of the peeper width or increase in the sediment contact area will reduce the equilibration time.

2.5.3 Device Material

The peeper body and cover are made from a variety of plastic materials. The choice of materials is based on the sediment conditions and pore water constituents under consideration. The plastic materials most often used are acrylic plastic (PMMA), high density polyethylene (HDPE) or polycarbonate (PC). For example, the Rickley Hydrological Company uses acrylic plastic in the manufacture of their peepers, while the US Army used polycarbonate peepers at Aberdeen Proving Ground, MD in 1995.

Dr. Richard Carignan has written numerous papers on dialysis sampling methods and heavy metals testing in pore water. Three of those papers dealt in part with peeper materials. He has determined that oxygen diffusion from plastics will affect redox sensitive metals like iron, manganese and dissolved reactive phosphate (DRP). His studies showed that polycarbonate was a particular problem as an orange-yellow color was seen on the membrane and chambers of peepers. In his experiments, polycarbonate peepers always resulted in lower concentrations of the redox sensitive metals. A related problem with the precipitation of ferric oxide is that the precipitate has a tendency to adsorb other trace metals (Bufflap and Allen, 1995). This results in a lower concentration reading of heavy metals than is actually in the sediment.

Carignan et al. (1994) determined the percent volume of oxygen of several types of plastics. They also determined the half life time for oxygen to diffuse out of the plastics. Their results showed that HDPE had an O_2 %Vol/Vol of 0.6 with a half life 3.7 days. Acrylic and polycarbonate were 1.8, 3.7 O_2 %Vol/Vol and 5.7, 1.6 days, respectively. From this data, they determined polycarbonate was not a fit material for heavy metal studies. In a similar study by Huerta-Diaz et al. (2007) polycarbonate was blamed for artifacts resulting in lower ion concentrations.

The material used for screws to fasten the peeper components is another item that could lead to artifacts in trace metal sampling. Bufflap and Allen felt that nylon screws should be used to eliminate any contamination. However in a 1985 study, Carignan et al. did not observe any effects from stainless steel screws.

2.5.4 Membrane

The membrane type and pore size is the most important component of dialysis samplers. Early researchers, like Hesslein and Brandl, used a cellulose membrane. However, since cellulose membranes are subjected to microbial attack, it is generally recommended that a biologically inert material be used (Mudroc and Azcue, 1995). Most researchers are currently using polytetrafluoroethylene (PTFE), polycarbonate, nylon or polysulfone (PS) for inorganic constituents, like trace metals, for pore water sampling. Polyethylene (LDPE) or PS are generally used for organic compounds.

The membrane pore size controls what molecules are allowed to pass into the sample chamber. The operational definition for dissolved phases is "a substance that will pass a 0.45 µm pore size filter". This is an industry standard that is based more on a manufacturing or operating conditions than on scientific data (Mudroc and Azcue, 1995). Carignan et al. in 1985 determined that there was no significant difference in pore water constituents or concentration with pore sizes as small as of 0.002 µm. Their study showed a further reduction in pore size resulted in incomplete equilibration or exclusion of metal complexes. Allen (1995) determined that colloidal material passed through a 0.40 µm filtration membrane. However, Carignan showed that there were no artifacts from colloidal material diffusing through a 0.45 µm membrane. These studies have confirmed that using the common membrane sizes of 0.2 µm and 0.45 µm are effective for trace metals evaluation.

A web site useful for choosing membranes was compiled by Nobis Inc. Their "Guide to Membrane References" recommends a membrane type based on the material being sampled and device used. For each of their selections, they list an appropriate reference. The web site url can be found in the reference section.

2.5.5 Preparation, Insertion and Removal

The peeper, as with any sampling device, must be contamination free when inserted into sediment. Proper preparation of peepers is the key to eliminating any contamination. Oxygen contamination is believed to be a particular problem when studying trace metals. Oxygen contamination can cause artifacts during preparation, insertion or removal of peeper sampling devices (Carignan, 1984) (Carignan et al., 1994) (Bufflap and Allen, 1995) (Allen, 1995). To eliminate oxygen diffusing out of plastic peeper components, Carignan recommends they be kept under an oxygen free atmosphere for at least 30 days prior to assembly. The peepers must also meet trace metal cleaning standards. Most peeper related studies used Carignan's 1984 paper as their source for proper peeper preparation and sample removal.

Carignan stated that proper preparation of the make up water is a critical preparation step. To guarantee the make up water does not contribute artifacts, it should be distilled then deoxygenated by bubbled nitrogen for 24 to 48 hours prior to use. Allen felt the removal of oxygen was so important that he further recommended using argon, a heavier element, instead of nitrogen. As with peeper components, Bufflap and Allen affirmed that there were differences in iron, manganese and DRP concentrations in peepers assembled with de-aerated water verses water not de-aerated.

Assembling the peeper is a tedious operation. Peepers require between 10 and 30 screws to attach the cover. The assembled peepers must also be free of any air bubbles. To mitigate adding air bubbles, the assembly process is best completed under water using the make up water deoxygenated in the peeper keepers. After assembly, the peeper should be immediately placed into the peeper keeper. The peepers are then deoxygenated for an additional 24 to 48 hours prior to insertion into the sediment.

To avoid contamination, peepers must be inserted into the sediment immediately upon removal from the peeper keeper. Depending on the sediment characteristics, vertically inserted devices can be pushed in by hand or pounded in with a mallet. Divers are used when inserting peepers under more than a few feet of water. Care must be taken to not damage the membrane during this process. As with the peeper designs, the insertion method is based on what the researcher is trying to accomplish.

Sample removal is completed using a syringe after the peepers have been removed from sediment. The fluid removed from the chamber should immediately be put into a vial and then acidified for storage. To reduce any oxygen-related artifacts, Carignan recommends that sample retrieval be done with in 5 minutes of the peeper being removed from the sediment. A related study by Loder showed Fe (II) losses in peeper samples were 75% after a 12 minute exposure to the atmosphere while a study by Lyons et al. had losses of 81% in 10 minutes. Bufflap and Allen suggest using a nitrogen or argon filled glove box as part of the sample retrieval procedure.

2.5.6 Pros & Cons

As stated earlier, the peeper is flexible and easily modified to fit sampling requirements. Most peeper designs only cause a small disturbance in the sediment or cap. Owing to its in-situ nature, there are few artifacts from temperature changes or exposure to atmospheric oxygen during the equilibration period (Carignan et al., 1985). The dialyzer yields an equilibrated sample of pore water which makes it the preferred device for trace metal examination.

The biggest drawback to using peepers is preparation. Deoxygenating adds at least two days to peeper preparation. The preparation difficulty is greatly increased if the field site is a long distance from your laboratory. Ryan Barth, of Anchor Environmental, described soaking his hotel room trying to prepare peepers there. Previously prepared peepers sent to a field site for Dr. Jeff Melton, of UNH Environmental Research Group, arrived with a damaged peeper keeper. This necessitated deoxygenating the peepers in his hotel room bath tub.

Assembly is difficult due to the number of screws used to attach membranes and trying to keep air bubbles out of chambers. Small sample size and difficult sample removal are drawbacks. Despite its shortcomings, peepers have become a valuable tool for sediment pore water sampling.

2.6 Direct Suction Samplers

2.6.1 Background

Direct suction samplers are an active in-situ device designed to collect sediment pore water samples. Direct suction methods increased in usage in the seventies when concentration changes were discovered in samples extracted by squeezing or centrifuging sediment. The artifacts were attributed to temperature and pressure difference (Mudroc and Azcue, 1995). The squeezing or centrifuging related artifacts are mitigated due to a suction sampler's ability to directly extract the pore water from the sediment. Like the peeper, oxygenation will affect redox sensitive constituents.

2.6.2 Device Specifics

Samplers can be as simple as a glass modified volumetric pipette or a long needle with a plastic syringe. The sampler works by inserting a rigid tube, typically made of glass, plastic or stainless steel, into the sediment and extracting the pore water with a suction device. The tube is sealed at the bottom but has slots or holes for extracting pore water samples. A filter sock, screening, inline filter or air stone can be used to eliminate solid sediment components from entering the sample container. The suction device can be a syringe or a mechanical pump, usually peristaltic type. One benefit of these devices are that Inline sensors can be included that allows pore water characteristics to be obtained "real time". These sensors can measure pH, conductivity, temperature and dissolved oxygen. The pore water sample is discharged into a vial or sealed bag. Use of the bladder keeps the sample from coming in contact with atmospheric oxygen. This eliminates oxygen being a problem when collecting anaerobic pore water samples.

Commercially manufactured apparatuses, incorporated with suction devices specifically designed for them, are commonly used. The simplest commercial device is the MHE Push Point. This unit is a $^1/_8$ or ¼ inch diameter stainless steel probe that is effective for collecting shallow water samples. At the other end of the spectrum is Coastal Monitoring's Trident Probe. The Trident Probe, when incorporated with the UltraSeep Meter, allows direct measurement of sediment characteristics.

2.6.3 Pros & Cons

Direct suction samplers offer many advantages. They require little training and are not difficult to use. The portable device can be deployed by wading in shallow water, from a boat, or by a diver. The sampler works best in sandy loose sediment. The sampler's holes or slots can easily become plugged is in fine sediment. Direct suction samplers do not offer depth resolution (Bufflap and Allen, 1995).

Their small size causes very litter disturbance in the evaluation site, thus making them useful for evaluating caps, environmentally sensitive regions, or repeated sampling in the exact area. The size allows them to be used for collecting samples from rocky or cobble type sediment. Devices with attached measuring equipment in the probe area, like the Trident, are not effective in hard bottom conditions.

The ability of the suction device to obtain a sample is limited as the water pressure increases due to depth (Bufflap and Allen, 1995). For example, the Trident is limited to a 40 foot depth for its push pole deployment method. The EPA noted that temperature reading may be affected by thermoclines in the water body or sunlight effects on the equipment.

Larger devices can be used to collect benthic biological samples. Rostron et al. (2001) pointed out that strong suction can damage delicate creatures. There is also a concern that the strength of the suction will break up colloidal material, possibly increasing measurements of bioavailable concentrations.

CHAPTER 3

METHODS & MATERIALS

3.1 Methods

3.1.1 Introduction

Each study in this thesis was designed to examine more than one aspect of the hypothesis. For example, the equilibration study also examined oxygen effects in the peeper makeup water and filtering options in sample removal. Sampling devices evaluated by the studies were vertical peepers, push point direct suction device and horizontal peepers.

Table 3.1: Sediment Location and Characteristics

	Cocheco River	Merrimack River	Squamscott River	Cottonwood Bay
Location	Dover, NH	Haverhill, MA	Newfields, NH	Dallas, TX
Sediment Conditions	1st 5" to 7" sandy, below clay	Sandy throughout	Very fine & silty	Very fine & silty
Vertical Peepers	Field Studies	Field & Laboratory Studies	Field & Laboratory Studies	
Horizontal Peeper	Mat Insertion Study			Mat Insertion Study

Sediment classification and location of sediment sites can be seen in table 3.1. Sediment from the Cocheco, Merrimack and Squamscott Rivers were used for field experiments. Merrimack and Squamscott River sediments were used to evaluate sampling devices under laboratory conditions. Insertion techniques for evaluation of reactive mats were completed in mats at the Cocheco River and Cottonwood Bay. Cocheco River sediment is sandy for the first five to seven inches and clay thereafter. Merrimack River sediment is sandy throughout. Squamscott River and Cottonwood Bay sediments are very fine and silty.

The purposes of the device studies were to:

1. Evaluate impact of peeper preparation on concentration observed
2. Evaluate sample removal methods
3. To compare dialysis and direction suction samplers
4. Evaluate horizontal peeper insertion techniques

The peeper preparation portion of the experiments compared oxygen levels in the makeup water. Sample removal studies compared filtered and non-filtered samples. The removal step for one of the experiments compared sample exposure to atmospheric conditions with sample removal in a closed nitrogen system.

For each experiment, peepers were scrubbed by hand with Citrad concentrated acidic non-phosphate detergent. They were then cleaned in the automatic washing machine with non-phosphate soap. Each peeper was acid washed following the Environmental Research Group standard acid wash procedure.

The acid wash procedure:

1. Pre-clean item or soak in cleaning tub
2. Soak for 48 hours in 50% Nitric Acid
3. Rinse in RO water at least seven times
4. Dry in oven (optional)

The peeper keepers and their components were washed by hand with the non-phosphate soap. They were rinsed thoroughly with RO water. Several cups of acid from the acid wash station were added the peeper keepers. The keepers were sealed then rotated so acid completely covered the inside. The acid was drained from the keepers and they were rinsed with RO seven times. The peeper keepers were subsequently rinsed with distilled RO water. With the exception of the bubbling stone, the peeper keeper components were soaked in the acid from the acid wash station for five minutes. These components were rinsed individually seven times with RO water. They were subsequently rinsed with distilled RO water. The keeper and its components were assembled and filled with distilled RO water.

The appropriate gas was bubbled into the peeper keeper for at least 24 hours prior to peeper assembly. The peepers were assembled under water, using the appropriate makeup water (bubbled air or nitrogen). The assembled peepers were placed into the appropriate peeper keeper and gas was bubbled for at least twenty four hours prior to insertion.

Peepers were transported to the evaluation site in the peeper keepers. The peepers were inserted immediately after being removed from the keeper. Peepers inserted into the Cocheco and Merrimack River's sediment were driven in with a hammer. Peepers in Squamscott River sediment were pushed in by hand. Each peeper's location and depth was recorded.

3.1.2 Equilibration Studies

The purpose of the equilibration experiments was to determine how long the peepers took to reach equilibrium in a variety of sediment types. Since these studies were performed in conjunction with the preparation experiments, they are also expected to show the effects of oxygen during the equilibration process. The experiments were performed under field and laboratory conditions.

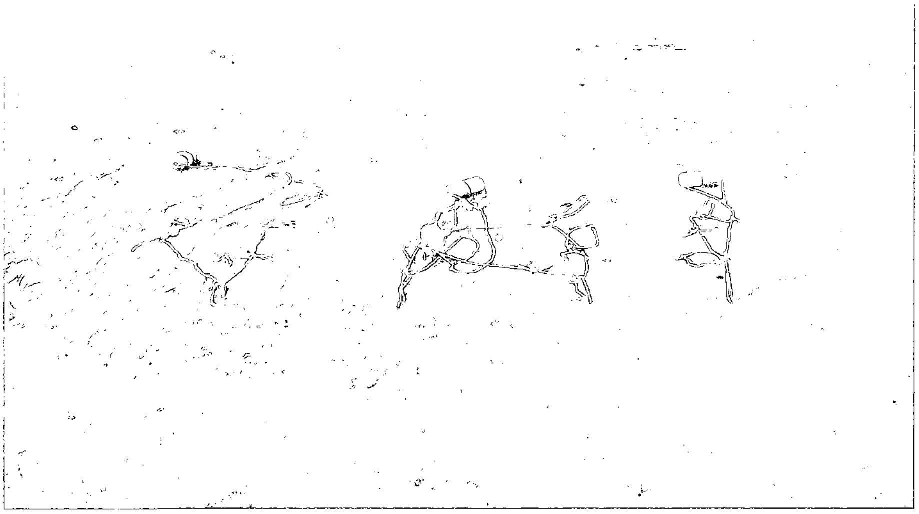


Figure 3.1: Cocheco Field Equilibration Matrix.
Peeper inserted in sediment to top of peeper. Peepers were grouped four to a row. Each group was attached to a float. The peepers from each group were removed on the same date.

The Cocheco River field study involved inserting five sets of peepers. The first four sets included four peepers that were also part of the preparation experiment. The last set had two peepers. The peepers were removed at weekly intervals for one to five weeks. A four by four matrix of was used for weeks one through four. Two peepers were inserted for week five. The peeper orientation can be seen in figure 3.1 “Cocheco Equilibration Matrix”. The peepers were inserted into the sediment in the intertidal zone at low tide. They were driven in so their tops were even with the top of the sediment. A loop was tied to each peeper then each row was attached to a float.

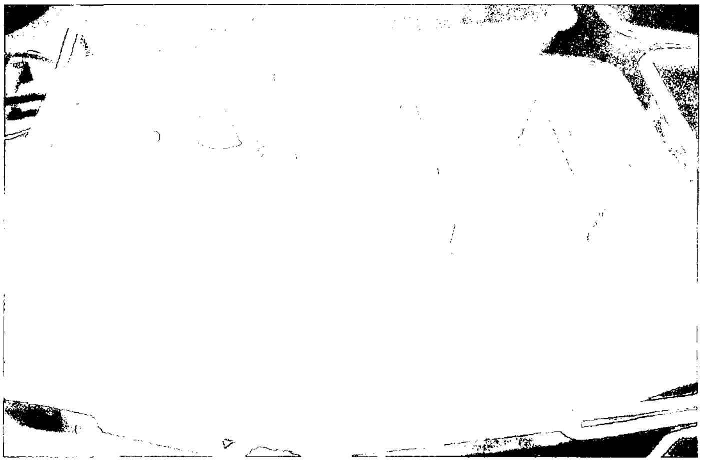


Figure 3.2: Laboratory Equilibration Layout.
Sediment tub with 1” of river water. Bottom of chamber #2 of peepers set at sediment/water interface.

Four peepers were put in tubs with sediment either from the Merrimack and Squamscott Rivers for the laboratory equilibration study. Each tub had at least 1” of the appropriate river water covering the sediment. The river water was exposed to the top two chambers of the peepers. The peeper layout is shown in figure 3.2 "Laboratory Equilibration Layout". Samples were extracted at weekly intervals starting with week two and ending with week five.

3.1.3 Post Equilibration Studies

The post equilibration studies evaluated peepers that already reached equilibrium with the pore water in the sediment. These peepers were in the sediment for four to five weeks. The experiments were run in conjunction with the preparation and sample removal evaluations. The laboratory experiments used the same tubs of sediment used during the equilibration studies. The peeper orientation was changed so different sediment came into direct contact with the peepers. The peepers were positioned in the field portion of these studies in a similar location as in the equilibration experiments. This allowed the last data point in the equilibration evaluation to be included with the post equilibration data.

3.1.4 Preparation

The preparation experiment was designed to evaluate the effect of dissolved oxygen in the peeper chambers prior to insertion. It compared makeup water that had oxygen removed by bubbling nitrogen gas into the peeper keeper with makeup water that had oxygen added by bubbling air into it. The oxygen effect will be evaluated by determining the concentration of dissolved iron species in the samples. Heavy metals concentrations will be examined to see if any are "co-precipitating" with or adsorbed the iron oxides.

A standard fish tank bubbler was used to add air. Ultra high purity nitrogen was introduced from a 300 ft^3 tank. Figure 3.3 shows the bubbler setups. The orange peeper keeper is attached to the fish tank bubbler while the blue keeper is attached to the nitrogen tank. Dissolved oxygen levels were measured with a YSI multipurpose probe before gas bubbling, prior to peeper assembly and prior to transporting to investigation site.

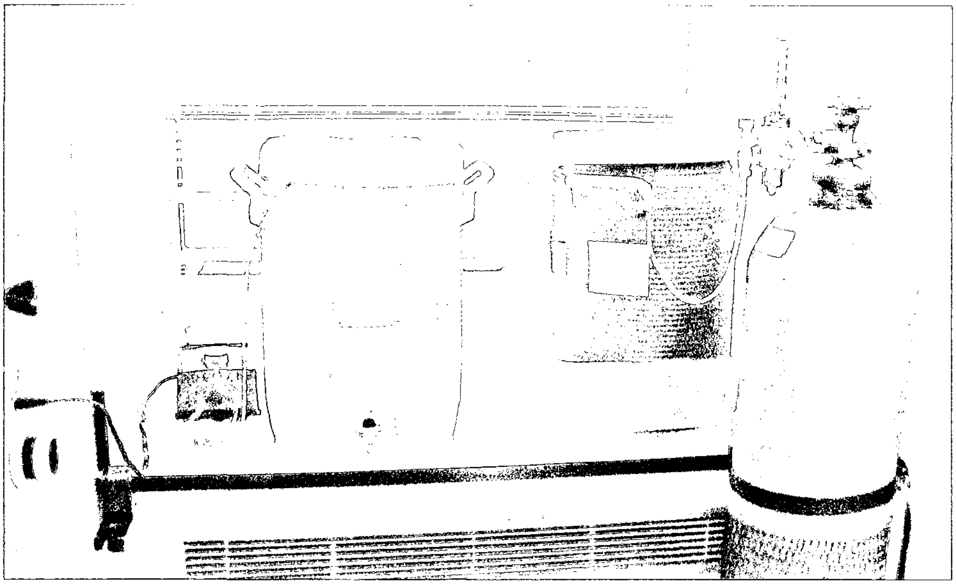


Figure 3.3: Makeup Water Preparation.
Orange peeper keeper with air bubbled. Blue peeper keeper with nitrogen bubbled.

The field study setup in the Cocheco River is shown in figure 3.1: Cocheco Field Equilibration Matrix. Samples were removed as part of the equilibration study. A set of two peepers, one prepared with air bubbling and one with nitrogen, were put into the Merrimack and Squamscott Rivers. They were inserted in the proximity of where the sediment was removed for the laboratory study. Samples from these peepers were removed after a five week equilibration time.

For the laboratory portion of the study, sediment from the Merrimack River was put into two tubs, as was sediment from the Squamscott River. One tub from each sediment type was labeled “Air” and the other was labeled “Nitrogen”. The arrangement can be seen in figure 3.4: “Laboratory Sediment Setup”. The light colored sediment on the left came from the Merrimack River. The darker sediment on the right came from the Squamscott River. Samples were extracted as described in the equilibration study.

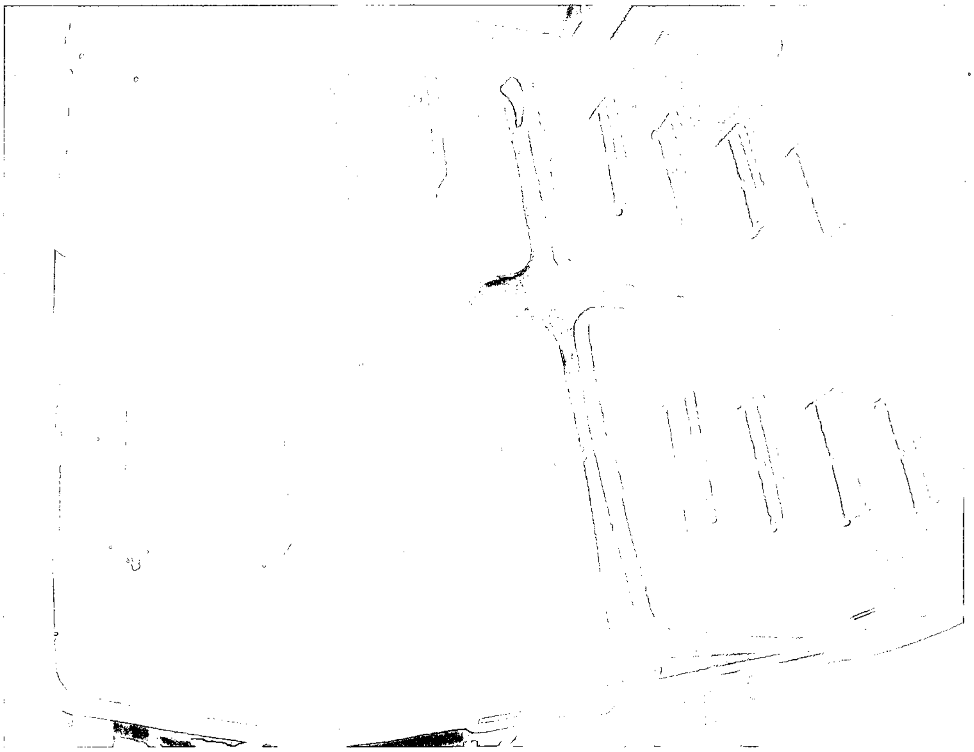


Figure 3.4: Laboratory Sediment Setup
Left tubs Merrimack River sediment. Right tubs Squamscott River sediment. Top tubs have nitrogen purged peepers. Bottom tubs have air purged peepers.

3.1.5 Device Comparison

The device comparison study evaluated pore water samples from vertical peepers and the push point direct sampling device. The purpose of this study was to compare results from the two devices. The study also compared push point extraction techniques. Standard procedure calls for removing pore water until the line is clear of most of the solids before collecting the sample. The study compared filtered, unfiltered and the initial unfiltered pore water samples with each other and the peepers. The purpose of filtering the direct suction samples was two fold. The first reason was to determine if solid components of the pore water are affecting the sample. Peeper samples go through a membrane as part of the dialysis process. Therefore, filtering push point samples will allow comparisons of device samples that have been through a 0.45mm filter. The extraction filtering technique will be discussed in a subsequent section.

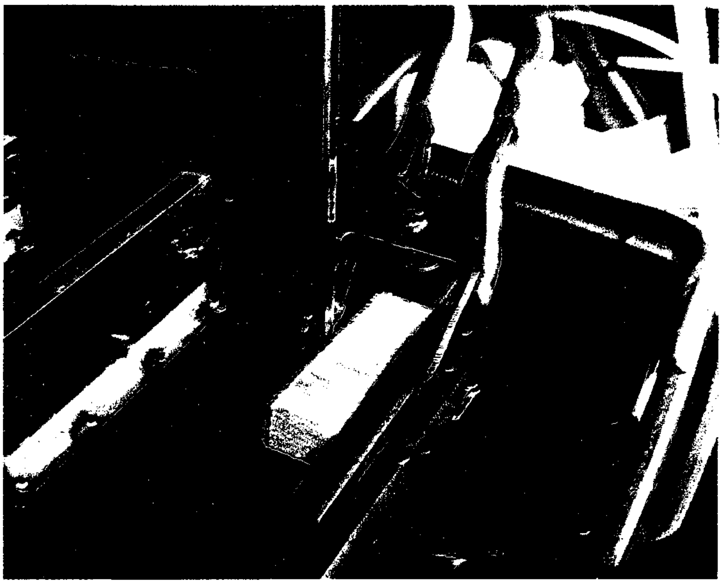


Figure 3.5: Push Point Extraction Setup
Push point extraction tube attached to peeper face with 1" thick block.

Push point samples were extracted approximately 1" from the face of the peepers just prior to their removal. The close proximity of the push point device was to extract pore water with the same constituent concentrations as was equilibrated in the peeper. The extraction setup can be seen in figure 3.5: “Push Point Extraction Setup”. The same spacer block was used for each extraction.

3.1.6 Extraction Techniques

In the first experiments, peeper samples were removed within two hours of peeper extraction. After it became evident that atmospheric oxygen may be causing a problem, sample removal started within five minutes of peeper extraction. A different disposable syringe was used for each of the peeper chambers. Figure 3.6: “Sample Removal with Syringe”, depicts a sample being removed from a peeper.

Figure 3.6: Sample Removal with Syringe

Part of the extraction procedure was to compare filtered and unfiltered peeper samples. This technique was designed to evaluate the amount of ferric oxide that may have precipitated in the chambers due to oxygen in the makeup water or device material. The comparison was conducted for both the equilibration and post equilibration studies. Figure 3.7: "Syringe & Filter" is a picture of the devices. Upon extraction of the sample, the needle is removed from the syringe and replaced with the filter. The sample is then pushed through the filter into a vial.

The syringe filter was used for the filter portion of the push point extraction study. Pore water was pumped into a vial from the suction device. The sample was then extracted from the vial with a syringe. It was then filtered, with the same technique as employed with the peepers, into a clean vial.

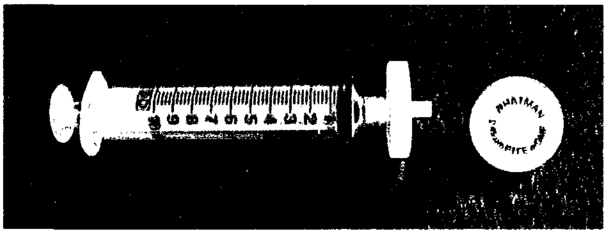


Figure 3.7: Syringe & Filter

Oxygen effects on sample removal were evaluated by comparing samples removed in a nitrogen filled glove box with those removed exposed to the atmosphere. This study was performed in conjunction with the laboratory post equilibration peeper experiment and the corresponding push point evaluation. For this study, all the needed sample extraction equipment was placed into the glove box. Nitrogen was forced into the vials and syringes to displace any oxygen. Time was allowed for the oxygen to leave the glove box before any samples were extracted. Peepers were immediately inserted into the glove box after removal from the sediment and the samples were extracted. The push point tubes were filled with nitrogen from the glove box prior to sample recovery. Afterwards, the samples were removed in the glove box using the previously defined push point procedure

3.1.7 Peeper Evaluation of Reactive Mats

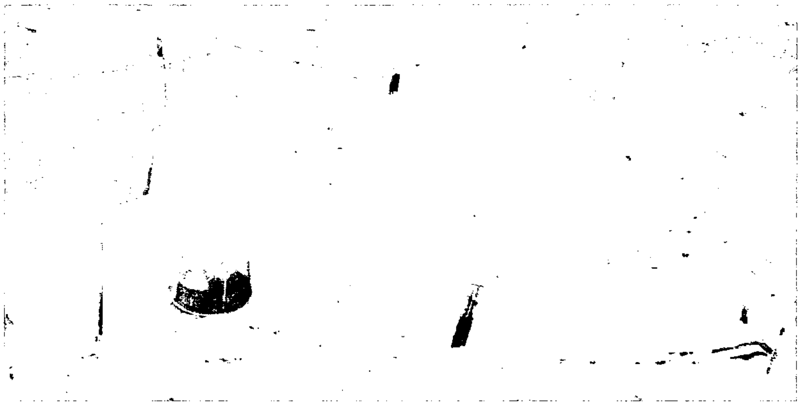


Figure 3.8: Cocheco River Reactive Mat with Peeper
Horizontal peeper is between strainer filled with sand and reactive mat. Paving block will sit on top of strainer to hold in place.

One of the objectives of this thesis was to determine the best method for evaluating the effectiveness of geo-textile reactive mats. It was determined, with significant input from Scott Greenwood, that the horizontal peeper design was the best tool for this purpose. Two field studies were designed to determine the best method for inserting the peepers. The Cocheco River study was performed on 6' x 6' mats previously placed in the intertidal zone. The corner of the mat was lifted to expose the sediment below it. A horizontal peeper was placed on top of the sediment and the mat was folded back over it. The method designed by Scott Greenwood for evaluating the top was to put the peeper inside a strainer lined with fine stainless steel screening and filled with sand. The strainer was flipped over on top of the mat above the peeper that was placed below the mat. The picture depicted in figure 3.8 "Cocheco River Reactive Mat with Peeper" shows the setup. A paving brick was placed on top of the strainer to hold it in place.

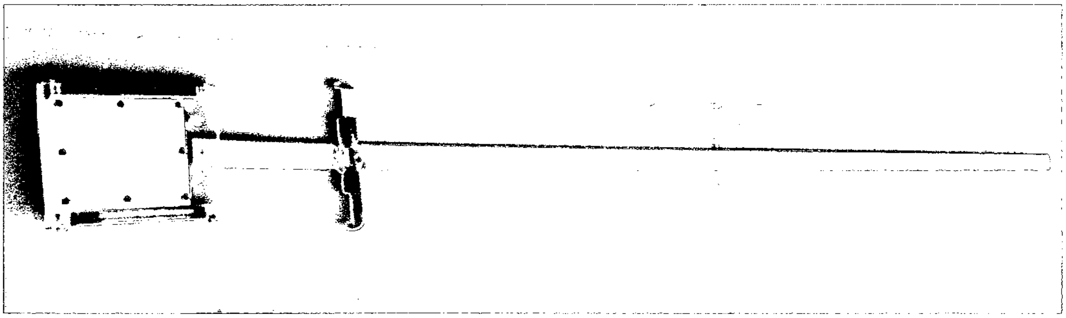


Figure 3.9: Horizontal Peeper With Bar & Attachments.
Two SPMEs are attached to the peeper sides. SPMD is attached to cross piece on bar.

The insertion exercise conducted at the Cottonwood Bay site was also designed in conjunction with Scott Greenwood. The Cottonwood Bay site has three mat arraignments that each covers a 25' x 25' area at a depth of approximately 6'. These arrangements include a mat with no cap, a mat with a sand cap and a double mat. A 5' multipurpose aluminum flat bar was designed to attach to the horizontal peeper to aid in insertion and removal. The bar was used to slide the peeper under the mats or between the double mats, approximately 4' in from the edge of the mats. The weight of the bar allowed it to be used to hold the peeper down when placed on top of the mats. Each bar was attached to one of the mat anchors. This was to keep the peeper secure and aid in finding them for removal. The insertions and removals were performed by a professional diver. The image in figure 3.9 shows the horizontal peeper attached to the bar with solid phase micro-extraction (SPME) and semi-permeable membrane (SPMD) sampling devices attached. These devices are designed to measure organic contamination in the pore water.

3.1.8 Analysis

A Varian AX Simultaneous Inductively Coupled Plasma Atomic Emission Spectrometer (ICP) was used to analyze pore water for twenty four metals. The list of metals included Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, V and Zn. Analysis for nitrate (NO_3^-), chloride (Cl^-) and sulfate (SO_4^{2-}) ions were performed on an ion chromatograph by the UNH Water Resources Research Center. The Water Resources Research Center also used a colorimeter to measure NO_2^- and the combination of $NO_3^- + NO_2^-$.

The amount of iron and manganese, redox sensitive elements, was used to determine the affects of oxygen on sample concentrations. Heavy metals with concentrations higher than the detection limits of the ICP were used to evaluate co-precipitation with iron and manganese oxides. The ions analyzed on the ion chromatograph and colorimeter were examined to understand the influence of oxygen.

Comparisons of metal and ion concentrations will be completed using the independent student's t-test. The equilibration study was evaluated by examining, on a line graph, time vs. concentration. Comparing the standard deviations of the points was considered for evaluating when the peepers reached equilibrium. Depth gradients were evaluated in a vertical bar graph.

3.2 Materials

3.2.1 Introduction

The sampling material and accompanying components are described in this section. Drawings, manufacturing specifics and descriptions of the devices designed by the author are included. These devices include the vertical peepers, horizontal peepers, the peeper keeper's inner components and the horizontal peeper insertion bar. Purchased devices, like the push point device and peristaltic pump, are described with their costs and purchase locations highlighted.

3.2.2 Vertical Peeper

The vertical peeper design, as described in section 2.5.1, is a modification of peepers availible from Rickley Hydrological Company. Those peepers were larger and more expensive than what was needed. The peeper body, seen in figure 3.10, has 15 chambers that are opened at the face. Twelve of the chambers have a volume of 13.5 ml. The other three chambers are split into two sections to accommodate attachment screws. The cover, seen in figure 3.11, is used to hold the membrane on the body. The cover configuration controls the active area of the peeper. For each chamber the active area is 1.688 in^2. The body and cover are attached with seventeen #10-32 5/8" long stainless steel screws. Socket cap screws were found to be easier to remove than Phillips head. Table 3.2 shows the part description, manufacturing/purchase location and cost.

Table 3.2: Vertical Peeper Purchasing Information

Description	Manufacturer/ Purchase location	Part #	Cost
Peeper Body & Cover	Plastic Supply Inc. 735 E. Industrial Park Dr. Manchester, NH 03709 800-752-7759 www.plasticsupply.com	Porewater Sampler Drawing 1-2 Mod 2	$86.88/unit
#10-32 5/8" long stainless steel screws	McMaster-Carr 562-463-4277 www.mcmaster.com	92949A267	$10.54/100

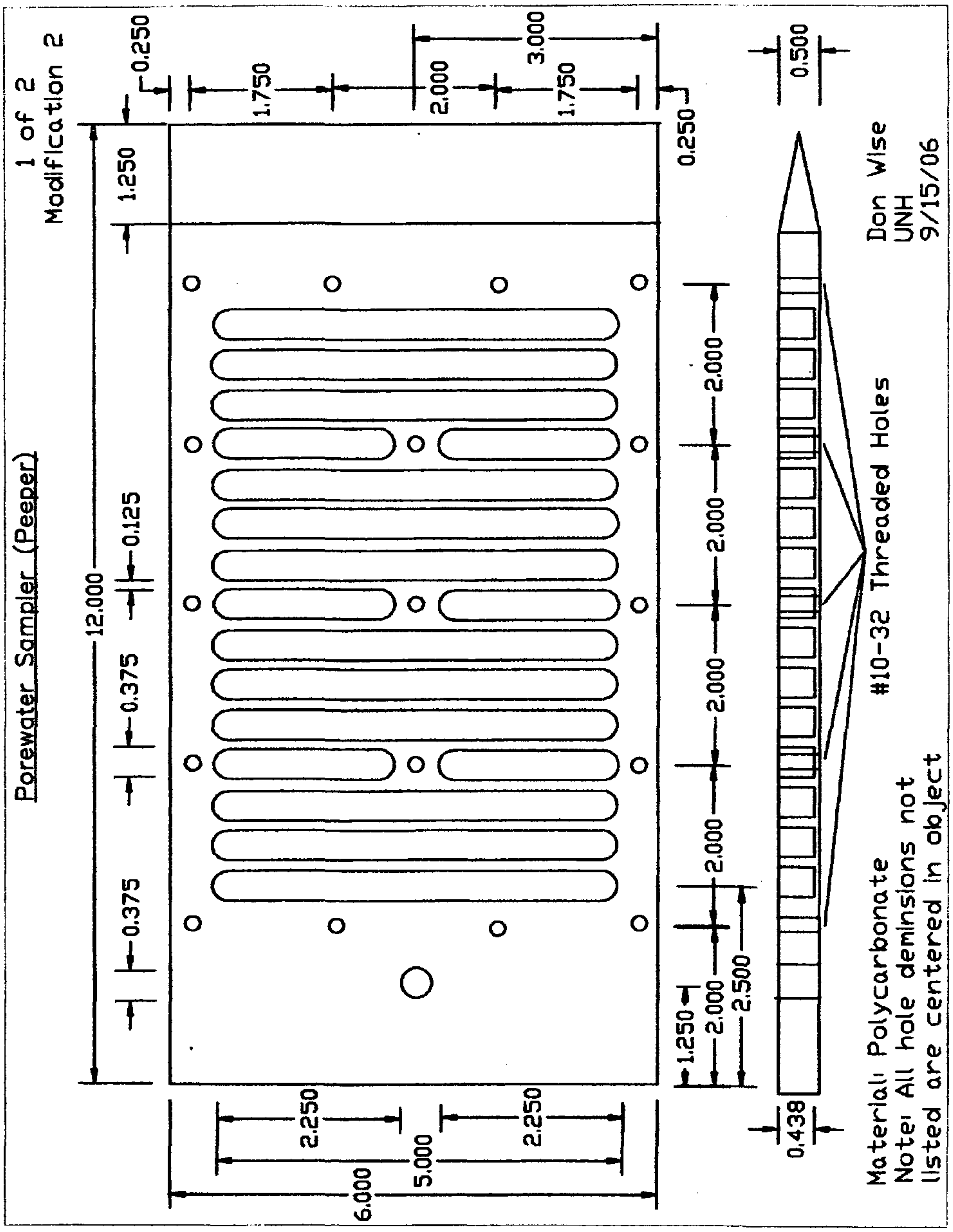


Figure 3.10: Vertical Peeper Body Drawing (1 of 2).

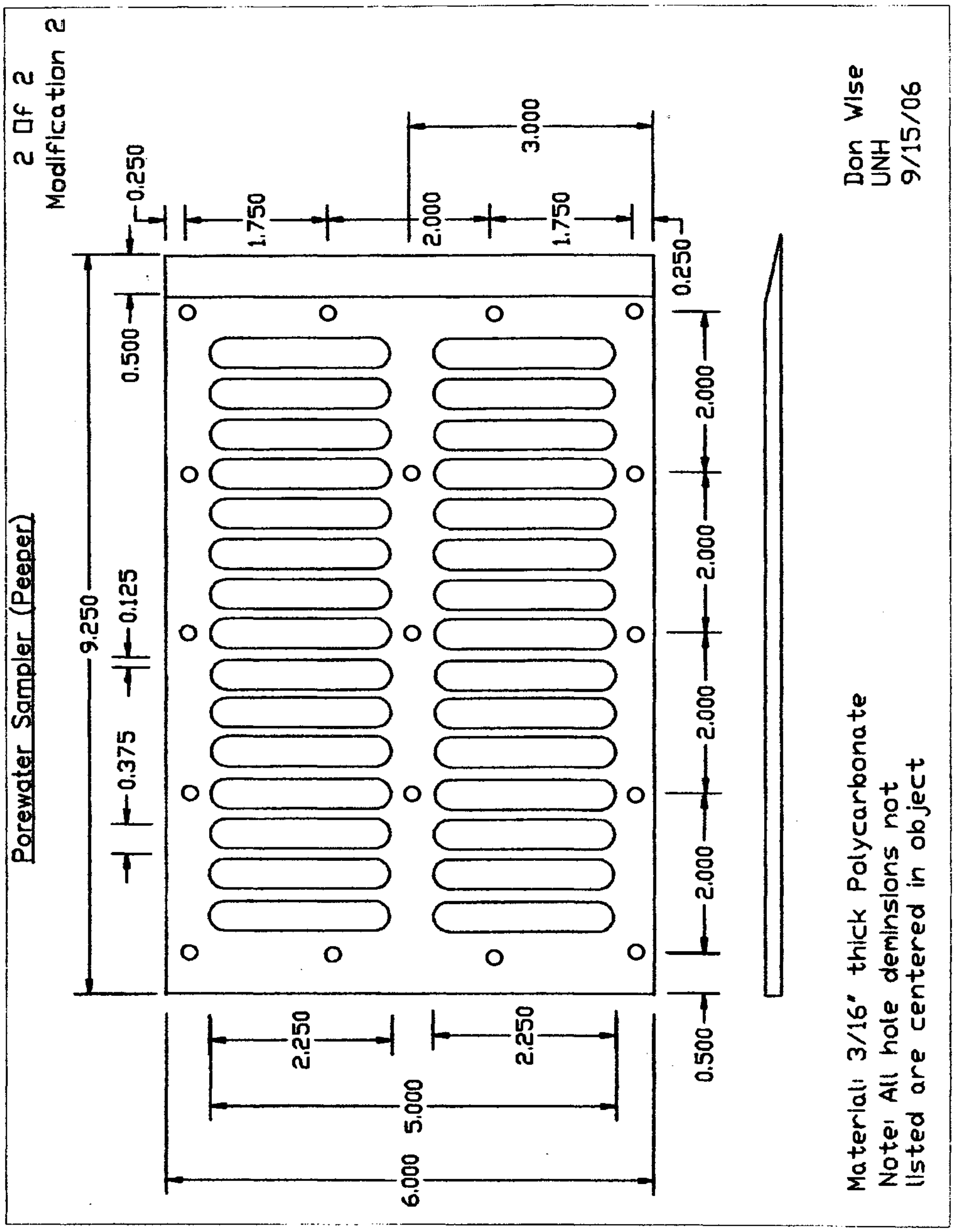


Figure 3.11: Vertical Peeper Cover Drawing (2 of 2).

3.2.3 Horizontal Peeper

The horizontal peeper design consists of three parts: a body and two covers. The body dimension and hole location drawings are shown in figures 3.12 and 3.13, respectively. The cover is shown the figure 3.14. The horizontal peeper is a three chamber device with the face and back open. The volume of each chamber is 27.5 ml. The body has two side attachment locations to accommodate SPME and SPMD devices. The cover openings are slightly smaller to help keep the syringe from penetrating through the back membrane when removing the sample. The resulting active area is 2.8 in^2 per side. Each cover is held in place with eight #10-32 5/16" long stainless steel screws for a total of sixteen screws per peeper. Phillips head screws were found to work well for the horizontal peepers. Table 3.3 shows the part description, manufacturing or purchase location and cost.

Table 3.3: Horizontal Peeper Purchasing Information

Description	Manufacturer/ Purchase location	Part #	Cost
Flat Peeper with SPME Chambers Body, Hole Layout & Cover	Plastic Supply Inc. 735 E. Industrial Park Dr. Manchester, NH 03709 800-752-7759 www.plasticsupply.com	Drawing 1-3, 1 Body & 2 Covers	$54.00/unit
#10-32 5/16" long stainless steel screws	McMaster-Carr 562-463-4277 www.mcmaster.com	91772A826	$9.74/100

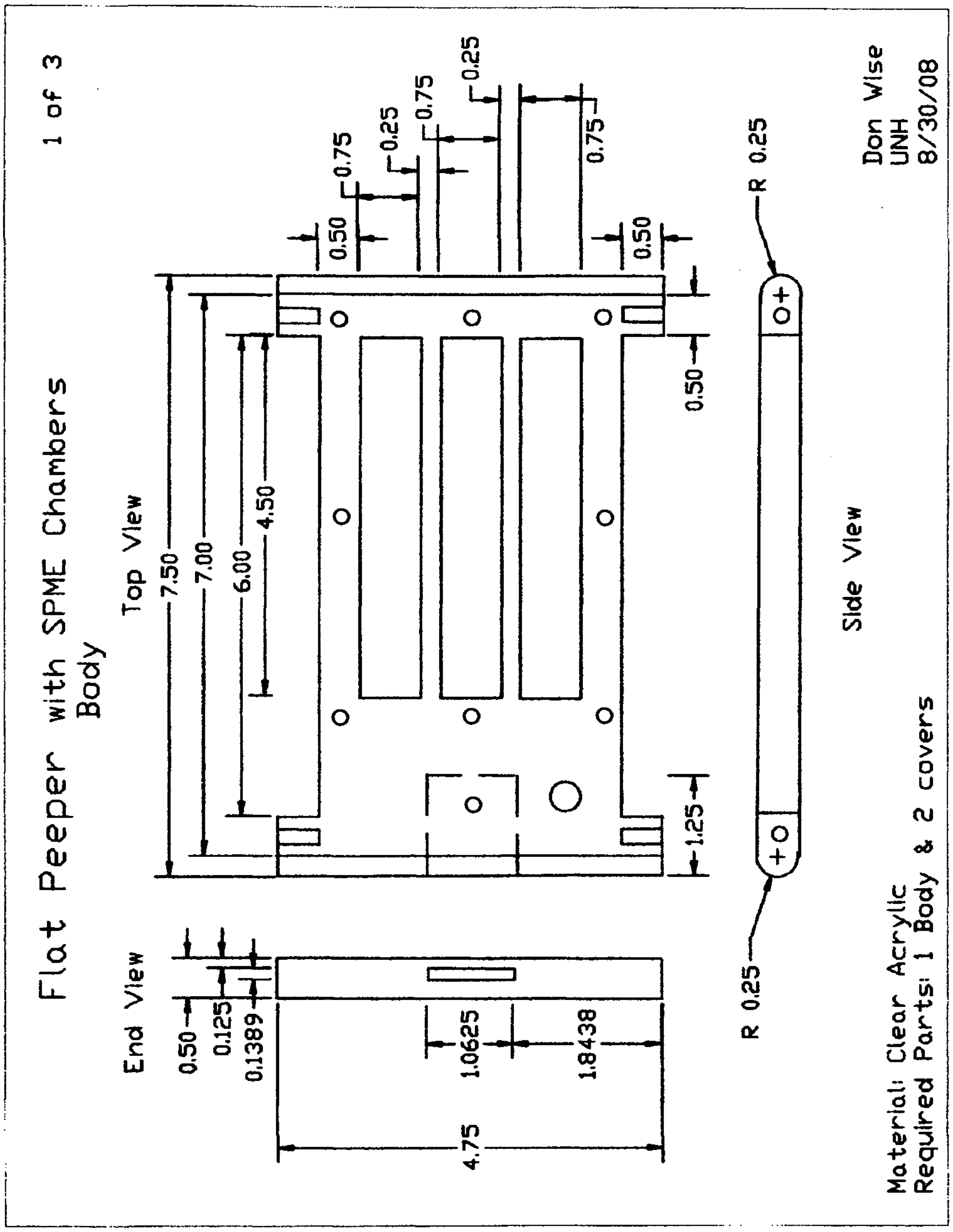


Figure 3.12: Horizontal Peeper Body Drawing with Bar & SPME Attachment sites (1 of 3).

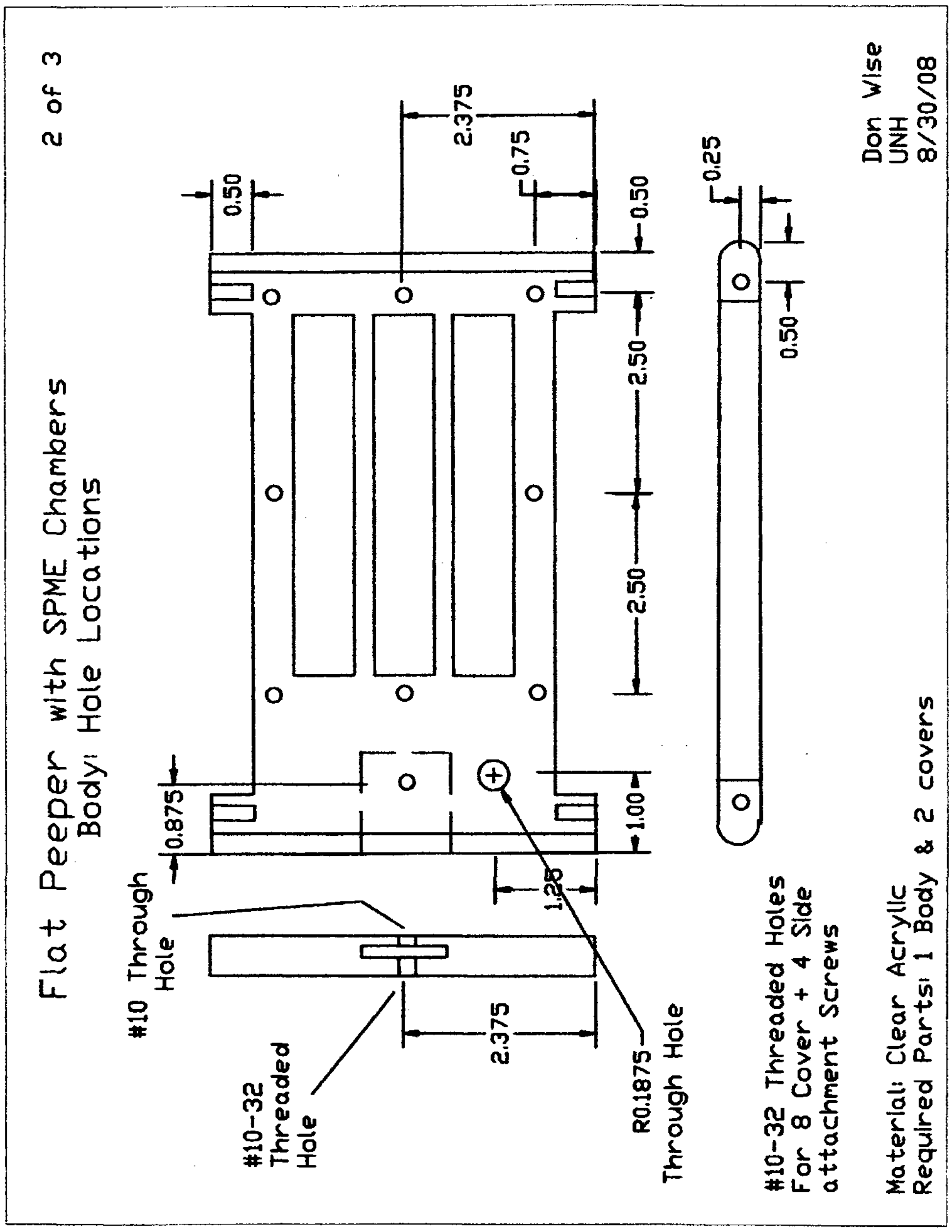


Figure 3.13: Horizontal Peeper Hole Location Drawing for Body with Bar & SPME Attachment Sites (2 of 3).

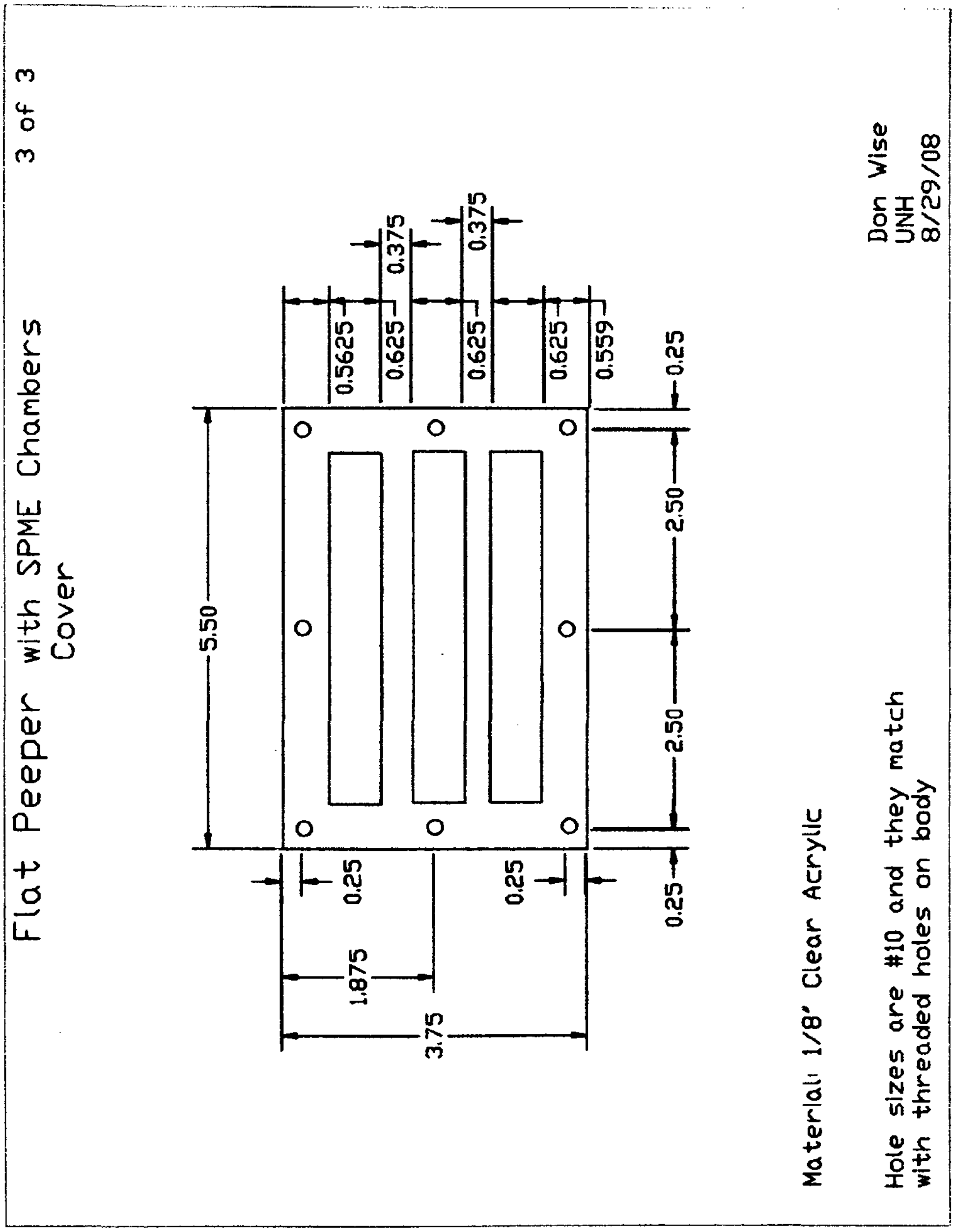


Figure 3.14: Horizontal Peeper Cover Drawing (3 of 3).

3.2.4 Membrane

The membrane chosen for these studies was the 0.2 μm HT Tuffryn© 200 membrane. A 12" x 50' roll was purchased from Pall Corporation (tel: 800-521-1520). The membrane's specifications can be seen in table 3.4.

Table 3.4: Membrane specifications

Filter Media	Hydrophilic polysulfone
Pore Size	0.2 μm
Typical Thickness	152 μm
Typical Water Flow Rate	14 mL/min/cm^2 at 0.7 bar
Cost	$282.80

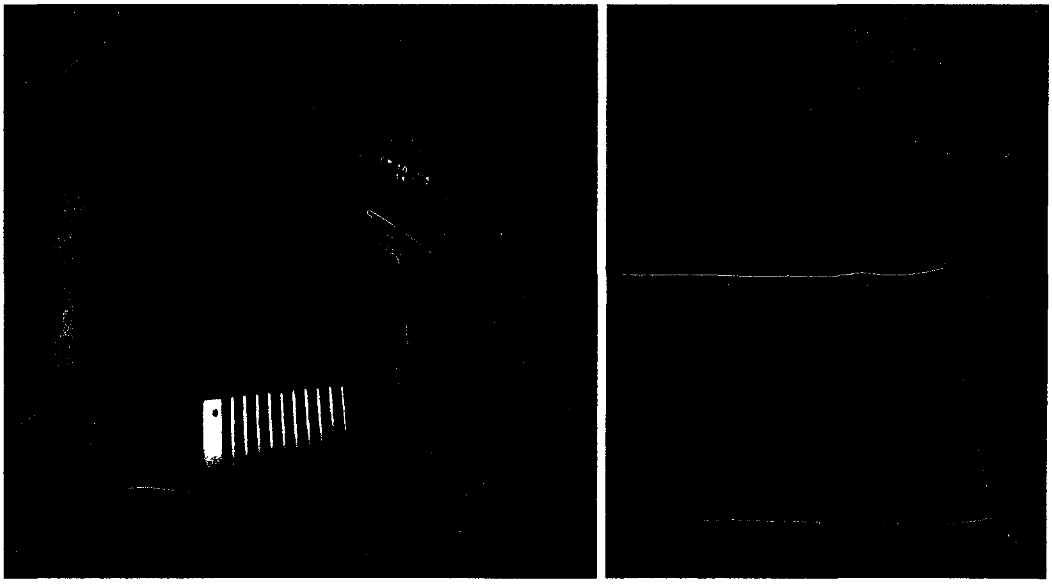


Figure 3.15: Membrane Roll & Sizing Equipment.
Peeper cover is used as template for cutting membrane to size.

Each peeper type required a different size membrane to be cut from the roll. Using the peeper cover as a template is the easiest way to guarantee the proper size. Care must be taken to keep the membrane free of any contamination. The equipment and cut membrane can be seen in figure 3.15.

3.2.5 Peeper Keeper

The purpose of the peeper keeper is to prepare the deoxygenated water and transport the peepers to the examination site. The keeper should be made of sturdy material to handle these functions. Rubbermaid® 5-gallon job site water cooler was chosen. A number zero rubber cork is used to seal the inside of the dispenser of the water cooler. The container can be seen in Figure 3.3: Makeup Water Preparation. A rack, made of acrylic, was constructed to hold the peepers above the gas bubbler. The bubbler was a standard fish tank bubbling stone. Figure 3.16 shows the internal peeper components.

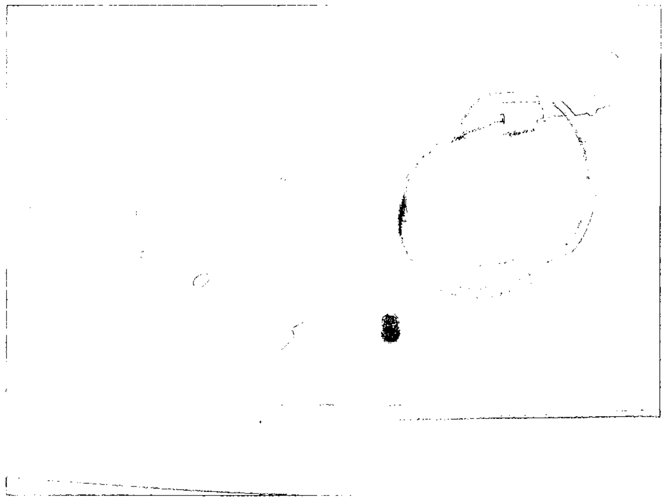


Figure 3.16: Peeper Keeper Components
Rack is used to keep peepers above aerator. Aerator is seen with attachment tubing. Rubber cork is used to plug keeper drain from the inside.

3.2.6 Push Point Samper

MHE Products Extreme (PPX36S) push point sampler was used in the device comparison studies. This direct suction sampler is a three foot long rigid 1/4-inch diameter stainless steel probe. Vertical slots are located one inch above the bottom of the unit. A battery operated Geopump™ peristaltic pump is used to pull the sample through the device and attached ¼" diameter tubing. The push point setup is shown in Figure 3.17 Push Point Field Setup. In the right side of the figure, the device is attached to a peeper. The pump and battery can be seen on the left side.

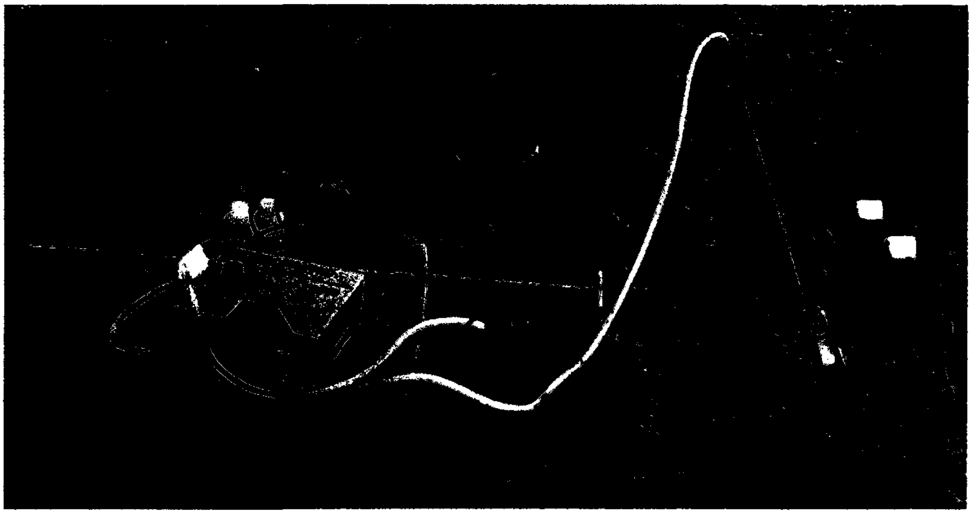


Figure 3.17: Push Point Field Setup.
Peristaltic pump with battery is attached with tubing to push point sample rod. The push point is attached to face of field peeper with 1" thick block separator.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Peeper Evaluation

4.1.1 Introduction

The purpose of the peeper evaluation section is to discuss the capabilities and limitations of the device. Selected data will be used to show how equilibration and depth profiling can be used to evaluate a contaminated sediment site. Each peeper was analyzed for twenty elements. This section will also determine which metals will be included for evaluating oxygen affects, peeper preparation and sample removal techniques. It should be noted that the laboratory tubs all exhibited out gassing when the peepers were inserted.

4.1.2 Heavy Metal Analysis

The first step in the analysis process was to determine which metals will be investigated. Iron and manganese were chosen due to being redox sensitive. To choose the other heavy metals to be analyzed, the results from each sediment type were examined to see which metals meet the selection criteria. The selection criteria included results from equilibrated peepers with chambers at least 1" below the sediment surface and concentrations above the minimum analysis detection level (MDL) in all sediment types. The selection criteria were determined so a consistent comparison can be made from the different sediment types.

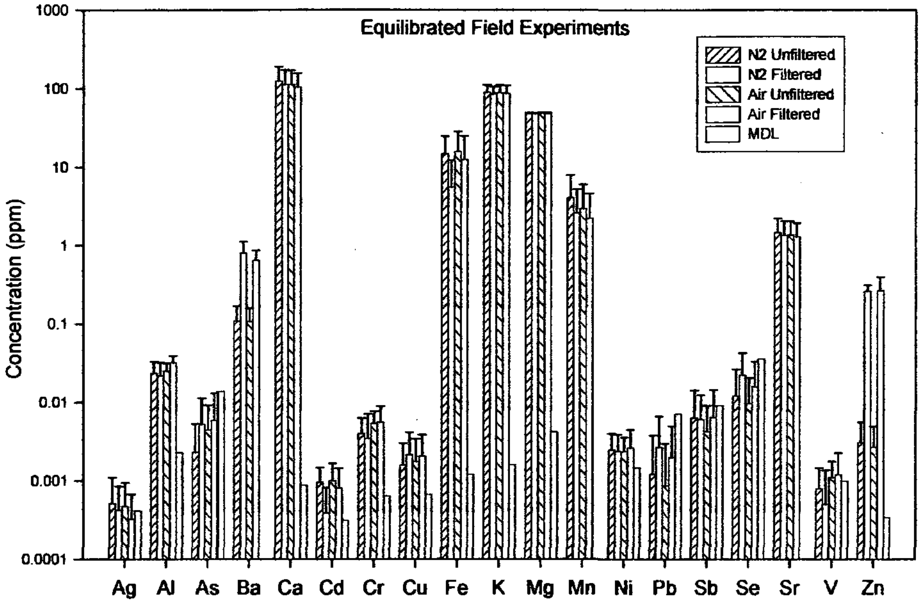


Figure 4.1: Cocheco River Sediment Metal Concentrations
Equilibrated field peeper sample concentrations. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers.

The data examined are from laboratory results of Merrimack and Squamscott Rivers and field results from the Cocheco River. The data was arranged in charts 4.1, 4.2 and 4.3. Each metal category is divided according to the purge gas and removal technique. The bar representing nitrogen purging is blue and the bar representing air is red. Unfiltered samples have hatched bars while filtered samples are a solid color. The fifth bar is the metal's MDL.

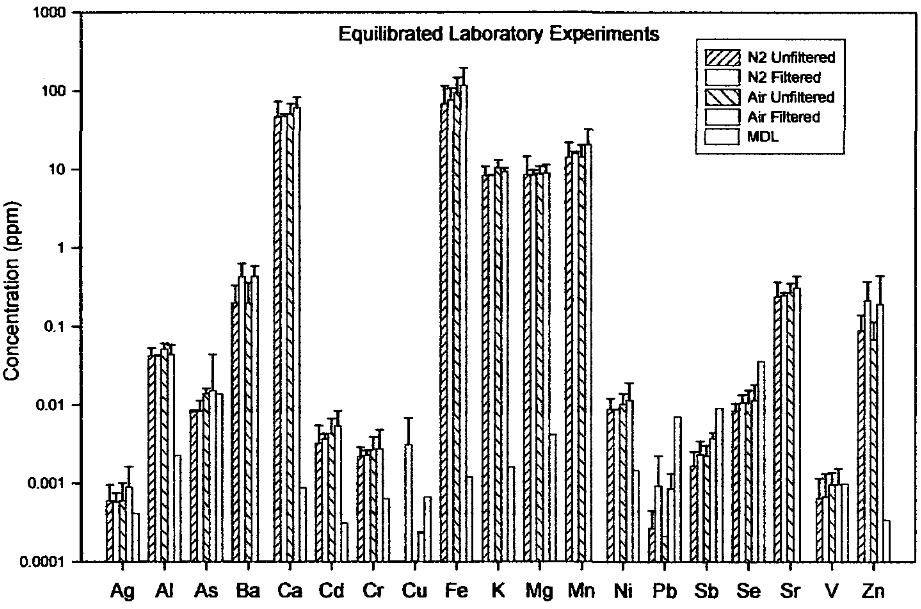


Figure 4.2: Merrimack River Sediment Metal Concentrations
Equilibrated laboratory peeper sample concentrations. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers.

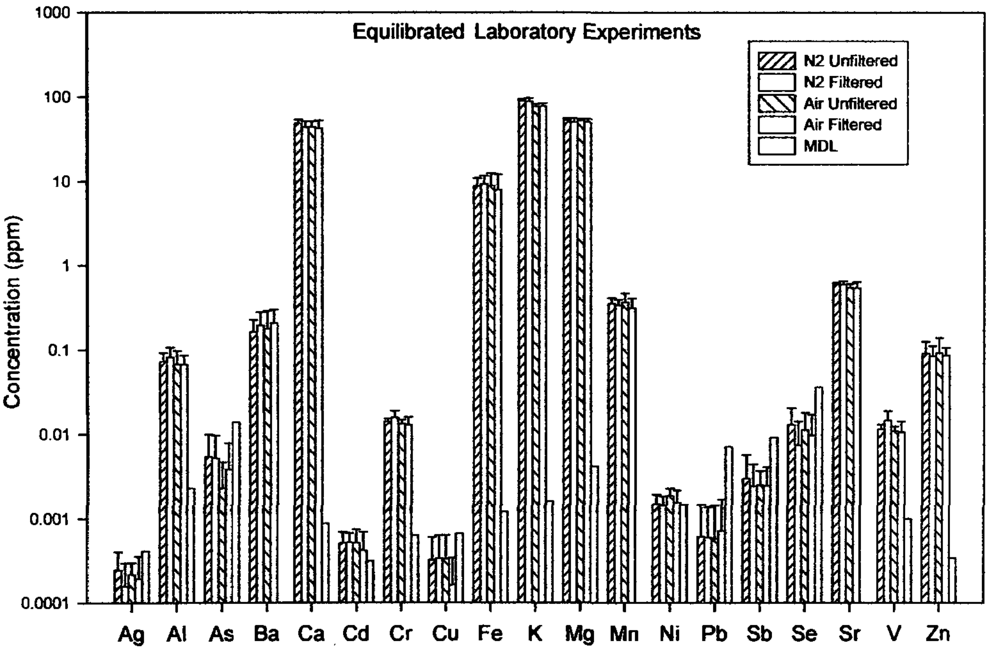


Figure 4.3: Squamscott River Sediment Metal Concentrations
Equilibrated laboratory peeper sample concentrations. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers.

Each sample required two vials, one for metal analysis by the ICP and one for anion analysis by the colorimeter. The colorimeter analysis requires vials to be topped off so there is no air pocket at the top. To accommodate the volume needs of the colorimeter, two chambers were needed to supply enough volume for each data point. This resulted in the fifteen chamber peepers being reported as seven samples. Sample one comprised of chambers 1 and 2. Sample two comprised of chambers 3 and 4. The pattern continued until chambers 13, 14 and 15 (the bottom chambers) were combined for sample seven. For the laboratory studies each peeper had the sediment water body interface between chambers 2 and 3. Chambers 3 through 7 were used for the analysis. For the field studies the equilibrated peepers (week five) from the equilibration/preparation studies were used. The peepers for the Cocheco field studies, which did not have anion data collected, were set at different levels in the sediment. The data was normalized for analysis of peepers. The chambers included in the average were from 2" below the sediment surface to the bottom of the peeper. For the laboratory analysis, the data from four to six peepers were used for the equilibrated average. The analysis of Cocheco field data was completed on two peepers from each category. The metals that met the selection criteria and were chosen for analysis, along with iron and manganese, were cadmium, chromium, strontium and zinc. The criteria for selection required each metal to be above the MDL in all of the sediments. Metal were also selected based on their toxicity. For example, calcium and magnesium were not chosen because they are rarely a health risk.

4.1.3 Equilibration

This section looks at equilibration in general with field and laboratory results compared. The field studies were performed in the intertidal zones on the Cocheco River. The resulting pore water movement through the sediment may have affected the equilibrium times. This movement can cause concentration changes in the pore water constituents by recharging or removing them from the area around the peeper. Increased hydraulic pressure may also force the constituents across the membrane. The laboratory experiments were performed on sediment from the Merrimack and Squamscott Rivers in stagnant tubs that had no pore water movement. Therefore, there are no outside forces present to affect the equilibration results. The equilibration time line is one of the indicators of oxygen effects from the peeper preparation. The equilibration time study comparing purge gas type will be examined in a subsequent section.

A linear regression t-test in Microsoft Excel was used to examine the equilibration trend lines for selected metals. The regression line calculation produces an r^2 with a value between 0 and1. A value r^2 of one indicates all of the data points are on the regression line. A value of zero means there is no relationship between the independent (time) and dependent (concentration) variables. That regression line will have a zero slope. The t-test will generate a P-value which is a determination of the probability the data points are on the regression line. The null hypothesis, slope is equal to zero, is true if the P-value is greater than the confidence level of the test. A zero slope indicates there is no relationship between time and concentration and that equilibration has been reached. The regression lines were tested at the ninety percent confidence level. The difficulty of using the regression tool for analysis of equilibration in this study is there are only four data points for each trend. The peepers used to determine equilibration trends in the field experiments were removed at weeks 1, 2, 3 & 5 while peepers for the laboratory experiments were removed at weeks 2, 3, 4 & 5.

Iron concentration equilibration trends are shown in figure 4.4 "Iron Equilibration Trends". A visual inspection of the graphs indicates that equilibration has been reached by week one in the field study on the Cocheco River. P-value is 0.55 and the r^2 is 0.2 which are also indicate equilibration has been reached. In the laboratory studies, the equilibration line is trending up to the four week point. Since three points are required for the regression test, equilibration can not be validated at four weeks. It should be noted that the Squamscott River trend line appears flat throughout but the r^2 is about 0.9 for the regression analyses consisting of weeks 2 through 5 and weeks 3 through 5.

Cadmium concentration trends shown in figure 4.5 are similar to those of iron but at different concentration levels. The regression line test are also similar, indicating equilibration has been reached in the Cocheco River by week one and in the Merrimack and Squamscott Rivers by week four.

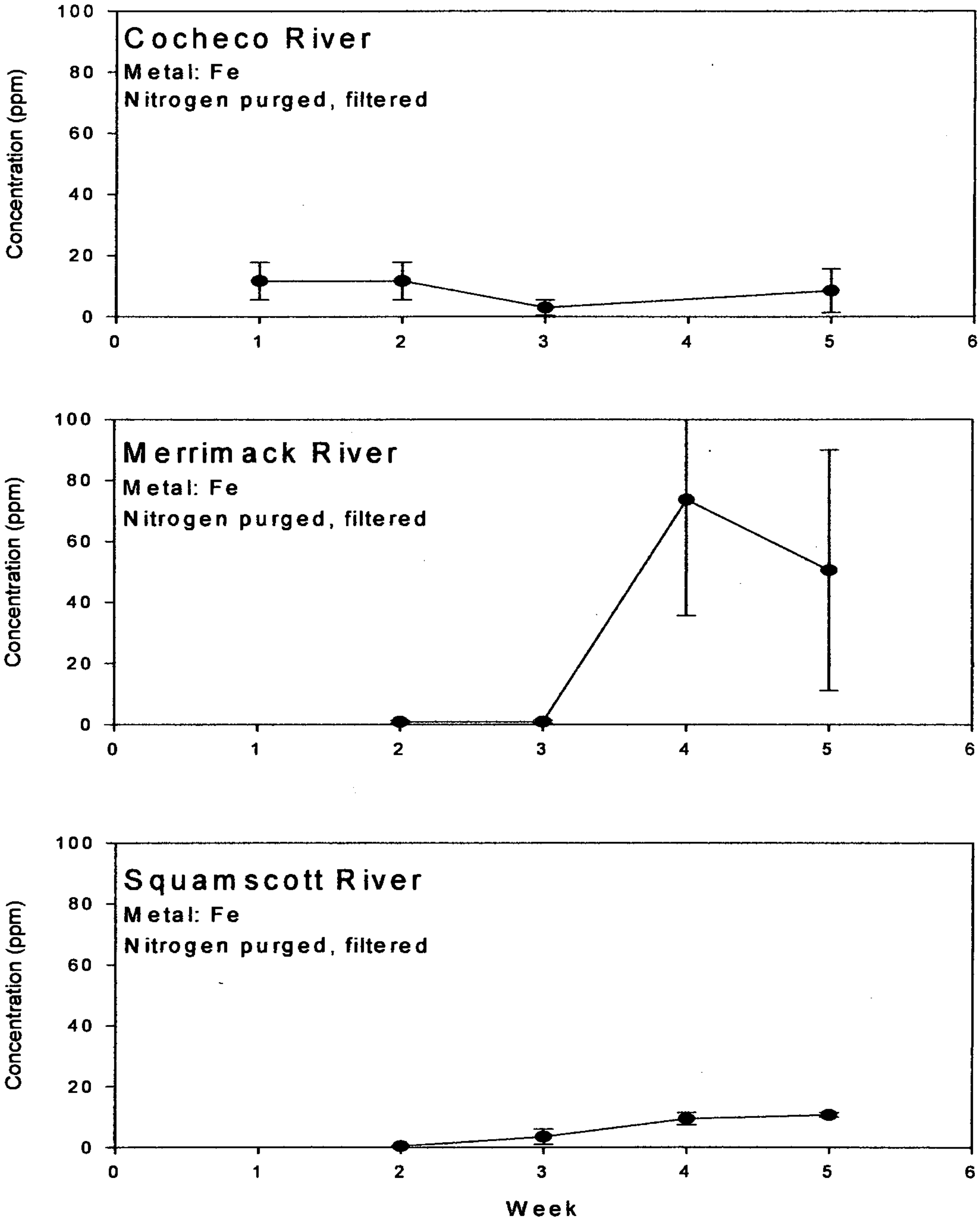


Figure 4.4: Iron Equilibration Trends

Cocheco River data is from field analysis. Merrimack and Squamscott River data is from laboratory analysis. Iron concentrations for each sample date are averages of peeper cells from 1" below the surface to the bottom of the peepers.

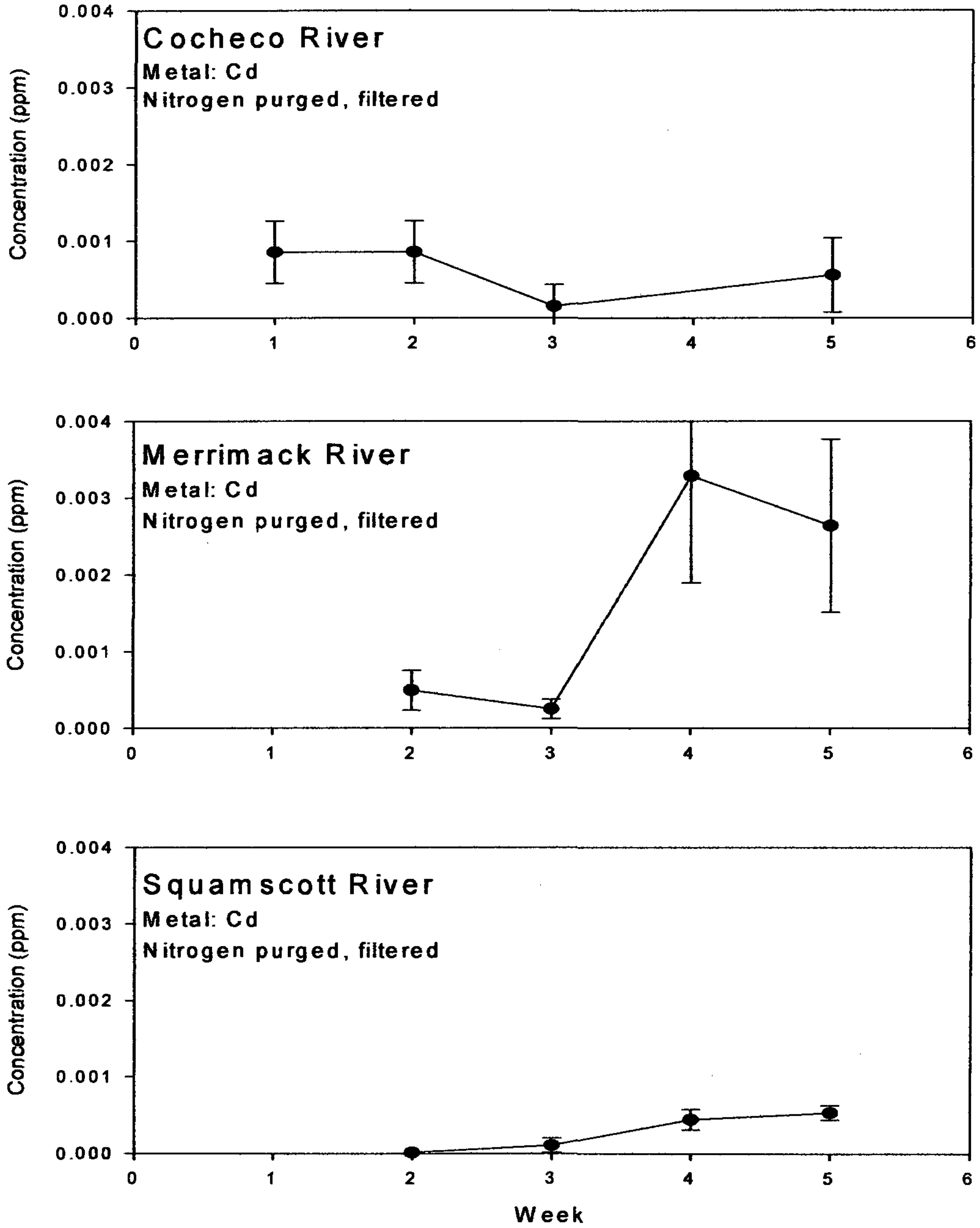


Figure 4.5: Cadmium Equilibration Trends
Cocheco River data is from field analysis. Merrimack and Squamscott River data is from laboratory analysis. Cadmium concentrations for each sample date are averages of peeper cells from 1" below the surface to the bottom of the peepers.

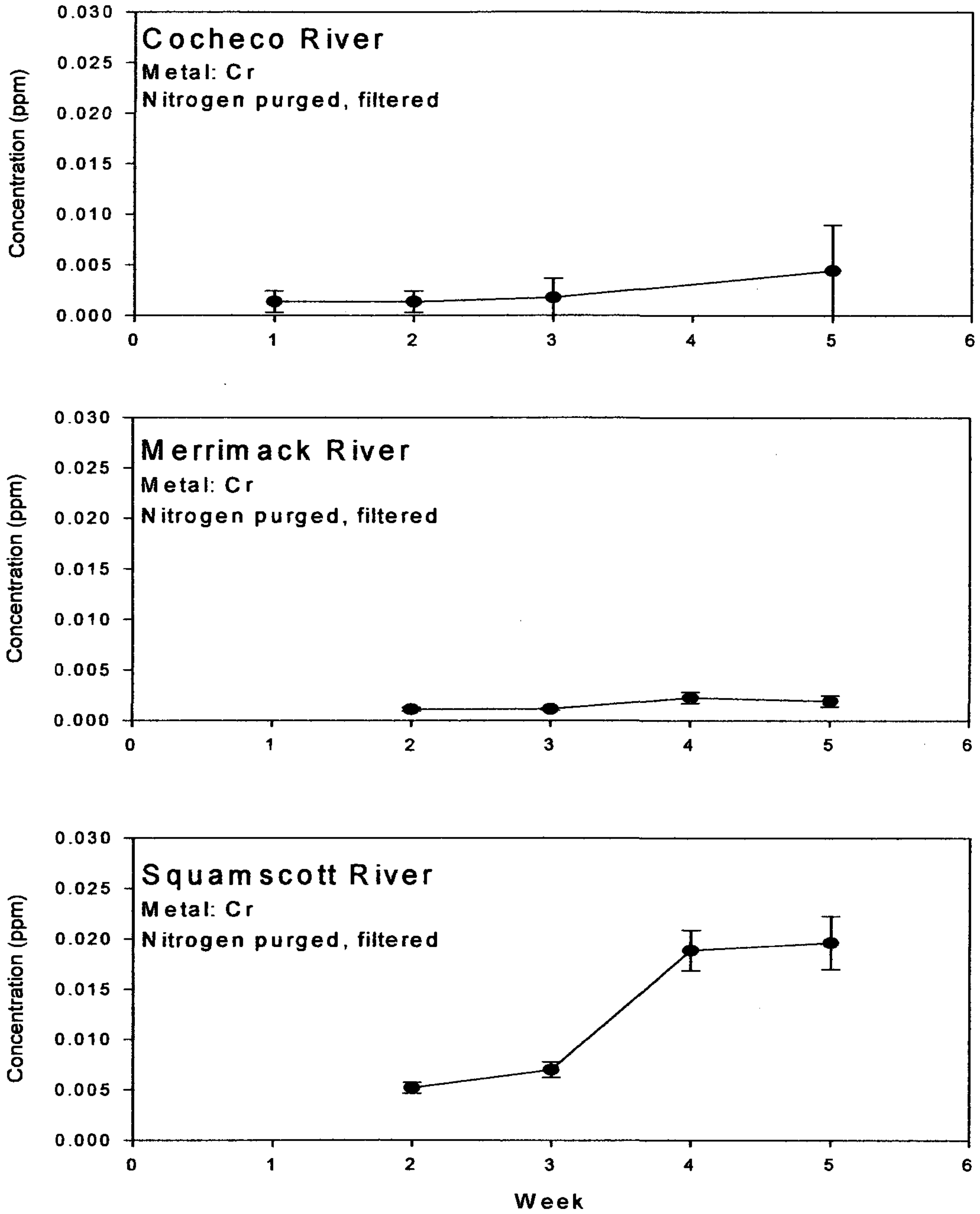


Figure 4.6 Chromium Equilibration Trends
Cocheco River data is from field analysis. Merrimack and Squamscott River data is from laboratory analysis. Chromium concentrations for each sample date are averages of peeper cells from 1" below the surface to the bottom of the peepers.

Chromium concentrations, seen in figure 4.6, for the Cocheco River appear visually to have reached equilibration by week four. However, r^2 is 0.85 for the regression analysis for weeks 1 through 5 and 0.95 for weeks 2 through 5 which indicates equilibration has not been reached. Equilibration of chromium concentrations in the Merrimack River looks like it has been reached by week one. The P-value for the regression analyses consisting of weeks 2 through 5 and weeks 3 through 5, pass the null hypothesis test. The r^2 value for those analyses is 0.6 and 0.5, respectively.

The regression tests for strontium in the Cocheco indicate it has not reached equilibration by week 3. Manganese and zinc both reached equilibration in the Squamscott by week one.

Another predicted trait of the equilibration time line is that the standard deviation should be reduced the longer the peepers stay in the sediment. This should be especially true for the laboratory studies where the sediment is not being recharged by pore water migration. A case can be made for standard deviation change in the field studies due to tidal influences, storm water runoff or ground water fluxes.

The Cocheco field study standard deviations were more consistent than those of the Merrimack River laboratory study (figures 4.4, 4.5 & 4.6). The Squamscott River sediment show similar consistency to that of the Cocheco River. A possible explanation for the consistency in the Cocheco River data is that only one peeper was used for each time period. One reason for the lack of consistency for the laboratory study is data for the equilibration trends came from multiple peepers. Deviations in the data may also be a result of differences in the concentration depth gradients of the peepers. It should be noted that the depth profiles will be evaluated in a subsequent section.

The general results for peeper equilibration were within those predicted by Carignan that equilibrium should take between two and three weeks depending on temperature and hydraulic conditions. The industry standard is between three and four weeks. It was expected that equilibrium should be reached somewhere between two to four weeks. Equilibrium in the field study on the Cocheco was reached between one and two weeks. In the laboratory studies in the Merrimack and Squamscott Rivers, it was reached after four weeks. Equilibration was different based on the metal. For example, iron and zinc equilibrated faster than strontium.

4.1.4 Depth Profile

One of the benefits of the multi-chambered vertical peeper is a depth profile of the sediment is available. The peeper seen in Figure 4.7 "Cocheco River Peeper" shows how the chambers can report a depth profile. In the picture the top of the peeper is to the right. The rubber band indicates the sediment/water body interface. The dark orange color, in chamber 5 through 7 (from the top), show the aerobic/anaerobic interface in the sediment.

A depth profile can be used to indicate movement direction of dissolved metal ions. Data from one peeper will give a profile of that spot in the sediment. Data from multiple peepers can be combined to characterize an area of sediment. To get a true picture of a sediment field, both methods are used.

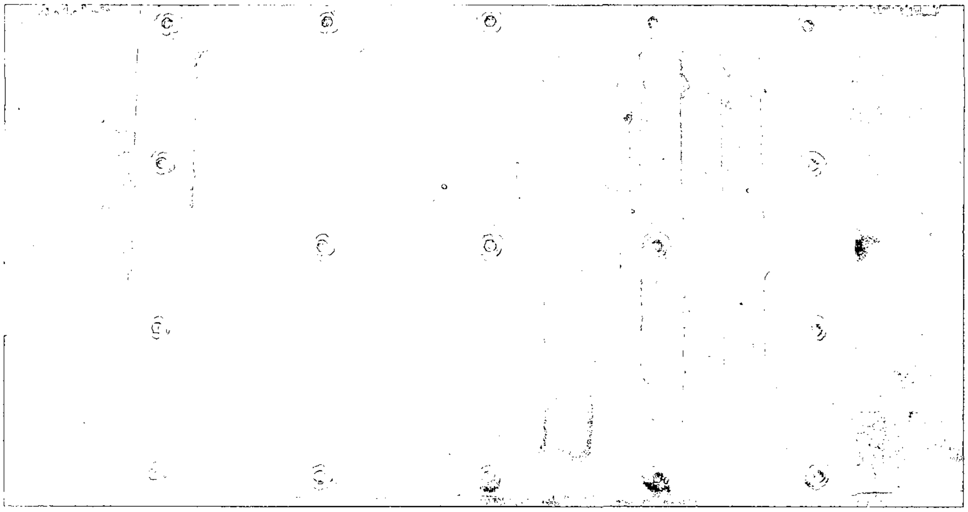


Figure 4.7: Cocheco River Peeper
Peeper removed from Cocheco River field site. Top of peeper is to right. Rubber band is set at sediment/river water interface. Dark orange just below the rubber band is aerobic area of sediment. Below the dark orange is the anaerobic area. This section was white when peeper was initially removed from the sediment (orange tint occurred after exposure to atmosphere).

Figure 4.8 "Merrimack River Iron Depth Profile" shows a depth profile of multiple peepers. The data is from the Merrimack River Laboratory experiment. The thin bars are iron concentrations of the individual peepers while the thick bar is the average. The standard deviation is indicated for the average concentrations. The general depth trend show iron concentration increases to a depth of 63mm where it then stays relatively consistent. Each individual peeper also shows this trend with the exception of the last value for peeper #2. The water body above the sediment shows very little iron. This is an indication of the redox environment throughout the sediment bed.

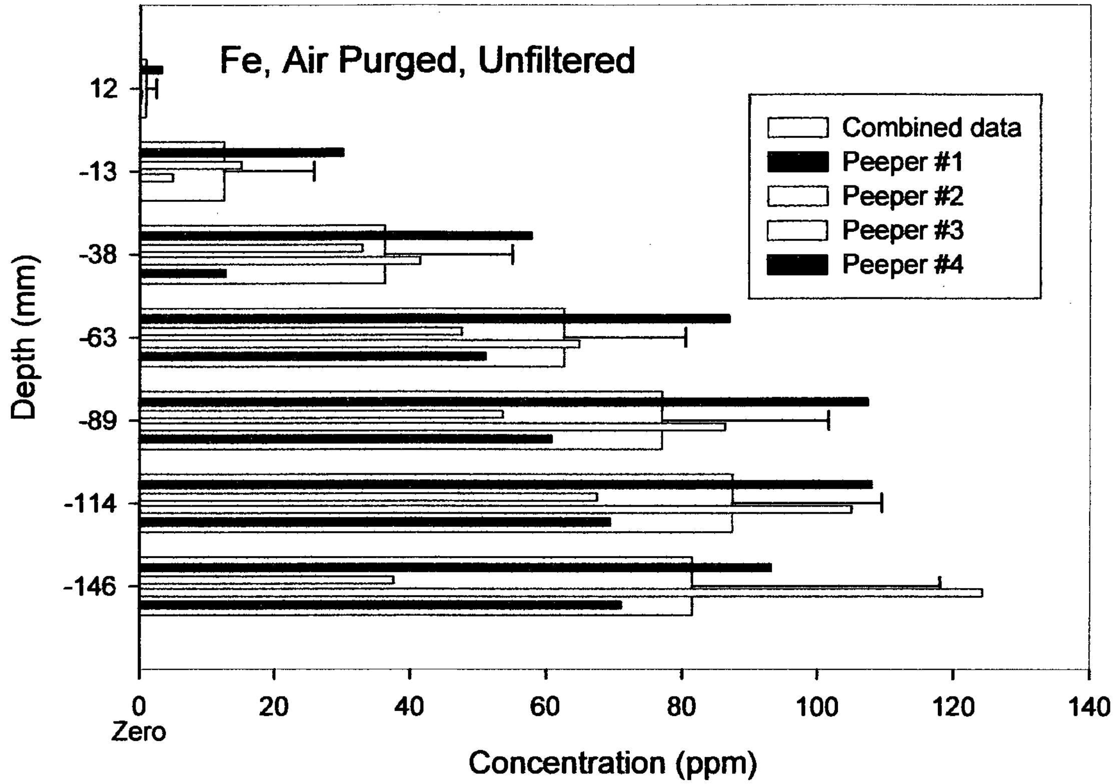


Figure 4.8: Merrimack River Air Purged, Unfiltered Iron Depth Profile
Depth profiles are from peepers removed from the Merrimack River laboratory sediment. The thin bars are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

Data from a series of individual peepers will show the anomalies responsible for the standard deviation. Figure 4.8 "Merrimack River Iron Depth Profile" is an example this concept. The average concentration for the depth of 146mm is 81.5ppm with a standard deviation of 36.5. The high standard deviation is due to peeper #2 having a concentration much lower than those of peepers #1 and #3.

The ability to provide a sediment pore water depth profile is a principal attribute of the vertical peeper. The depth profile is a key tool used to evaluate how the pore water is interacting with the water body above the sediment and the ground water below it. It also provides information on historical contamination and possible ecological impacts

4.2 Evaluation of Oxygen Effects

4.2.1 Introduction

Evaluating the effects oxygen has on peeper material, preparation and sample removal is a central theme of this thesis. This section will examine influences that oxygen introduction has by looking at how the purge gas type and filtering techniques affect metal concentrations determined from sediment sampling. Since oxygen introduction affects redox sensitive metals by changing their state, they will be looked at first. The selected heavy metals will then be evaluated.

4.2.2 Redox Sensitive Metal Equilibrated Analysis

This section will evaluate oxygen effects on sampling of redox sensitive metals iron and manganese. Analysis of filtered and unfiltered samples from nitrogen and air purged peepers will be compared. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers.

The results shown in Figure 4.9 "Overall Iron and Manganese Concentrations" are for peepers equilibrated for four to five weeks. The graphs show iron in peeper samples with nitrogen purged gas preparation was equal or less than iron in air purged ones. The difference between filter options, which will be discussed in detail in a later section, were mixed and showed no trend.

Merrimack River sediment has high standard deviations for iron in three of the four categories displayed. The manganese results were also mixed and showed no trends. The average concentration and standard deviations for manganese in Merrimack River pore water were similar to those for iron.

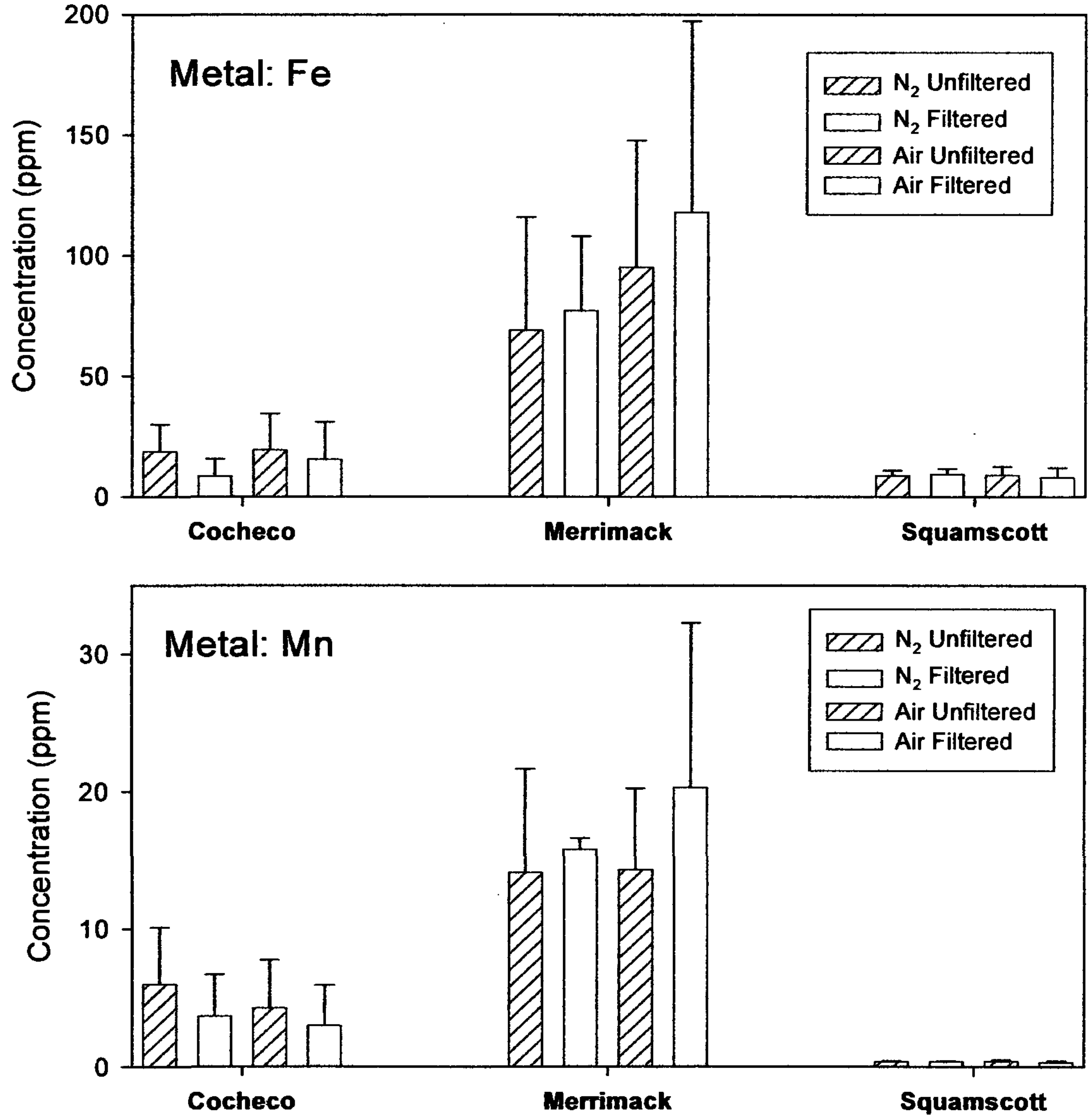


Figure 4.9: Overall Iron and Manganese Concentrations

Charts are equilibrated concentrations of redox sensitive metals, Fe & Mn. Cocheco River data is from field analysis. Merrimack and Squamscott River data are from laboratory results. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers. Each sediment analysis shows the purge gas the peepers were prepared with and the filtering option the sample was removed with.

The depth profiles for metals in the Merrimack River sediment equilibrated in laboratory studies were expected to be low near the surface and increase with depth. Figure 4.10, "Merrimack River Iron Depth Profile" represents the two tubs the laboratory experiments were conducted in. Both tubs show dilution from the river water sitting above the sediment. The peepers profiled are from two equilibrated peeper studies. Variations in the nitrogen purged, filtered peepers can be attributed to the concentration differences between peepers 8-1PMN and 8-3PMN (figure 4.10). In the air purged, filtered, large variations are seen in peepers 8-3PMA and 10-6PMA (figure 4.10). This phenomenon is especially evident at the depth of -146mm in both purge gas types.

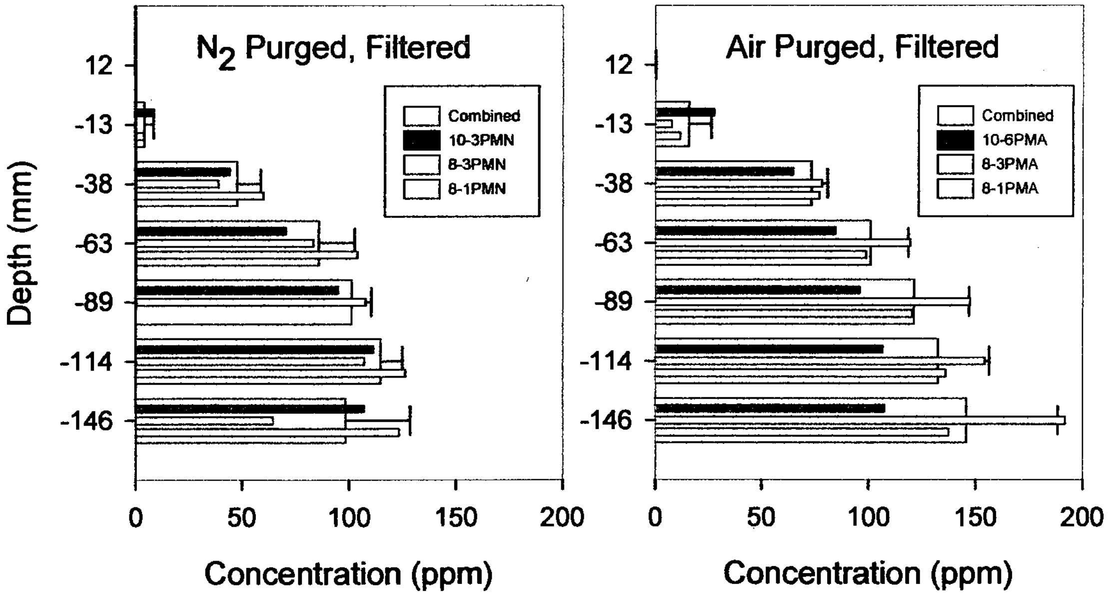


Figure 4.10: Merrimack River Filtered Iron Concentration Depth Profiles
Iron depth profiles are from peepers removed from the Merrimack River sediment laboratory analysis. The chart on the left is from peepers prepared with nitrogen purged gas. The chart on the right is peepers purged with air. The thin bars are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

The depth profiles for the Squamscott River (figure 4.11), also a laboratory study, was expected to be similar to those of the Merrimack River. The concentration of the nitrogen purged peepers at each depth had low standard deviations. Depths -63mm to -114 had consistent iron concentrations. The air purged tub showed an increasing trend from top to bottom. The depth profile of peepers purged with nitrogen and air in the laboratory studies behaved as predicted. Iron concentrations were expected to be low near the surface and increase with depth.

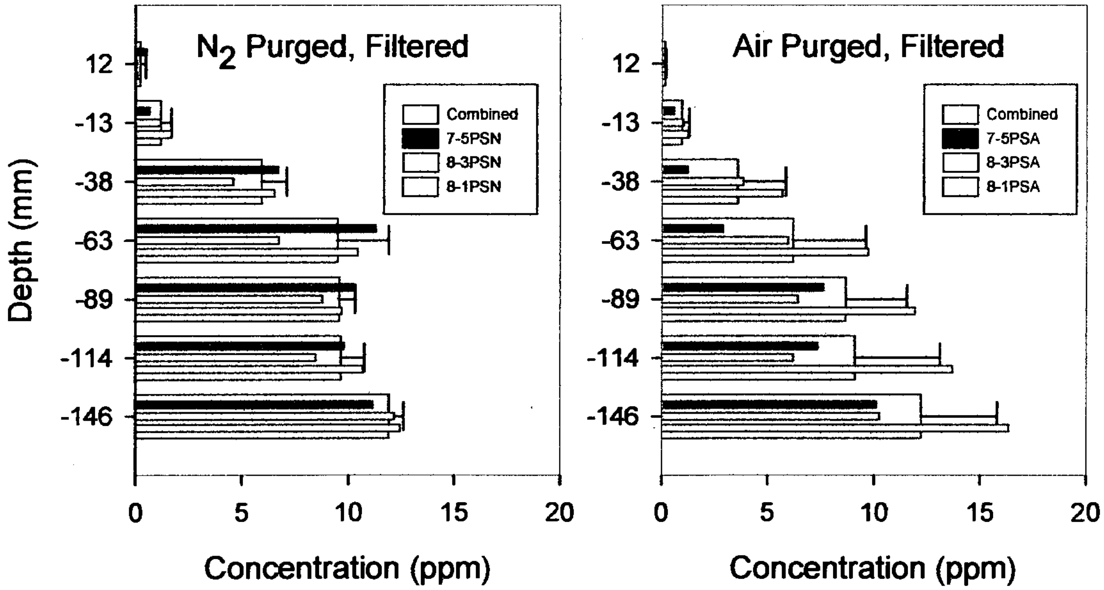


Figure 4.11: Squamscott River Filtered Iron Concentration Depth Profile
Iron depth profiles are from peepers removed from the Squamscott River sediment laboratory analysis. The chart on the left is from peepers prepared with nitrogen purged gas. The chart on the right is peepers purged with air. The thin bars are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

The depth profile for the Cocheco River, depicted in Figure 4.12 "Cocheco River Iron Depth Profile", is from two studies for equilibrated peepers. The iron concentrations were significantly different so they were shown in separate graphs. Data from 9-1FC study is on the left while 1-6OXY study is on the right.

The Cocheco river studies did not include anion data so each chamber had a depth reading associated with it. In the 1-9FC study the peeper chamber #3 was at the water body/sediment interface. In the 1-6OXY study the top of the peeper was set at the top of the sediment. The peepers from both studies have depth reading between 64mm and 152mm below the sediment. The studies were done approximately fifty feet from each other.

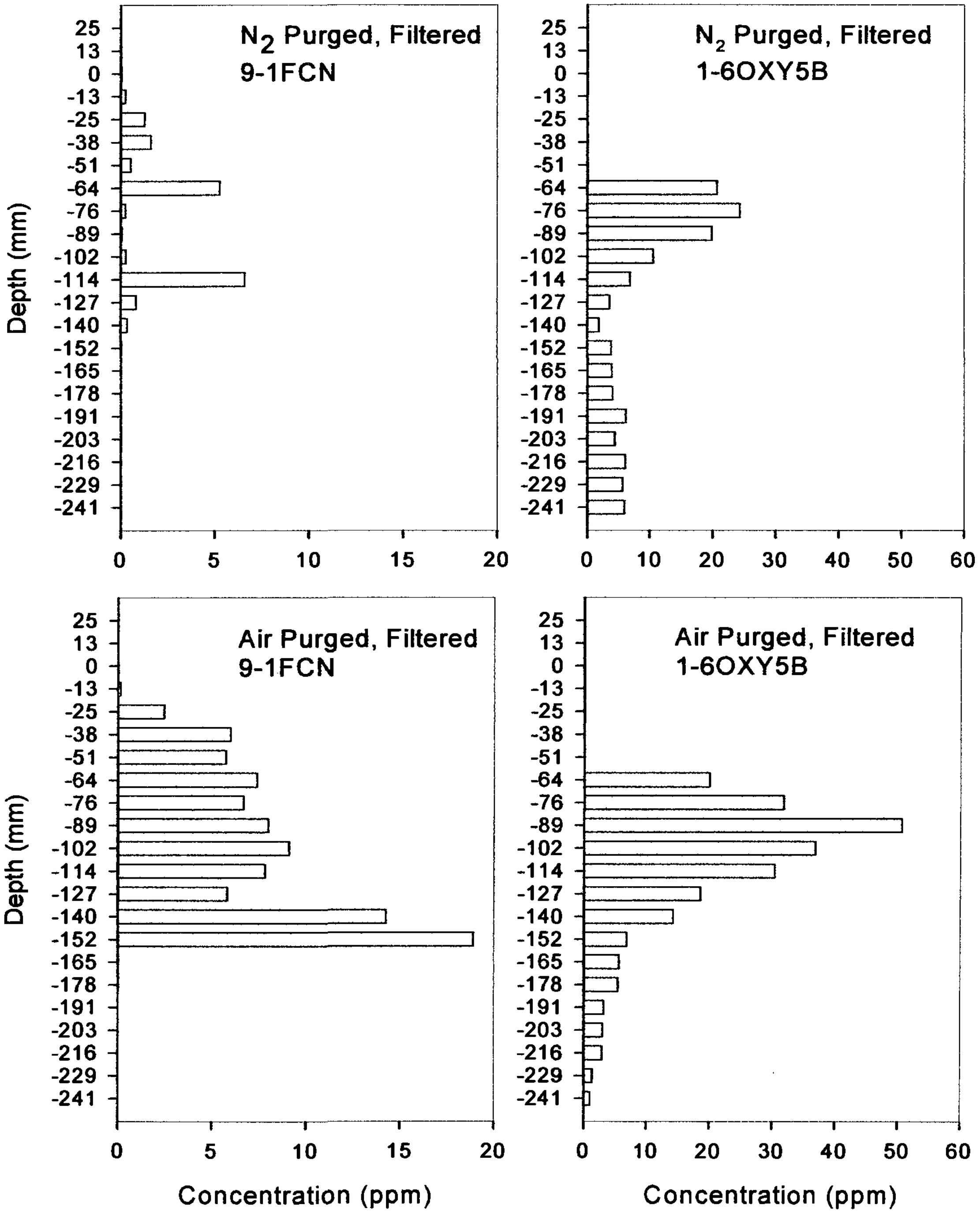


Figure 4.12: Cocheco River Filtered Iron Concentration Depth Profile

Iron depth profiles are from peepers removed from the Cocheco River sediment field analysis. Each chart is from a single peeper. The third chamber of peepers for the charts on the left was set at the sediment water interface. The top of peepers for the charts on the right was set at the sediment water interface. Charts on the top are from peepers prepared with nitrogen purged gas. Charts on the bottom are from peepers purged with air.

In both studies, air purged peepers have higher iron concentrations than nitrogen purged peepers. Similar to the Merrimack and Squamscott River data, the Cocheco had very little iron in the water body above the sediment. Iron concentrations below 114mm for the nitrogen purged 1-6OXY5B peeper were consistent. The air purged peeper for that study had a trend of reducing concentrations. There were not trends evident in the 1-9FC study.

The independent t-tests for redox metals are shown in Table 4.1. They were determined with a 95% confidence level for each category. The independent t-test was chosen as an evaluation tool due to differences in laboratory sediment tubs and peeper chambers. Also, since the analysis was completed for constituent average concentration, the averages were based on individual chambers for all the peepers in a category.

The results were mixed for iron concentrations in the Cocheco River (table 4.1). Unfiltered peeper t-tests indicated there was no difference in the purge gas type. While the filtered data showed that air purged peepers had a higher concentration. Both filtering options for iron in the Merrimack River pore water indicated that air purged peeper peepers had a higher concentration (table 4.1). In the Squamscott River zero was included in the interval so there was no apparent difference between purge gas types (table 4.1). Zero was included in all the difference intervals for manganese in all the sediment. The exception was Merrimack River filtered peepers.

Table 4.1: 95% Confidence Independent t-tests for Redox Metals

Preparation purge gas comparisons are equilibrated concentrations of redox sensitive metals, Fe & Mn. Cocheco River data is from field analysis. Merrimack and Squamscott River data are from laboratory results. Concentrations used in the comparison are averages of peeper cells from 1" below the surface to the bottom of the peepers. df = degree of freedom; $t_{df,0.025}$ are from student t-test tables

Metal	Sediment	Comparison	df	t	Interval (ppm)	
Fe	Cocheco	N_2 vs. Air Unfiltered	50	2.009	5.415	-7.167
		N_2 vs. Air Filtered	50	2.009	-1.354	-12.44
	Merrimack	N_2 vs. Air Unfiltered	38	2.024	-7.418	-44.88
		N_2 vs. Air Filtered	37	2.026	-13.72	-67.88
	Squamscott	N_2 vs. Air Unfiltered	18	2.101	2.672	-2.828
		N_2 vs. Air Filtered	28	2.048	10.56	-7.821
Mn	Cocheco	N_2 vs. Air Unfiltered	50	2.009	3.026	-0.841
		N_2 vs. Air Filtered	50	2.009	1.775	-1.002
	Merrimack	N_2 vs. Air Unfiltered	38	2.024	2.198	-2.570
		N_2 vs. Air Filtered	37	2.026	-0.1808	-8.835
	Squamscott	N_2 vs. Air Unfiltered	18	2.101	0.0658	-0.0908
		N_2 vs. Air Filtered	28	2.048	0.2360	-0.1860

The prevailing evidence is that there is no difference in equilibrated peeper concentration for redox sensitive metals with or without oxygen present during preparation.

4.2.3 Redox Sensitive Metal Equilibration Trend Analysis

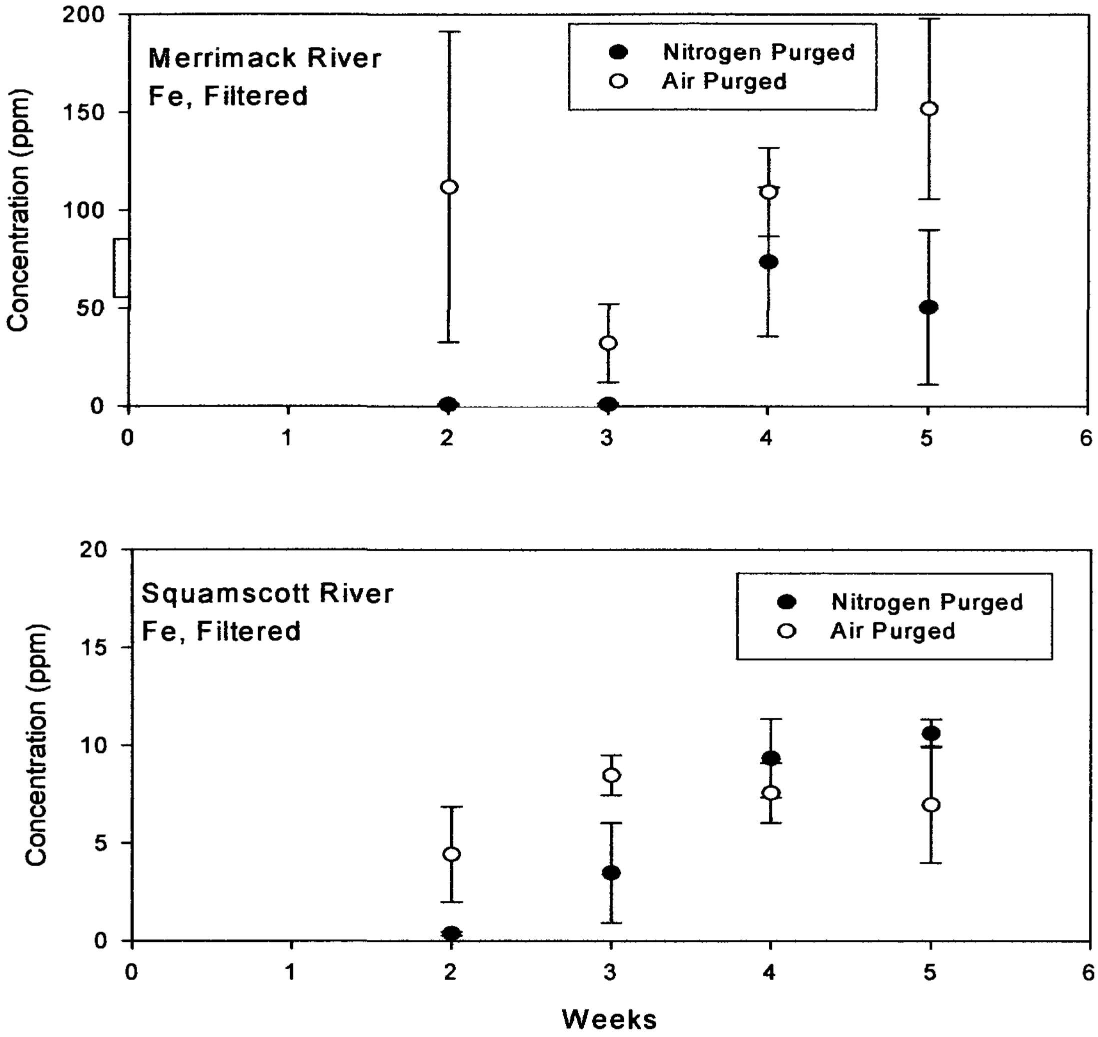


Figure 4.13: Merrimack & Squamscott Rivers Iron Equilibration Trend
The iron equilibration trends are from laboratory analysis of filtered peeper samples for average cell concentrations for depths 63mm to 145mm below the sediment.

A major part of the theory presented in this thesis is that oxygen effects will be mitigated the longer the peeper is kept in the sediment. Any oxygen present in the peeper material or makeup water will be dissipated in the sediment or consumed by microbial activity during the equilibration period. Since redox metals have reduced concentrations near the sediment surface, the depth range chosen for analysis of equilibration trends was 63mm to 145mm below the sediment. Laboratory results are depicted in Figure 4.13 "Merrimack & Squamscott Rivers Iron Equilibration Trend". The Squamscott River and nitrogen purged Merrimack River peepers appear to have reached equilibrium at the four week mark. The air purged Merrimack River results are still trending upwards. The Merrimack River trends have a large standard deviation while those for the Squamscott River are more consistent. In the Merrimack River, the air purged concentration for iron is higher for all points. In the Squamscott River the trend changes after the peepers have reached equilibrium.

The depth profile for the individual Merrimack River peepers can be seen in Figure 4.14 "Merrimack River Iron Equilibration Trend Depth Profile". The results for the nitrogen purged peepers at a depth of 145mm are suspect. The results for Week 4 peepers, at 145mm, have a much greater concentration than the peepers from the other weeks. However, the results seem to be in line with week 4 results from other depths. The week 3 results, for air purged peepers, are lower than those in week 2 for depths 89mm to 145mm. The significant concentration variation between the peepers at each depth is responsible for the large standard deviation in the Merrimack River equilibration trends (figure 4.13).

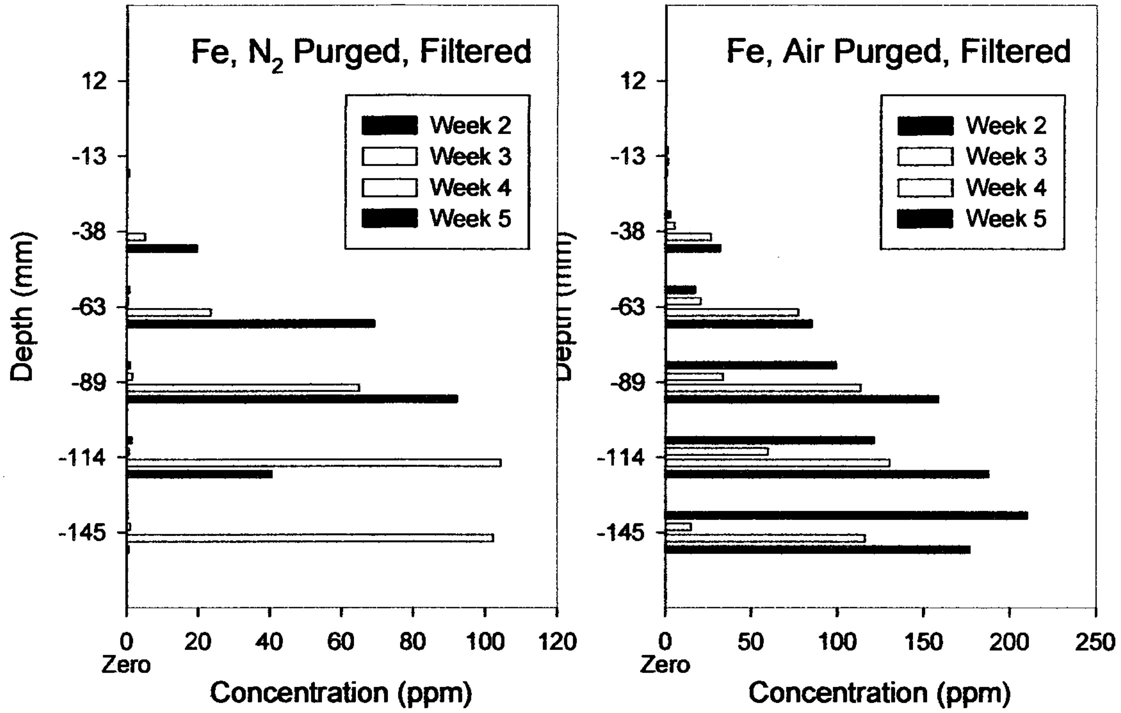


Figure 4.14: Merrimack River Iron Equilibration Trend Depth Profile
Iron concentration depth profiles of filtered peeper samples removed from the Merrimack River sediment for laboratory evaluation of equilibration trends. The peepers used for the chart on the left were purged with nitrogen during preparation. The peepers for the chart on the right were purged with air.

The laboratory analysis of manganese equilibration trends can be seen in Figure 4.15 “Merrimack & Squamscott Rivers Mn Equilibration Trend”. The manganese concentrations for the Squamscott River peepers reached equilibration at week 3. The Merrimack River manganese trends were a little erratic. Nitrogen purged peepers appeared to reach equilibration at four weeks while the air purged peepers were still trending up at five weeks. Squamscott River manganese results had a smaller standard deviation than those for the Merrimack River. The manganese results and standard deviations for the Merrimack River were more consistent than the iron results.

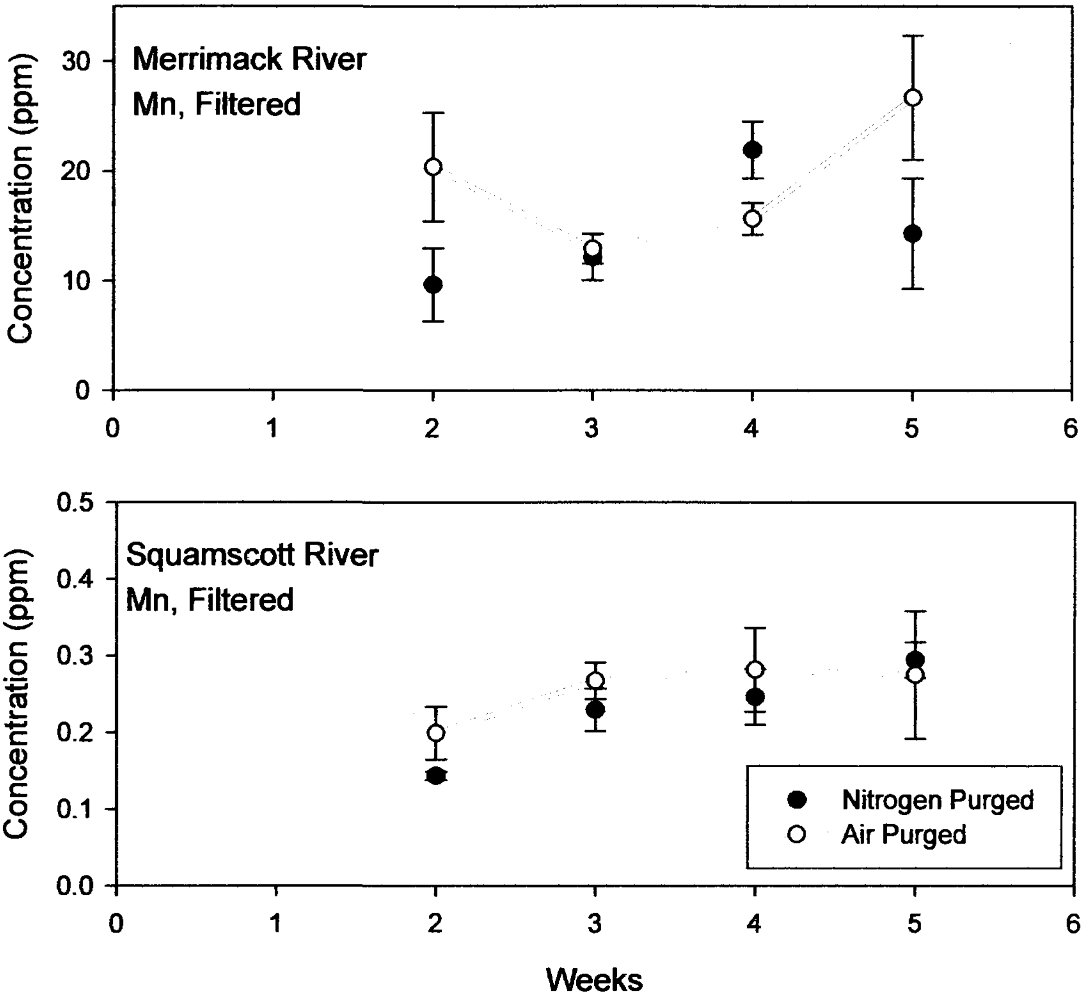


Figure 4.15: Merrimack & Squamscott Rivers Mn Equilibration Trend
The manganese equilibration trends are from laboratory analysis of filtered peeper samples for average cell concentrations for depths 63mm to 145mm below the sediment.

The paired t-tests for the Merrimack and Squamscott Rivers were performed at 95% Confidence with a $t_{3,0.025}$ of 3.182. The paired t-test was used because comparisons were made at each time period. The comparisons used data from figures 4.14 and 4.15. Depths from 63mm to 145mm were compared for nitrogen and air purged gases to mitigate the near surface redox metal concentration effects. Since the individual depths were compared, the paired t-test was used.

Table 4.2: Paired t-tests for Redox Metals Equilibrated Results

Sediment is from laboratory studies. Preparation purge gas comparisons used data from figures 4.14 and 4.15. Depths from 63mm to 145mm were compared for nitrogen and air purged gases. $t_{3,0.025} = 3.182$

Metal	River	Week	Interval	
Fe	Merrimack	2	-237.543	15.2709
		3	-63.179	0.634952
		4	-65.6636	-5.54084
		5	-218.309	15.47596
	Squamscott	2	-7.97294	-0.15791
		3	-9.59367	-0.40514
		4	0.815909	2.731446
		5	-1.52908	8.819598
Mn	Merrimack	2	-23.7135	2.2398
		3	-5.55014	4.065706
		4	2.315631	10.21243
		5	-26.973	2.220524
	Squamscott	2	-0.11039	-0.00074
		3	-0.10198	0.026545
		4	-0.08375	0.012628
		5	-0.14483	0.183914

The iron results for the Merrimack River had larger intervals than those for the Squamscott. As stated earlier, this was due to the large variation between peeper chamber concentrations. Zero was included in the interval for three of the four weeks evaluated. Although the interval was large and zero was near the positive endpoint, this is an indication there was no difference between the purge gas types. Week 4 had a negative interval. This is an indication that air purged peepers had a higher concentration. The Squamscott River iron t-test difference intervals for weeks 2 & 3 were negative. This suggests air purged peepers have higher concentrations than nitrogen. Weeks 4 interval difference included zero, while week 5 had a positive interval.

The manganese results were consistent for both rivers with zero included in six of the eight comparisons. Significantly, the last week's difference interval included zero for the Merrimack and Squamscott rivers. This is an indication that at equilibrium, there is no difference in concentration analysis whether oxygen is introduced during preparation or not.

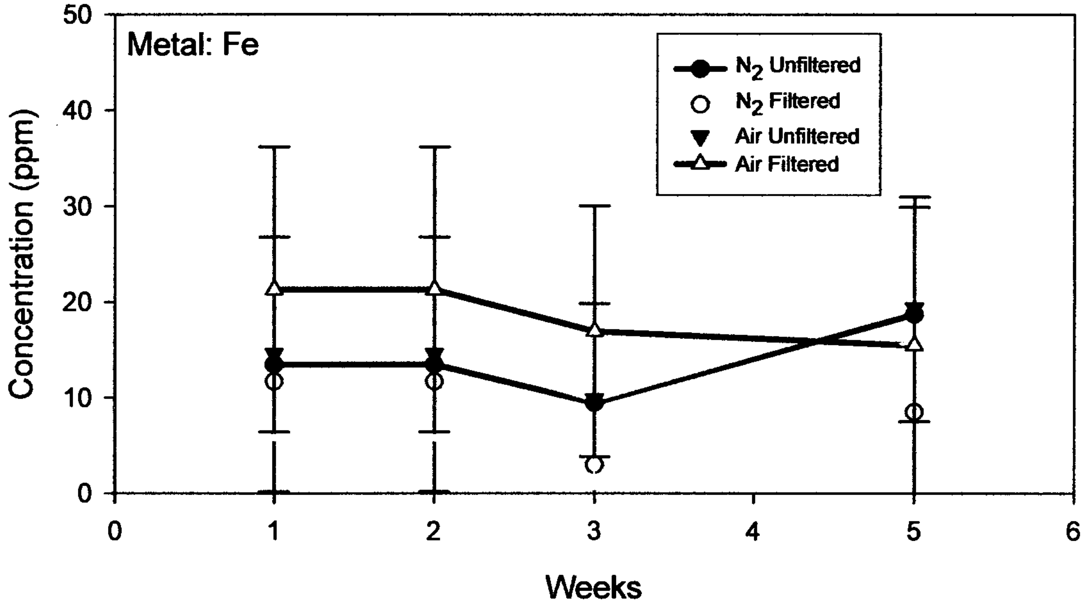


Figure 4.16: Cocheco River Iron Equilibration Trends
The iron equilibration trends are from field analysis of cell concentrations averaged over the entire peeper for each data point. Four peepers for each time period were evaluated based on preparation purge gas and filter option for sample removal.

Each point in Figure 4.16 "Cocheco River Iron Equilibration Trends" and Figure 4.17 "Cocheco River Manganese Equilibration Trends" are an average of all fifteen chambers representing depth from 64mm to 241mm. The depth range was chosen to mitigate the surface effects of the redox metals. Iron concentration reached equilibration by week one. The trend is flat with a similar standard deviation as those in the laboratory studies. The unfiltered results were essentially the same for both purge gas types.

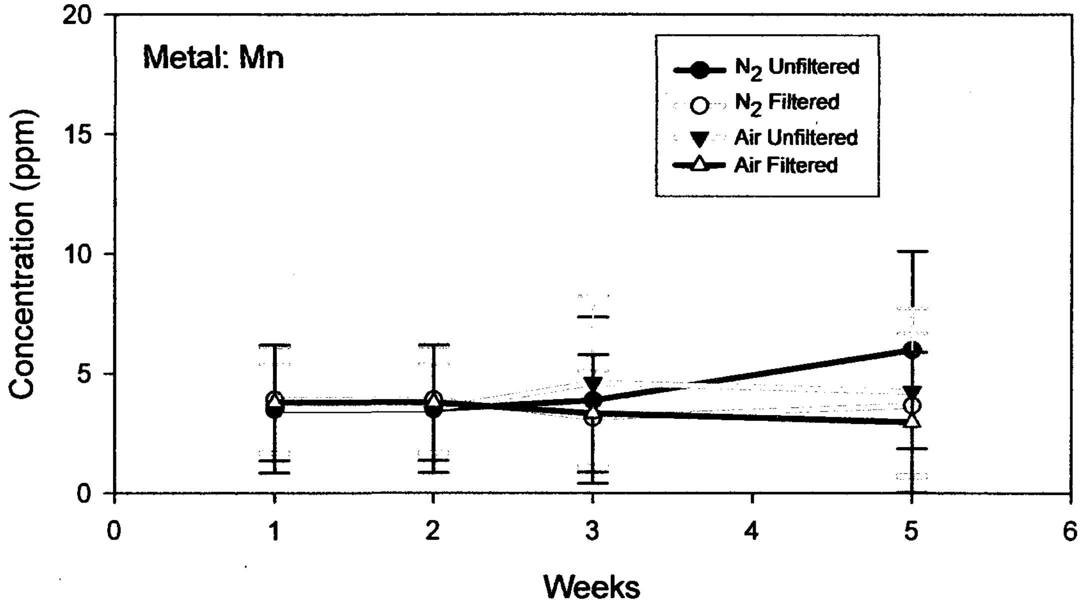


Figure 4.17: Cocheco River Manganese Equilibration Trends
The manganese equilibration trends are from field analysis of cell concentrations averaged over the entire peeper for each data point. Four peepers for each time period were evaluated based on preparation purge gas and filter option for sample removal.

Week 1 and 2 manganese concentrations were almost identical for both purge gas types and filtering options. At week 3, the unfiltered air purged peeper concentration was higher than the unfiltered nitrogen peeper concentration. The results were reversed for week 5. The filtered sample concentrations were close for both purge gas types throughout the trend period.

Table 4.3: Cocheco River Paired t-tests for Redox Metals

Sediment is from field studies. Preparation purge gas comparisons used data from figures 4.16 and 4.17. Depths from 63mm to 241mm were compared for nitrogen and air purged gases. $t_{14,0.025} = 2.145$

Metal	Removal Technique	Week	Interval	
Fe	Filtered	1	0.904083	1.57246
		2	-15.068	-4.13166
		3	-20.4247	-7.50287
		5	-13.5333	-0.37348
	Unfiltered	1	-0.69457	-0.09553
		2	1.387202	4.404815
		3	2.929202	10.84217
		5	4.702053	17.03358
Mn	Filtered	1	-0.24878	0.015225
		2	-0.3191	0.586707
		3	-0.52071	0.137876
		5	0.283386	1.114444
	Unfiltered	1	0.162999	0.451861
		2	-0.70539	-0.11443
		3	0.433492	2.524042
		5	0.014761	1.165205

Table 4.3: "Cocheco River Paired t-tests for Redox Metals" are t-tests for iron and manganese equilibrated trends. The t-test was performed at 95% Confidence with a $t_{14,0.025}$ of 2.145. Depths from 63mm to 241mm were compared for nitrogen and purged gas. The filtering removal technique options were also included. The paired t-test was used because comparisons were made at each time period and to stay consistent with the laboratory experiments.

The iron concentration difference intervals were small for the Cocheco field study as compared to the Merrimack River laboratory experiment. Filter samples for iron t-test difference intervals for weeks 2, 3 and 5 was negative for air purged peepers. This suggests that air purged peepers had higher equilibrated iron concentrations than the filtered nitrogen purged peeper samples. The unfiltered t-test difference intervals were positive for those time periods indicating nitrogen peepers had higher concentrations. If oxygen was present causing iron oxide precipitation, the expected results would be opposite.

As with all of the sediment types, manganese had smaller difference intervals. A small t-test interval is indicates there is little difference between the subjects being compared. In the filtered option, there was no apparent difference between the purge gas types for weeks 1, 2 and 3. Week 5 had a positive t-test difference interval. In the unfiltered option, the last two time periods had a positive difference interval. This suggested nitrogen purged peepers had a higher manganese concentration.

The overall results of the redox sensitive metal show that there is no difference between the purge gas types. This is an indication that oxygen has little affect on peeper preparation or material for redox metals given sufficient equilibration time.

4.2.4 Selected Metal Analysis

The purpose of this section is to evaluate how oxygen affects heavy metal concentration from peeper sampling. The figures and tables on the following pages will be used for this evaluation. Pore water samples equilibrated for four or five weeks were analyzed for Cadmium, Chromium, Strontium and Zinc. Their sample concentrations were compared for nitrogen purged and air purged peeper preparation.

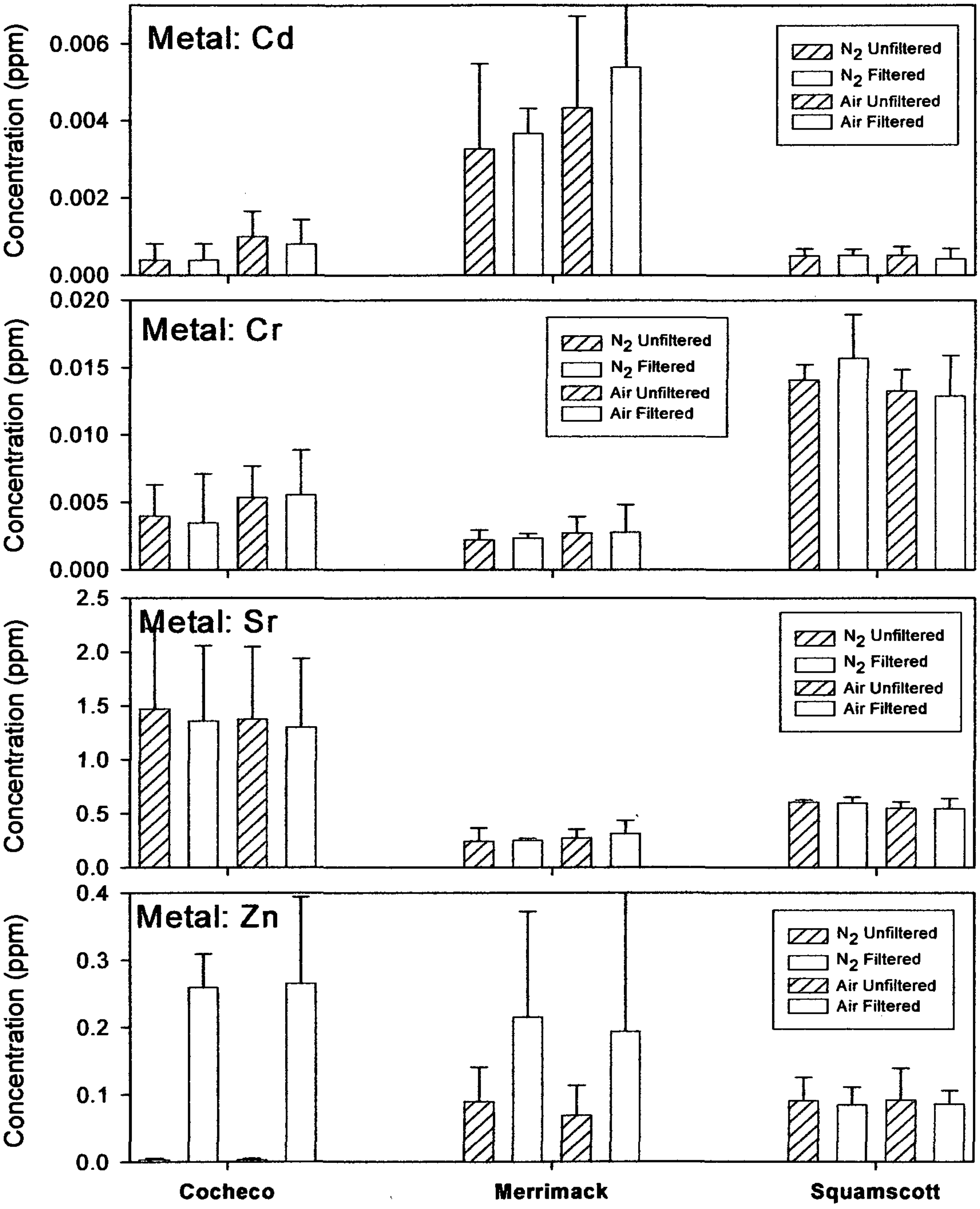


Figure 4.18: Selected Equilibrated Metal Concentrations
Charts are equilibrated concentrations of Cd, Cr, Sr & Zn. Cocheco River data is from field analysis. Merrimack and Squamscott River data are from laboratory results. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers. Each sediment analysis shows the purge gas the peepers were prepared with and the filtering option the sample was removed with.

In figure 4.18 “Selected Equilibrated Metal Concentrations”, cadmium concentrations are greater and there is a larger standard deviation in the Merrimack River sediment pore water. In the Cocheco and Merrimack River pore water, peepers with air purging during preparation have a higher cadmium concentration than those purged with nitrogen. The peepers in the Squamscott River are close to equal concentration regardless of the gas purged during preparation.

The equilibrated concentrations for chromium have mixed results for the different sediments (figure 4.18). The Squamscott River pore water has the highest chromium concentration with nitrogen purged peepers being slightly higher that air purged ones. The Cocheco River pore water has air purged peepers with slightly higher chromium concentrations (figure 4.18). Chromium concentrations in the Merrimack River pore water are similar for the different preparation purge gas types. Standard deviations for the Cocheco and Squamscott Rivers are in the same range (figure 4.18). Those for the Merrimack River are slightly lower.

Strontium concentrations in the Cocheco River sediment pore water are essentially equal for the different sampling categories in that pore water (figure 4.18). The Cocheco River sediment has the highest concentration as well as the largest standard deviations. Strontium concentrations in the Merrimack River pore water are similar for each of the sampling categories; each category has a low standard deviation (figure 4.18). Squamscott River strontium concentrations follow a similar pattern as those in the Merrimack River.

Equilibrated Zinc concentrations in the Squamscott River sediment pore water are similar for the purge gas and filtering options (figure 4.18). The standard deviations in the Squamscott River results are small. Filtered samples in the Cocheco and Merrimack Rivers have higher zinc concentrations than corresponding unfiltered samples for both preparation purge gas types. The standard deviations are also higher in the filter samples (figure 4.18).

Table 4.4: Independent t-tests for Selected Metals

Preparation purge gas comparisons are equilibrated concentrations of selected elements, Cd, Cr, Sr & Zn. Cocheco River data is from field analysis. Merrimack and Squamscott River data are from laboratory results. Concentrations used in the comparison are averages of peeper cells from 1" below the surface to the bottom of the peepers. df = degree of freedom; $t_{df,0.025}$ are from student t-test tables

Metal	**Sediment**	**Comparison**	**df**	**t**	**Interval (ppm)**	
Cd	Cocheco	Unfiltered	50	2.009	0.0003	-0.0004
		Filtered	50	2.009	-0.0001	-0.0007
	Merrimack	Unfiltered	38	2.024	-0.0003	-0.0018
		Filtered	37	2.026	-0.0006	-0.0029
	Squamscott	Unfiltered	18	2.101	0.0002	-0.0002
		Filtered	28	2.048	0.0007	-0.0005
Cr	Cocheco	Unfiltered	50	2.009	-0.0001	-0.0027
		Filtered	50	2.009	-0.0001	-0.0040
	Merrimack	Unfiltered	38	2.024	-0.0001	-0.0009
		Filtered	37	2.026	0.0001	-0.0010
	Squamscott	Unfiltered	18	2.101	0.0021	-0.0005
		Filtered	28	2.048	0.0115	-0.0059
Sr	Cocheco	Unfiltered	50	2.009	0.4928	-0.3010
		Filtered	50	2.009	0.4315	-0.3155
	Merrimack	Unfiltered	38	2.024	0.0007	-0.0589
		Filtered	37	2.026	-0.0154	-0.1075
	Squamscott	Unfiltered	18	2.101	0.0985	0.0144
		Filtered	28	2.048	0.2610	-0.1537
Zn	Cocheco	Unfiltered	50	2.009	0.0017	-0.0009
		Filtered	50	2.009	0.0487	-0.0605
	Merrimack	Unfiltered	38	2.024	0.0615	-0.0195
		Filtered	37	2.026	0.1173	-0.0745
	Squamscott	Unfiltered	18	2.101	0.0379	-0.0402
		Filtered	28	2.048	0.0594	-0.0623

The Independent t-tests in table 4.4 compares equilibrated concentrations preparation purge types, nitrogen vs. air, for the selected metals. Concentrations for metals, Cd, Cr, Sr & Zn, are averages of peeper cells from 1" below the surface to the bottom of the peepers. Cocheco River data is from field analysis. Merrimack and Squamscott River data are from laboratory results. It should be noted that a negative difference interval indicates air purged peepers have the higher concentration. A positive difference suggests nitrogen purged peepers have the higher concentration. If zero in included in the t-test interval difference then the evidence indicates there is no difference.

The cadmium unfiltered independent t-test interval differences for the Cocheco River and both filtering options for the Squamscott River include zero in the interval (table 4.4). This indicates there is no cadmium concentration differences between the preparation purge gas types. The Merrimack River and filtered samples for the Cocheco River have a negative interval for cadmium concentration (table 4.4). A negative interval suggests peepers with air purged have a higher concentration than those with nitrogen.

The independent t-test for chromium concentration difference intervals for the Squamscott River include zero (table 4.4). The difference interval for unfiltered peepers in the Merrimack River sediment include zero while filtered results have a negative interval (table 4.4). For the Cocheco River, chromium concentration difference intervals for both filtering options are negative (table 4.4).

The independent t-tests for strontium, an alkaline earth metal, are mixed. Zero is included in the concentration difference in both filter options for the Cocheco River sediment pore water (table 4.4). The Merrimack River concentration difference for unfiltered peepers includes zero while the filtered peeper samples have a negative difference interval (table 4.4). The Squamscott River unfiltered peepers have a positive t-test difference interval. Filtered peepers from the Squamscott River have zero in the difference interval.

Zero is included in the independent t-test difference interval for zinc concentration for all the filter options and sediment pore water (table 4.4). This suggests there is no difference attributed to oxygen during sediment sampling for zinc concentrations with peepers.

Cadmium concentration depth profiles, shown in figure 4.19, are from filtered samples of equilibrated laboratory peepers removed from the Merrimack and Squamscott Rivers. The thin bars are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers. The depth profiles of cadmium in the Merrimack and Squamscott Rivers follow a similar trend as the iron profiles with cadmium concentrations low near the surface and increasing with depth. Peeper 8-1PSA for air purged Squamscott River sediment is significantly greater than the other peepers at depths of -89mm, -114mm and -146mm. This peeper is responsible for the large standard deviations at those depths.

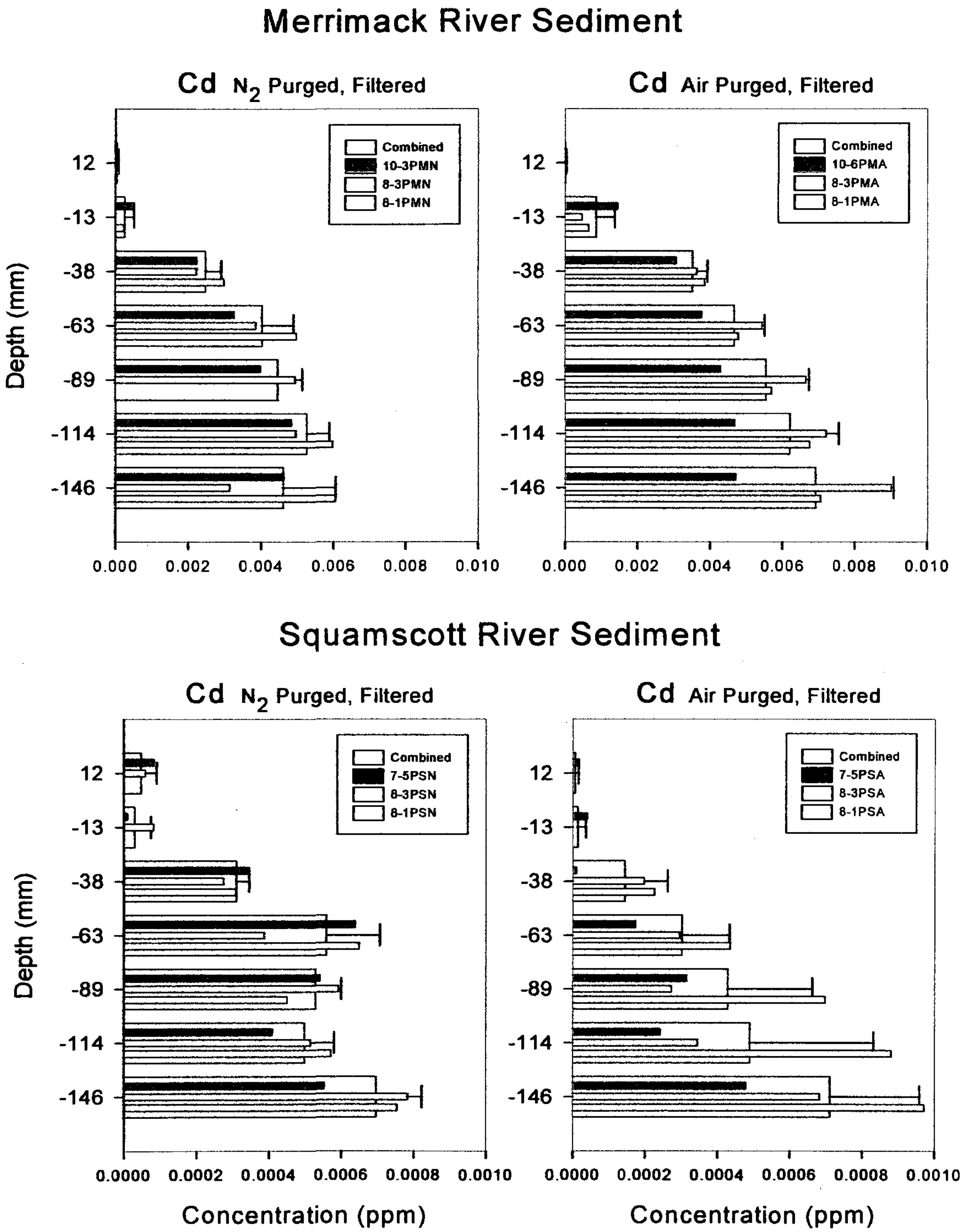


Figure 4.19: Merrimack & Squamscott Rivers Depth Profile for Cd
Cadmium concentration depth profiles are from filtered samples for equilibrated peepers removed from the Merrimack & Squamscott Rivers laboratory sediment. The thin bars are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

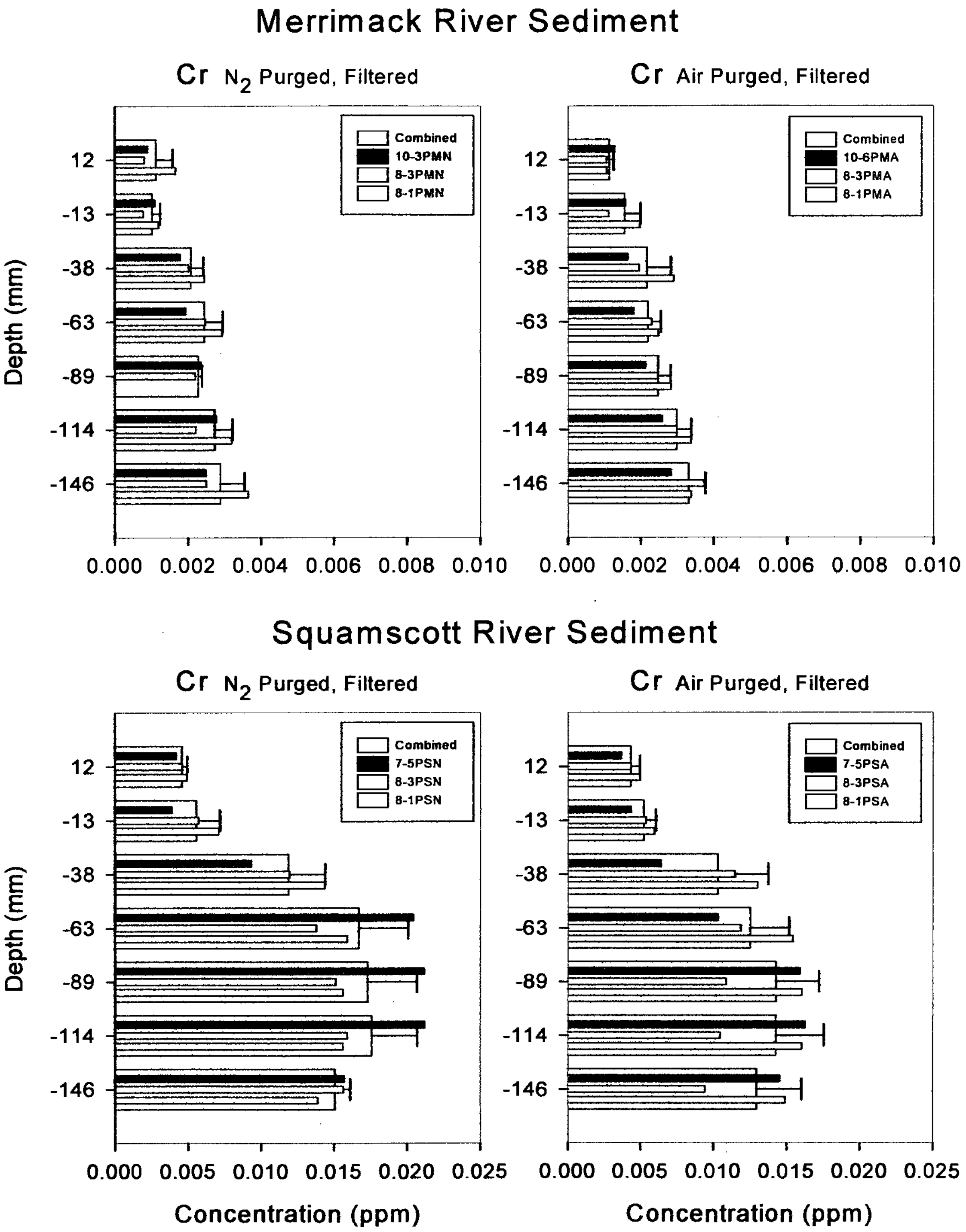
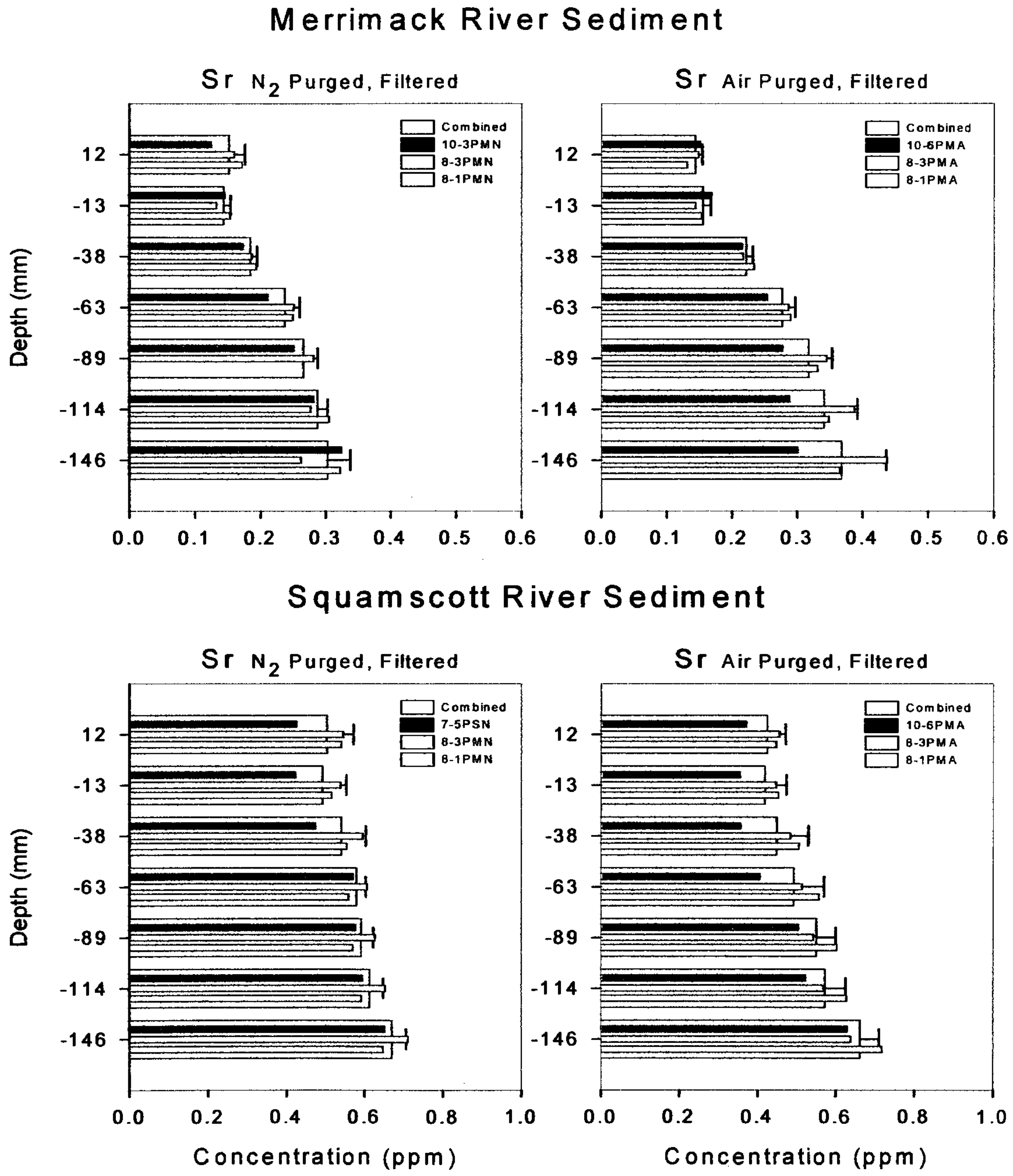


Figure 4.20: Merrimack and Squamscott Rivers Depth Profile for Cr
Chromium concentration depth profiles are from equilibrated peepers removed from the Merrimack and Squamscott Rivers laboratory sediment. The thin bars are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

Chromium concentration depth profiles, shown in figure 4.20, are from filtered samples of equilibrated laboratory peepers removed from the Merrimack and Squamscott Rivers. Chromium concentration depth profiles follow the expected trend as those seen in iron. The chromium concentration in Squamscott River sediment pore water is greater than in the Merrimack River. Both Rivers have a similar trend and concentration level for air and nitrogen purged peepers (figure 4.20).

Strontium concentration depth profiles, shown in figure 4.21, are from filtered samples of equilibrated laboratory peepers removed from the Merrimack and Squamscott Rivers. Strontium concentrations in the Merrimack River follow the expect trend of increasing concentration with increasing depth. Squamscott River concentrations are consistent throughout the depth profile, including strontium concentration is the river water. There is a similar depth profile for Strontium concentration air and nitrogen preparation purged peepers in both sediments. The peepers at each depth for both sediments and purge gas types have consistent concentration. As a result, their standard deviations are small (figure 4.21).

Zinc concentration depth profiles, shown in figure 4.22, are from filtered samples of equilibrated laboratory peepers removed from the Merrimack and Squamscott Rivers. There is a similar trend for purge gas types, air and nitrogen, in both sediments. The depth profile for the sediments is relatively consistent from the river water to the bottom of the peepers. Data from laboratory experiment #10, peepers 10-3PMN and 10-6PMA, have higher values than those from experiment #8 (figure 4.22).


Merrimack River Sediment

Sr N_2 Purged, Filtered

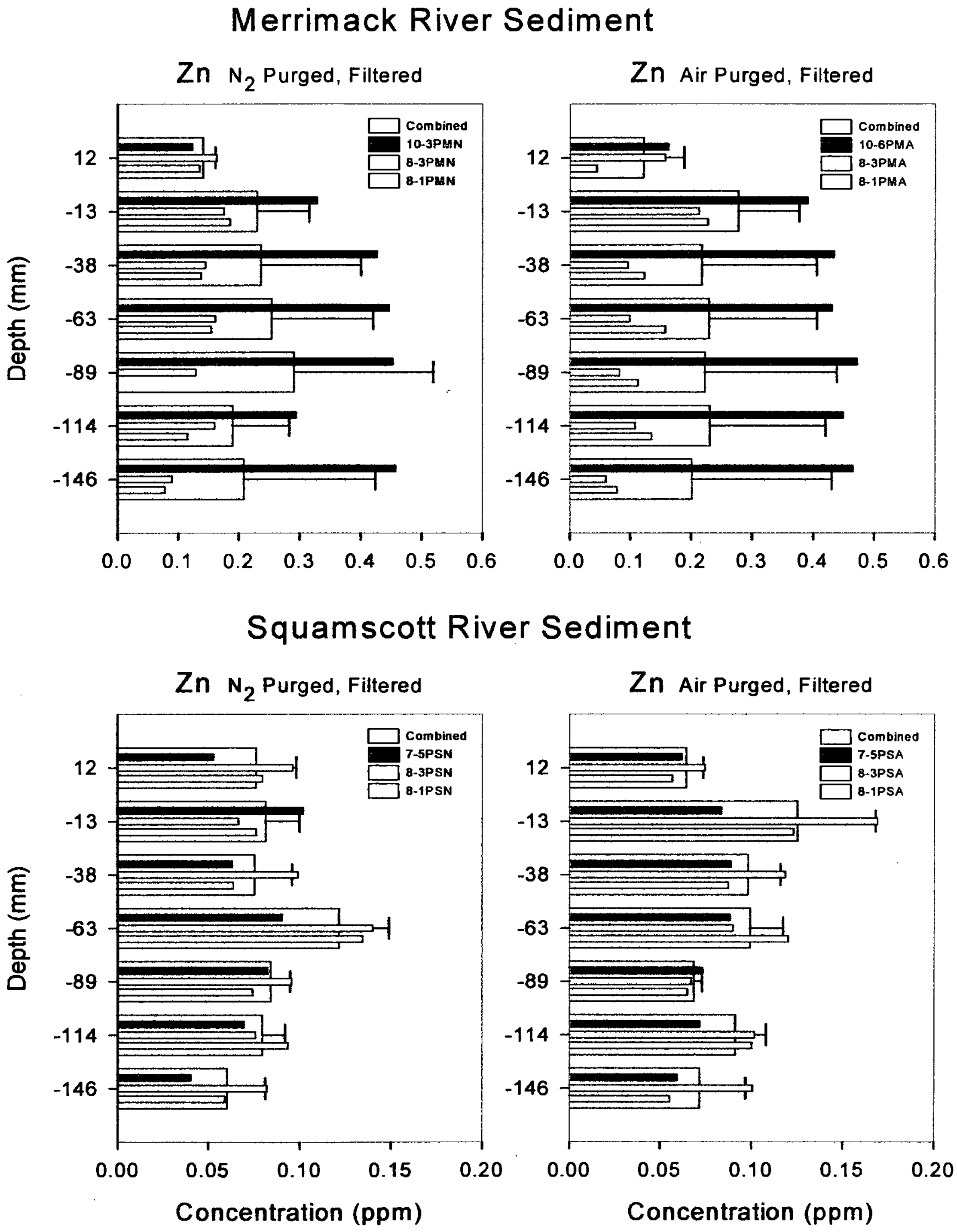
Sr Air Purged, Filtered

Squamscott River Sediment

Sr N_2 Purged, Filtered

Sr Air Purged, Filtered

Figure 4.21: Merrimack and Squamscott Rivers Depth Profile for Sr
Strontium concentration depth profiles are from equilibrated peepers removed from the Merrimack and Squamscott Rivers laboratory sediment. The thin bars are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.



Merrimack River Sediment

Squamscott River Sediment

Figure 4.22: Merrimack and Squamscott Rivers Depth Profile for Zn

Zinc concentration depth profiles are from equilibrated peepers removed from the Merrimack and Squamscott Rivers laboratory sediment. The thin bars are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

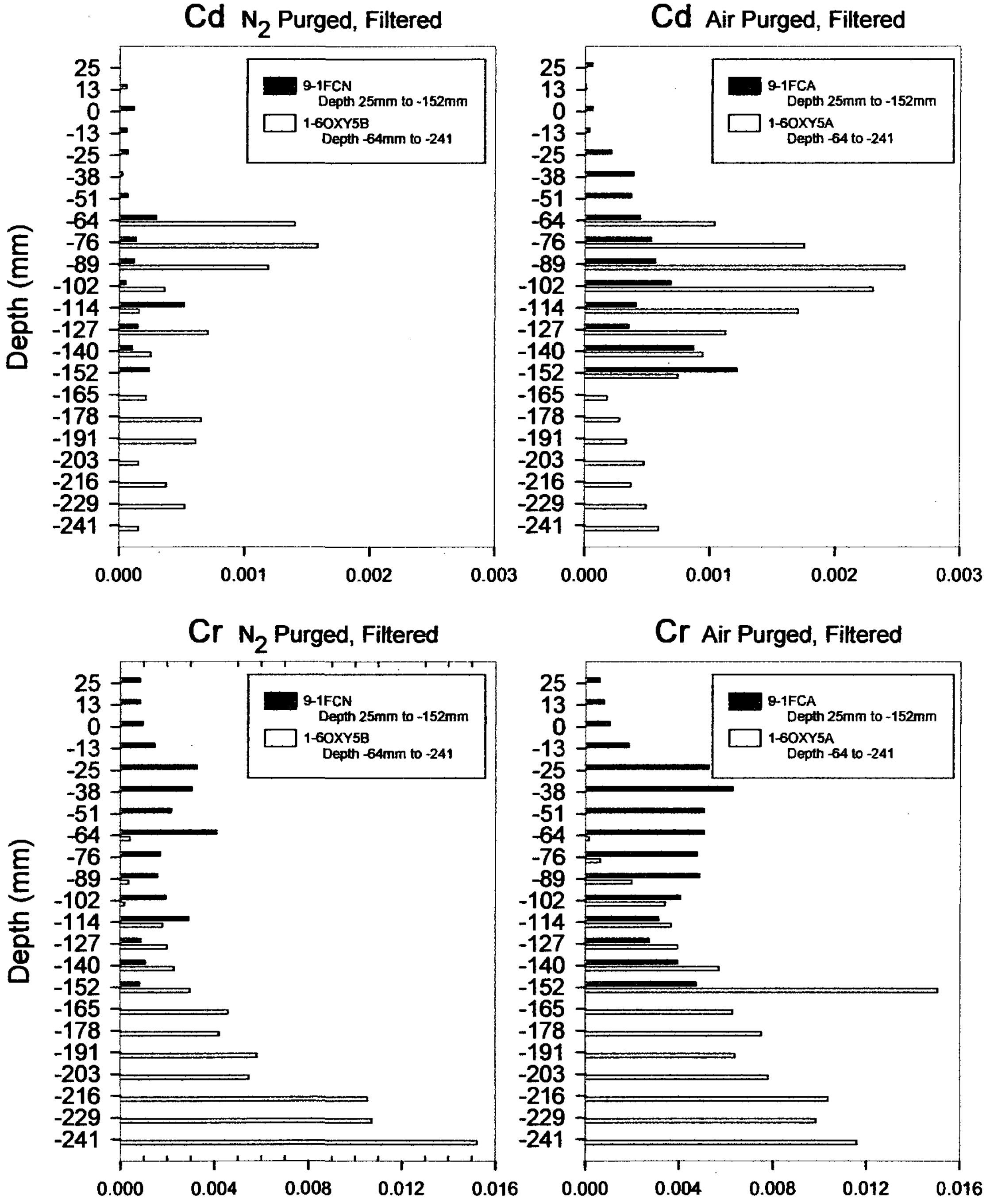


Figure 4.23: Cocheco River Depth Profile for Cd & Cr
Cadmium and chromium equilibrated concentration depth profiles for Cocheco River sediment pore water field studies. Fifteen chambers from peepers 9-1FC* correspond to depths 25mm to -152mm. Fifteen chambers from peepers 1-6OXY5* correspond to depths -64mm to -241mm.

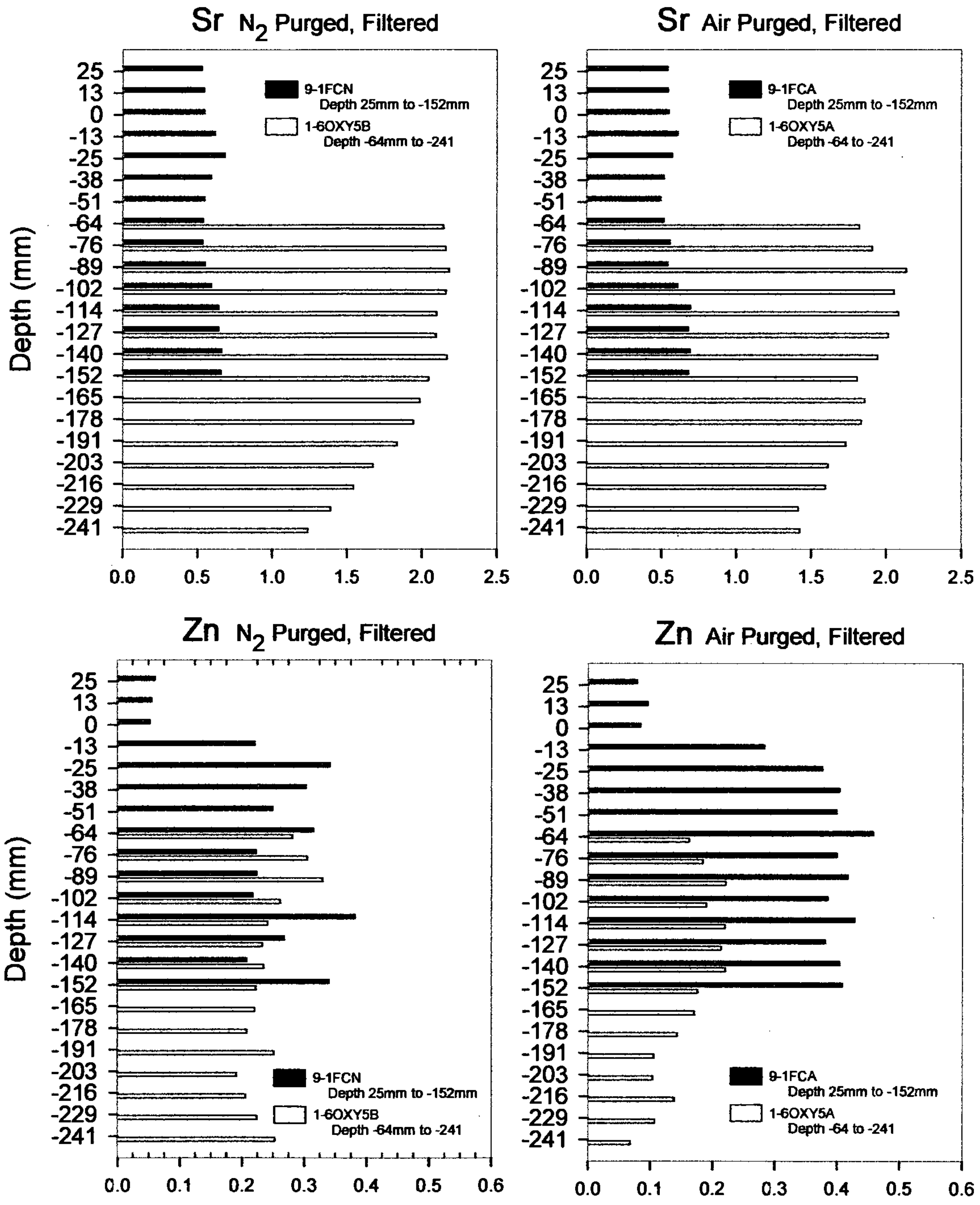


Figure 4.24: Cocheco River Depth Profile for Sr & Zn

Strontium and zinc equilibrated concentration depth profiles for Cocheco River sediment pore water field studies. Fifteen chambers from peepers 9-1FC* correspond to depths 25mm to -152mm. Fifteen chambers from peepers 1-6OXY5* correspond to depths -64mm to -241mm.

Cadmium concentration depth profiles, shown in figure 4.23, are from filtered samples of equilibrated field peepers removed from the Cocheco River. There is very little cadmium in the top portions of the sediment and in the river water. Peepers from the 1-OXY study have a higher concentration than those from the 9-1FC study. Peepers with air purged during preparation have a larger cadmium concentration than those with nitrogen purging (figure 4.23).

Chromium concentration depth profiles, shown in figure 4.23, are from filtered samples of equilibrated field peepers removed from the Cocheco River. There is a lower concentration of chromium in the river water than in the sediment pore water. Peeper purged with air during preparation have a high concentration than those purged with nitrogen in depths -25mm to -230mm. Depths from -216mm to -241mm have chromium concentrations that are similar for both air and nitrogen purged peepers (figure 4.23).

Strontium concentration depth profiles, shown in figure 4.24, are from filtered samples of equilibrated field peepers removed from the Cocheco River. Peepers from the 1-OXY study have a higher concentration than those from the 9-1FC study. Strontium concentrations in each peeper are consistent for all depths or chambers (figure 4.24). In each study, there is no difference between air and nitrogen purged peepers.

Zinc concentration depth profiles, shown in figure 4.24, are from filtered samples of equilibrated field peepers removed from the Cocheco River. There is very little zinc in the river water. Similar to strontium, zinc concentrations are consistent between individual peeper chambers and purge gas type.

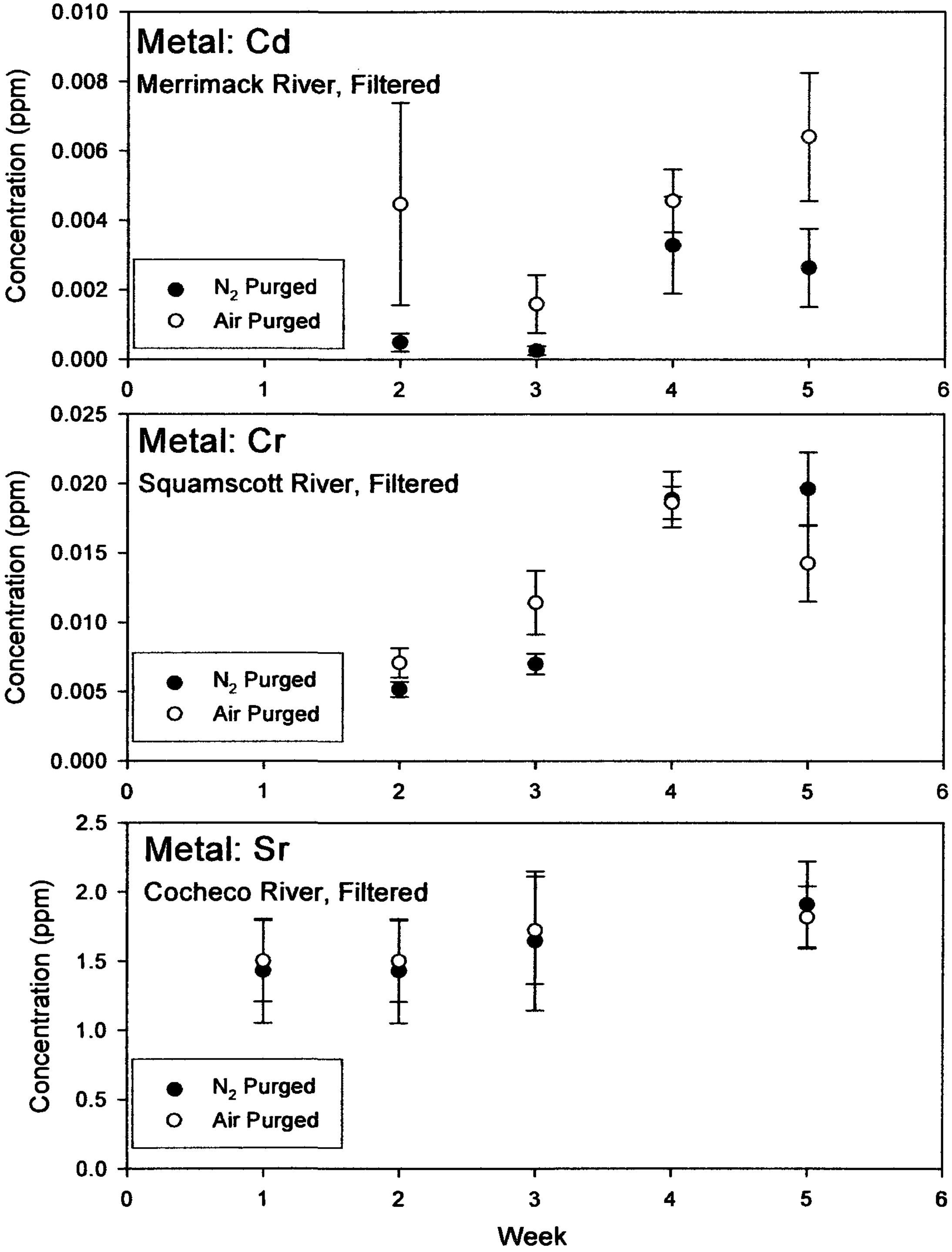


Figure 4.25: Selected Metal Trends

Cocheco River data is from field analysis. Merrimack and Squamscott River data is from laboratory analysis. Metal concentrations for each sample date are averages of peeper cells from 1" below the surface to the bottom of the peepers.

Equilibration trends for selected metals are shown in figures 4.25 and 4.26. The concentrations for each sample period are averages of peeper cells from 1" below the surface to the bottom of the peepers. Each metal has trends for peepers purged with nitrogen and air during preparation.

Cadmium laboratory equilibration trends for filtered peeper samples in Merrimack River sediment can be seen in figure 4.25. Peepers purged with air during preparation have higher concentration than those purged with nitrogen for each time period. Cadmium concentration is still rising for air purged peepers at the five week time period. For nitrogen purged peepers, the concentration at five weeks is lower than at four weeks (figure 4.25). However with only one time period of reduce concentration, equilibration can not be confirmed.

Chromium laboratory equilibration trends for filtered peeper samples in Merrimack River sediment can be seen in figure 4.25. The trends for peepers purged with nitrogen and air converged at week four. Nitrogen purged peeper sample concentrations were flat between four and five, while air purged peeper concentration went down at week five (figure 4.25). Again with only one time period of reduce or flat concentration levels, equilibration can not be confirmed.

Strontium field equilibration trends for filtered peeper samples in Cocheco River sediment can be seen in figure 4.25. The trends for peepers purged with nitrogen and air during preparation were similar for all time periods. Concentration levels were rising from week three to week five. Equilibration could not be verified for strontium in the Cocheco River during the study period.

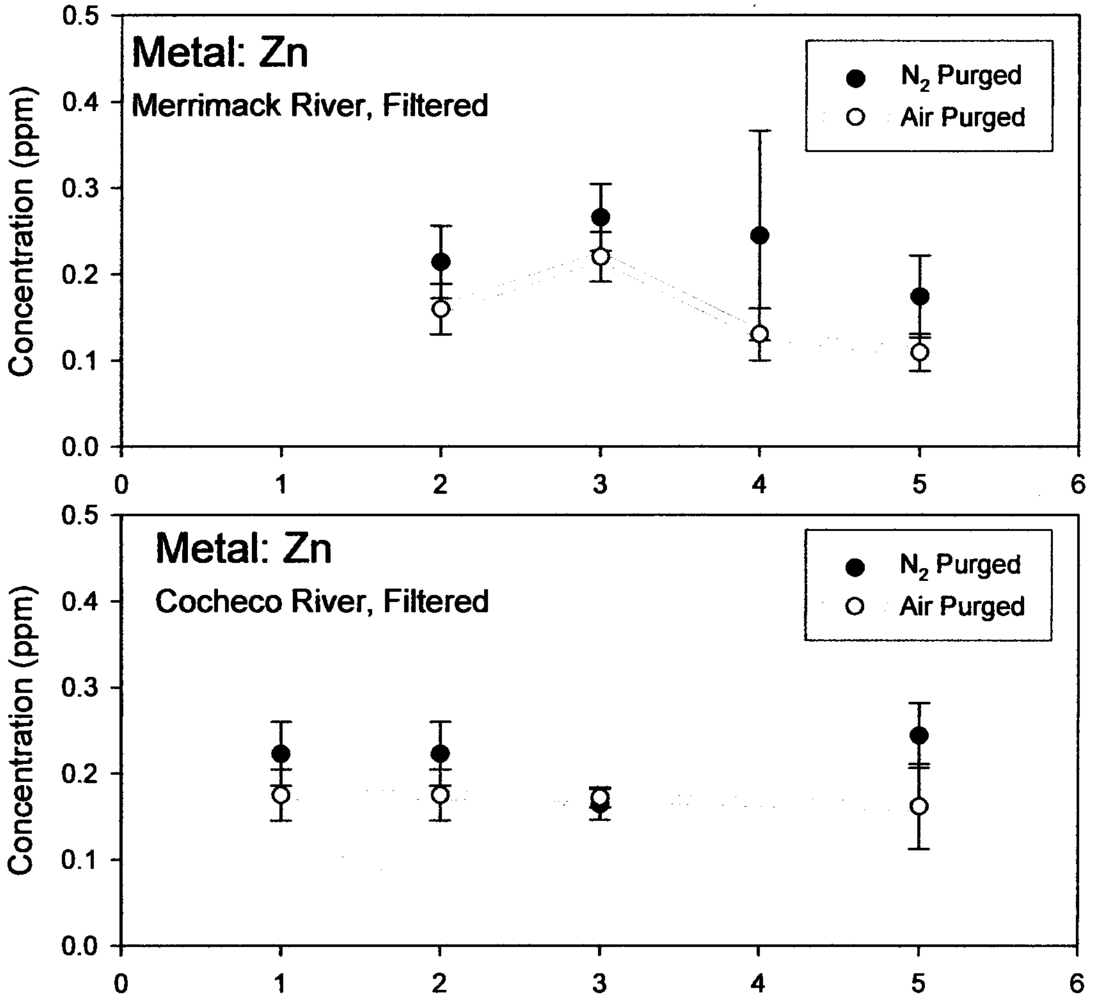


Figure 4.26: Zn Trends in Selected Sediments
Cocheco River data is from field analysis. Merrimack and Squamscott River data is from laboratory analysis. Zinc concentrations for each sample date are averages of peeper cells from 1" below the surface to the bottom of the peepers.

Zinc equilibration trends in the laboratory study for the Merrimack River and the field study for the Cocheco River sediments, for filtered peeper samples, can be seen in figure 4.26. Trends for zinc concentrations in the Merrimack River had a similar pattern for both purge gas types. Concentration increased from week one to week two then decreased to week five. Nitrogen purged peepers in

Merrimack River sediment had a higher concentration for all of the time periods. In Cocheco River Sediment, zinc concentrations were relatively flat for the entire study. Nitrogen purged peepers had higher concentrations than air purge peepers for weeks 1, 2 and 5. Equilibration was reached in the Cocheco River by week one and by week three in the Merrimack River.

Overall the oxygen effects on the selected metals were negligible. Most of the difference intervals for the independent t-tests included zero. The majority of those that did not were negative, which indicated air purged peepers had a higher concentration. The results were similar to those of the redox sensitive metals. The depth profiles for the selected metals were also similar to those for the redox sensitive metals. Peepers reached equilibration between week four and six.

4.2.5 Oxygen Effect on Anion Concentration

Anion analysis was performed on Merrimack and Squamscott River sediment pore water. In the laboratory studies, anion data was collected for all the peepers. Two peepers were analyzed at each field location close to where the sediment was collected. One was prepared with nitrogen purged gas and one with air purged gas. The field peeper samples were all filtered.

Part of the theory of this thesis is that oxygen effects will be mitigated by microbial activity. Microbes will consume any oxygen introduced into the sediment by the peepers, which will cause the redox conditions to return to their original state. Microbes use nitrate as a terminal electron acceptor by converting nitrate to nitrite. Therefore, the relationship between nitrite and nitrate was investigated. Microbial activity should cause the ratio of nitrite to nitrate plus nitrite to increase over time. Chloride and sulfate concentrations were also measured. Equilibrated peeper concentrations can be seen in Figure 4.27: "Equilibrated Anion Concentrations".

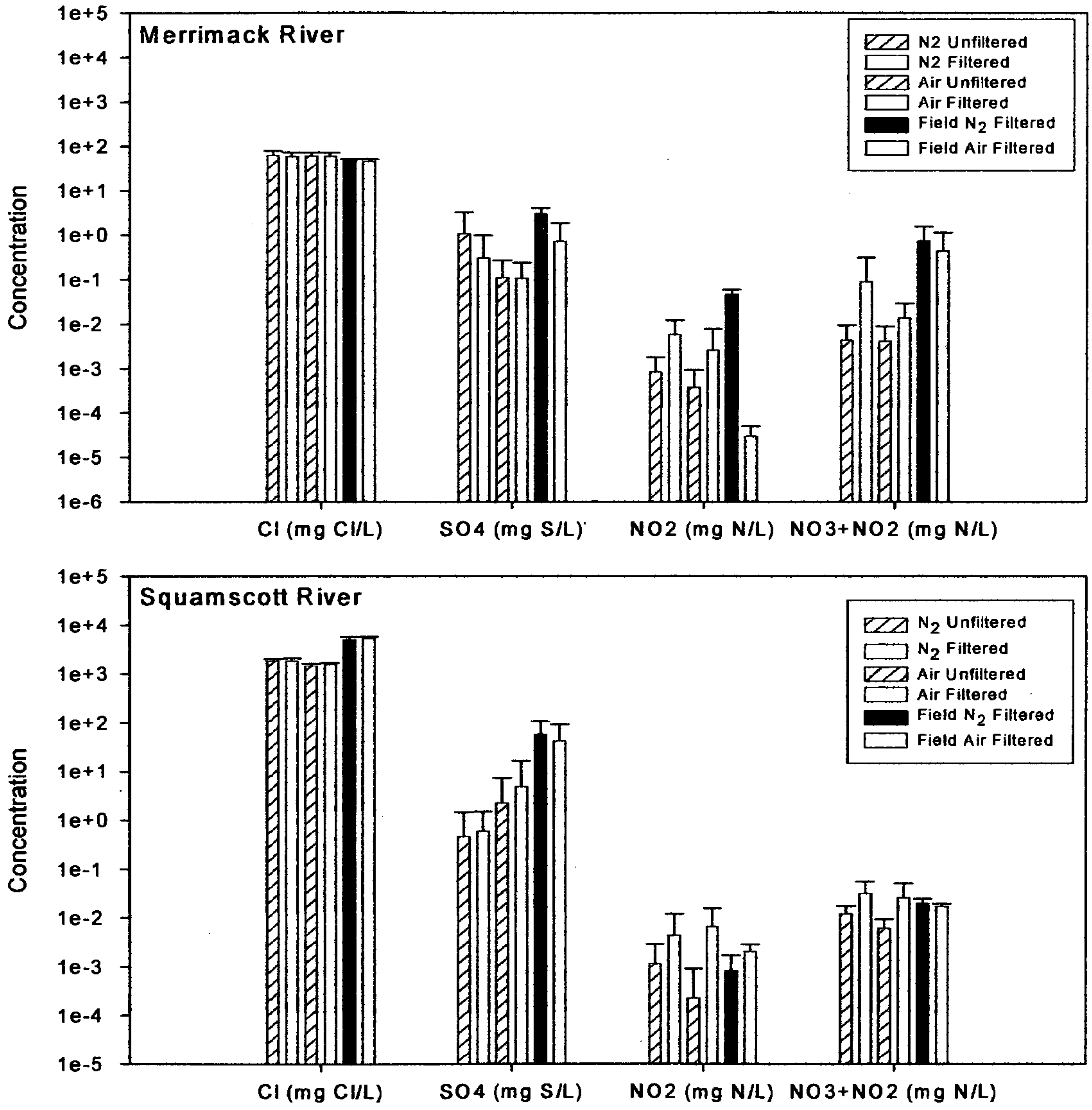


Figure 4.27: Equilibrated Anion Concentrations
Equilibrated laboratory and field peeper sample concentrations for the Merrimack and Squamscott Rivers. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers. Chloride and sulfate were analyzed on an ion chromatograph. Nitrite and nitrate + nitrite were analyzed on a colorimeter.

The Chloride concentrations in the Merrimack River sediment were of similar magnitude for field and laboratory experiments (figure 4.27). Field samples from the Squamscott River were than the laboratory samples. In both sediments, nitrogen and air purged peepers in each category had similar concentrations. The independent t-tests for the Merrimack River sediment included zero in the difference interval for all the options (table 4.5). The t-test on field sediment of the Squamscott River also included zero in the difference interval. Laboratory sediment from the Squamscott River had a positive t-test interval for both filtering options. It is expected and confirmed, by figure 4.27, that the chloride ion is not influenced by oxygen introduced into the sediment.

Sulfate concentrations are greater for filtered field peepers in the Merrimack River than for the filtered laboratory peepers (figure 4.27). In the Squamscott River, field samples have a greater sulfate concentration the filtered or unfiltered laboratory samples (figure 4.27). There are mixed results, in both river sediments, for the comparison between nitrogen and air purged peepers. For example in Squamscott River, nitrogen purged peeper have a higher sulfate concentration than air purge peepers in the field study while air purged peepers have the higher concentration in laboratory study (figure 4.27). The independent t-test interval difference includes zero in all but Merrimack River field sediments (table 4.5). A zero difference interval indicates that oxygen introduced into the sediment has no effect on sulfate concentration.

Table 4.5: Anion Independent t-tests

Preparation purge gas comparisons are equilibrated concentrations of selected anions, Cl^-, SO_4^{2-}, NO_2^- & $NO_3^- + NO_2^-$. Merrimack and Squamscott River data are from laboratory and field results. Concentrations used in the comparison are averages of peeper cells from 1" below the surface to the bottom of the peepers. df = degree of freedom; $t_{df,0.025}$ are from student t-test tables

Anion	Sediment	Comparison	df	t	Interval (ppm)	
Cl^-	Merrimack Laboratory	Unfiltered	18	2.101	15.49	-11.32
		Filtered	28	2.048	8.555	-10.95
	Squamscott Laboratory	Unfiltered	18	2.101	563.4	246.7
		Filtered	28	2.048	407.1	119.2
	Merrimack Field	Filtered	8	2.306	0.6869	-9.219
	Squamscott Field	Filtered	8	2.306	431.5	-1115
SO_4^{2-}	Merrimack Laboratory	Unfiltered	18	2.101	2.426	-0.5188
		Filtered	28	2.048	0.5644	-0.1572
	Squamscott Laboratory	Unfiltered	18	2.101	1.614	-5.182
		Filtered	28	2.048	1.885	-10.36
	Merrimack Field	Filtered	8	2.306	-0.7379	-3.947
	Squamscott Field	Filtered	8	2.306	89.57	-59.55
NO_2^-	Merrimack Laboratory	Unfiltered	18	2.101	0.0012	-0.0003
		Filtered	28	2.048	0.0076	-0.0013
	Squamscott Laboratory	Unfiltered	18	2.101	0.0022	-0.0003
		Filtered	28	2.048	0.0040	-0.0084
	Merrimack Field	Filtered	8	2.306	-0.0346	-0.0591
	Squamscott Field	Filtered	8	2.306	0.0000	-0.0025
NO_3^- + NO_2^-	Merrimack Laboratory	Unfiltered	18	2.101	0.0049	-0.0045
		Filtered	28	2.048	0.1938	-0.0436
	Squamscott Laboratory	Unfiltered	18	2.101	0.0101	0.0018
		Filtered	28	2.048	0.0243	-0.0133
	Merrimack Field	Filtered	8	2.306	0.7831	-1.386
	Squamscott Field	Filtered	8	2.306	0.0080	-0.0033

Nitrogen purged field peepers had the highest nitrite concentrations while the air purged field peepers had the lowest (figure 4.27). Nitrite concentrations for filtered laboratory peeper samples were greater than the unfiltered samples. In the Squamscott River, the filtered sample concentrations were greater than unfiltered samples for all categories. Nitrogen and air purged peepers had mixed results. Unfiltered nitrogen peeper samples had a greater nitrate concentration than the unfiltered air peepers. However, the filtered samples of air purged peepers were greater than the nitrogen purged peepers (figure 2.27). Except for the field study in the Merrimack River, all the independent t-test intervals for sediment comparison of purge gas type included zero (table 4.5).

Nitrate + nitrite concentrations in the Merrimack River field study were greater than those in the laboratory study (figure 4.27). Filtered sample concentrations were larger than the unfiltered on in the Merrimack River laboratory. The Merrimack River laboratory filtered sample removal option had higher nitrate + nitrite concentrations for nitrogen purged peepers than air purged peepers. The preparation gas purge types had similar concentrations for Merrimack River unfiltered samples (figure 4.27). In the Squamscott River sediment, filter samples had greater nitrate + nitrite concentrations than unfiltered for all purge gas types (figure 4.27). Nitrogen and air preparation purge samples had similar concentrations when compared by filtering option (figure 4.27). Except for the unfiltered laboratory study in the Squamscott River, all the independent t-test intervals for sediment comparison of purge gas type included zero (table 4.5). It should be noted that a difference interval that include zero suggests oxygen introduced into the sediment by the peepers has no effect on nitrate or nitrite concentration.

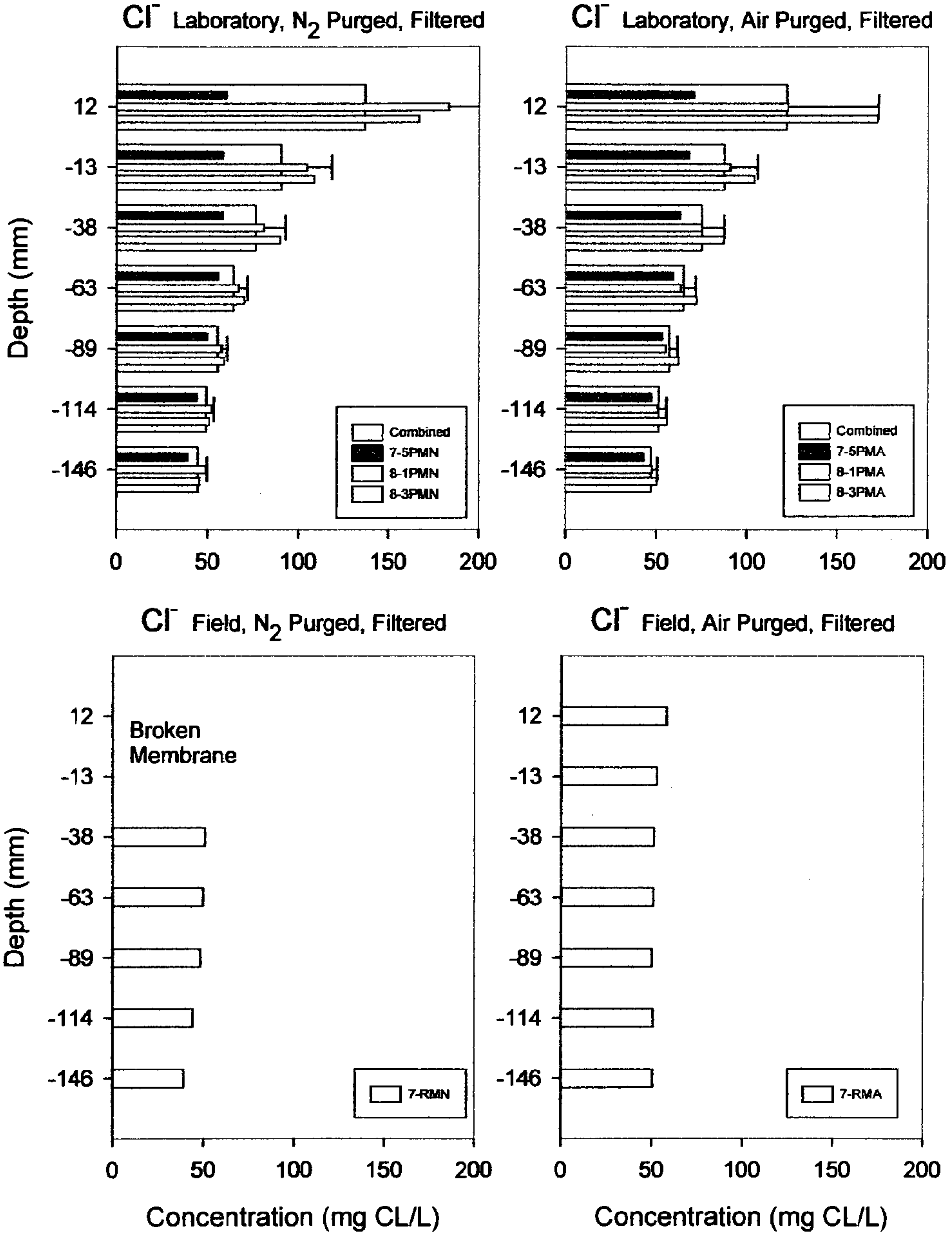


Figure 4.28: Merrimack River Chloride Anion Depth Profile

Chloride concentration depth profiles of filtered peeper samples removed from the Merrimack River sediment in laboratory and field studies. The peepers used for the chart on the left were purged with nitrogen during preparation. The peepers for the chart on the right were purged with air. The thin bars on the laboratory sediment are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

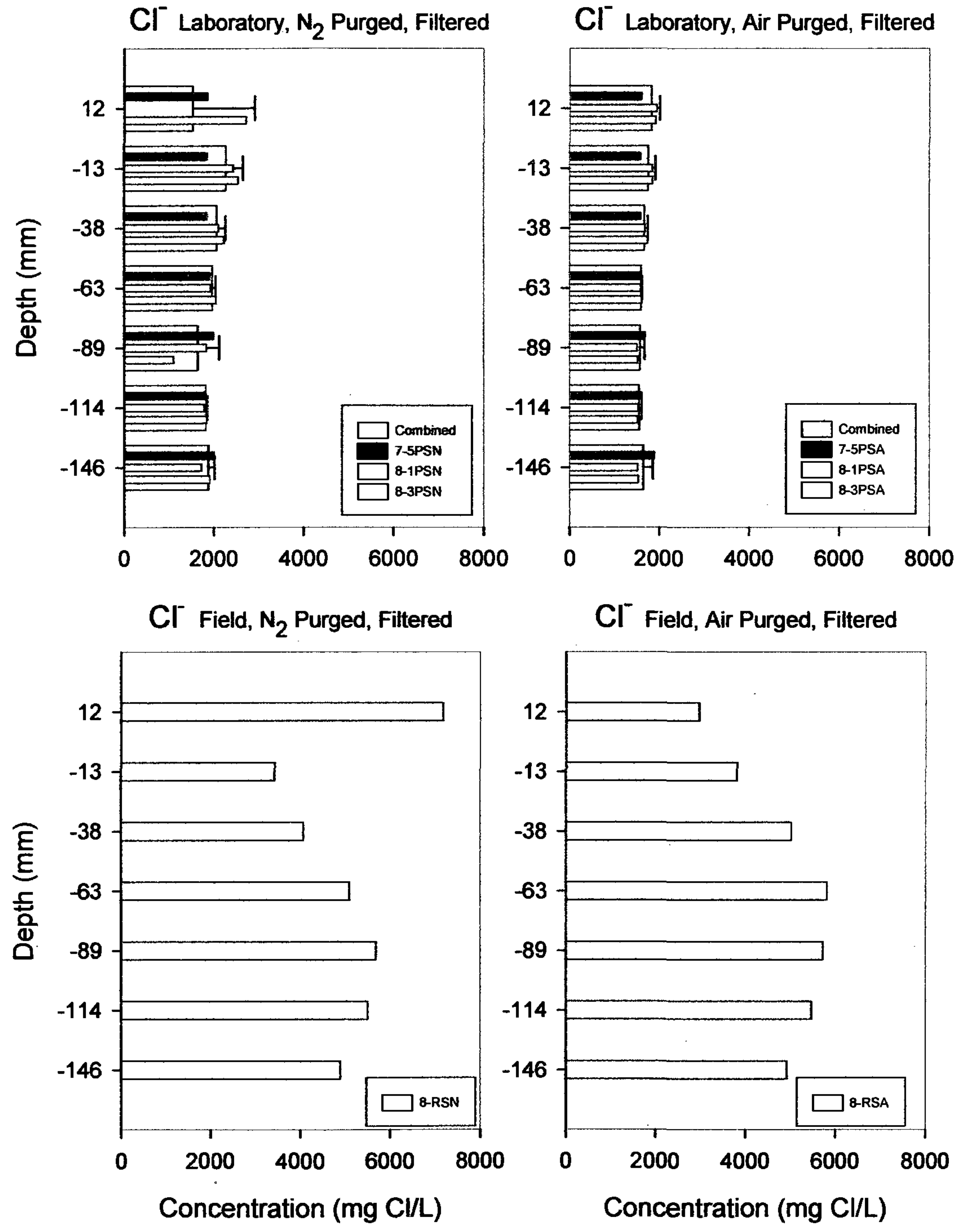


Figure 4.29: Squamscott River Chloride Anion Depth Profile
Chloride concentration depth profiles of filtered peeper samples removed from the Squamscott River sediment in laboratory and field studies. The peepers used for the chart on the left were purged with nitrogen during preparation. The peepers for the chart on the right were purged with air. The thin bars on the laboratory sediment are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

The Merrimack River depth profile for chloride in laboratory studies shows a higher concentration in the river water than in the pore water for both purge gas types (figure 4.28). Chloride concentration in the Merrimack River laboratory study is gradually reduced to approximate 50 mg Cl^-/L. The field results show a consistent concentration throughout the depth profile at 50 mg Cl^-/L (figure 4.28). Squamscott River chloride concentrations are consistent throughout the depth profiles for both purges types in both field and laboratory studies (figure 4.29). However, the field results are much higher than those for laboratory studies.

The sulfate anion concentrations in the Merrimack and Squamscott Rivers laboratory study were higher in the river water and upper sediment (figure 4.30 & 4.31). There was very little sulfate below -33mm. The exception was that the air purged Squamscott River peeper had a high concentration at -146mm. The Merrimack River air purged field peeper had a consistent concentration to -89mm at near 4 mg S/L (figure 4.30). The field nitrogen peeper for the Merrimack River had a broken membrane so the results were suspect. The Squamscott River field peepers had sulfate to a depth of -89mm.

It should be noted that sulfide-rich sediment can be affected by air introduction by causing metal sulfides to dissolve. Although, the sediment was not analyzed for sulfide, the Squamscott River sediment constituents were used in the computer modeling program Visual Minteq. Each constituent concentration (from the laboratory analysis), temperature, pH and atmospheric pressure was entered into the program. The model resulted in a very low sulfide partial pressure, 9.47×10^{-23} and no sulfide in the sediment. There also was no tell-tale scent of hydrogen sulfide. The concentration detectable by humans is 0.0047ppm. This is an indication that the sediment is not sulfide rich.

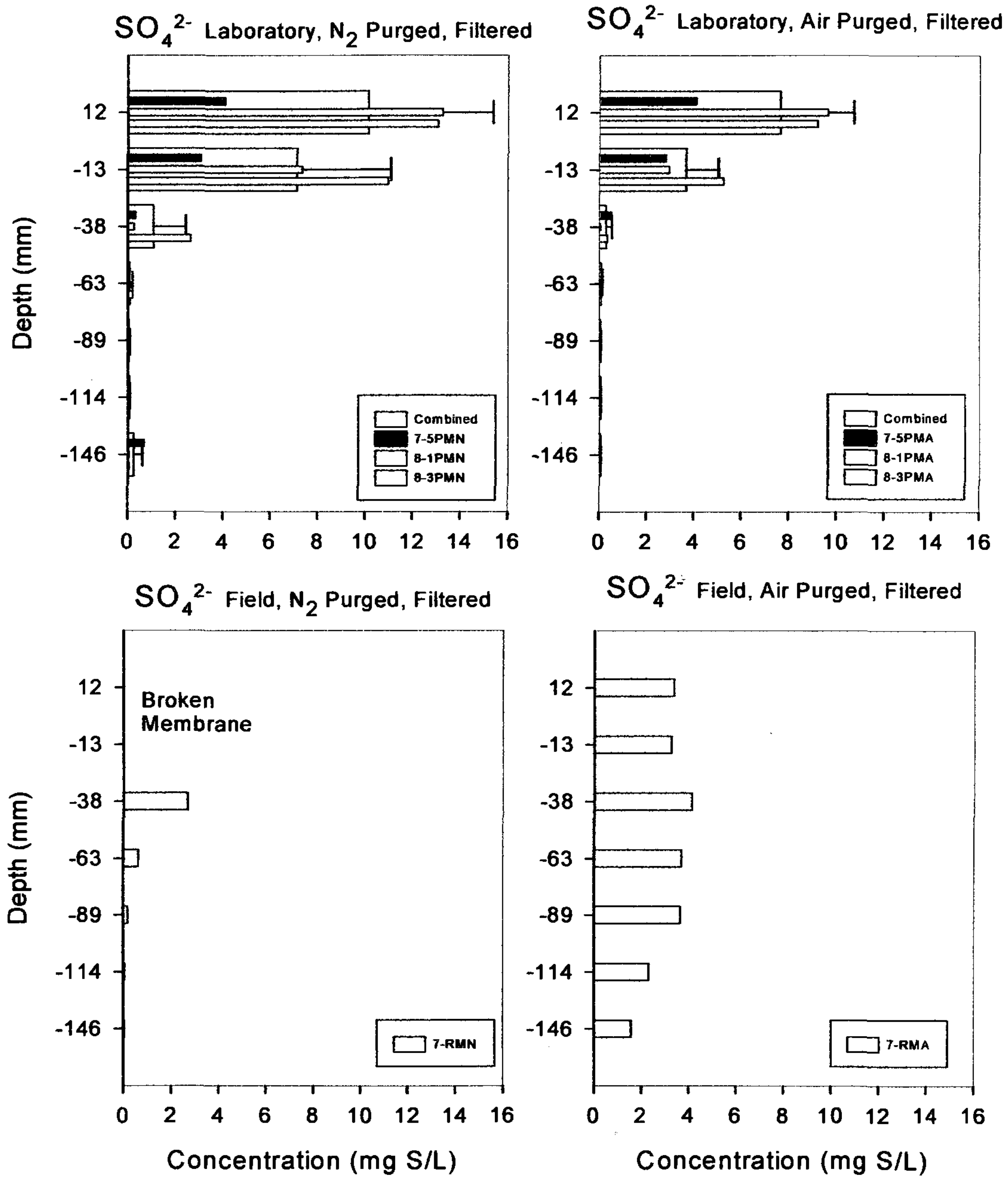


Figure 4.30: Merrimack River Sulfate Anion Depth Profile Figure
Sulfate concentration depth profiles of filtered peeper samples removed from the Merrimack River sediment in laboratory and field studies. The peepers used for the chart on the left were purged with nitrogen during preparation. The peepers for the chart on the right were purged with air. The thin bars on the laboratory sediment are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

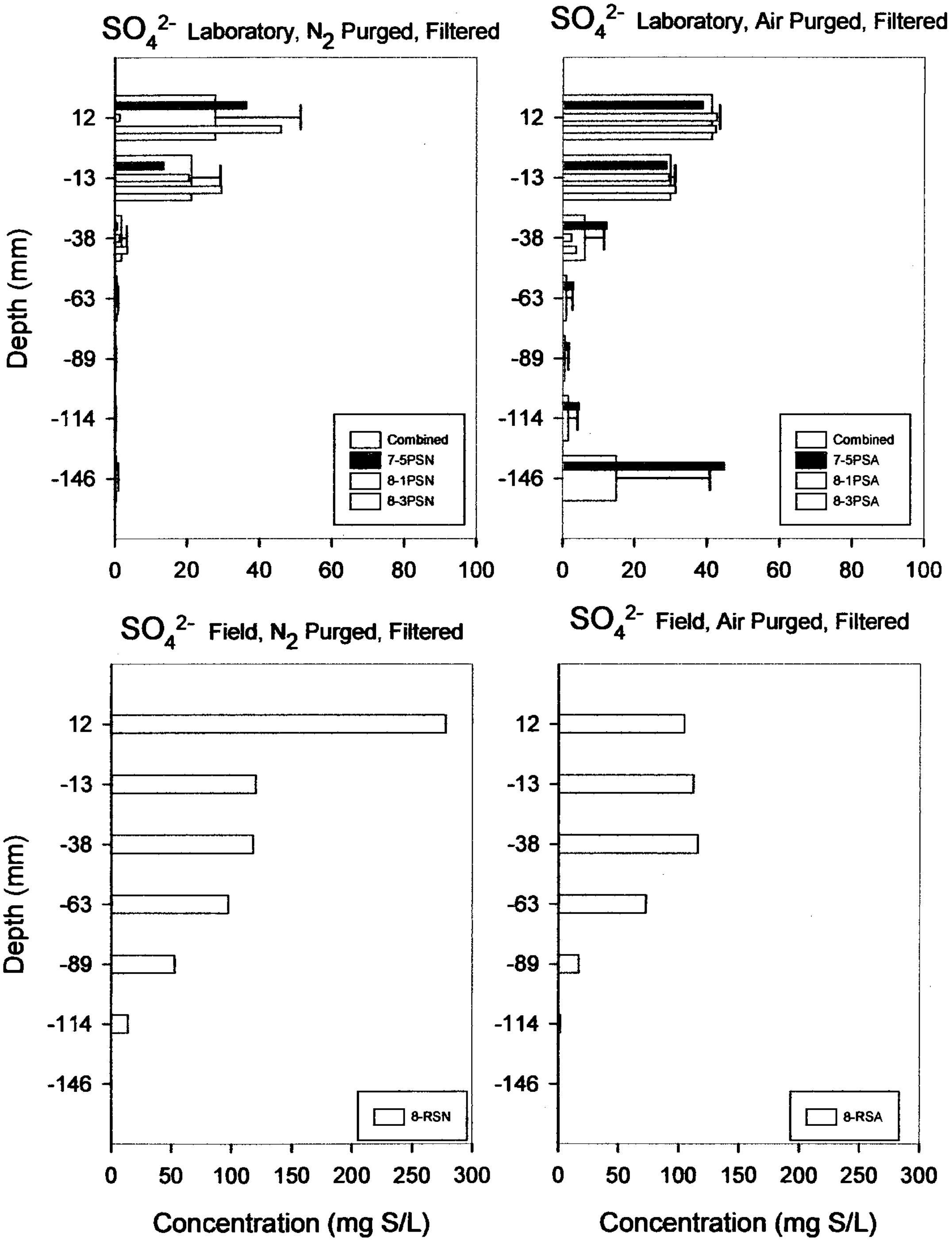


Figure 4.31: Squamscott River Sulfate Anion Depth Profile
Sulfate concentration depth profiles of filtered peeper samples removed from the Squamscott River sediment in laboratory and field studies. The peepers used for the chart on the left were purged with nitrogen during preparation. The peepers for the chart on the right were purged with air. The thin bars on the laboratory sediment are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

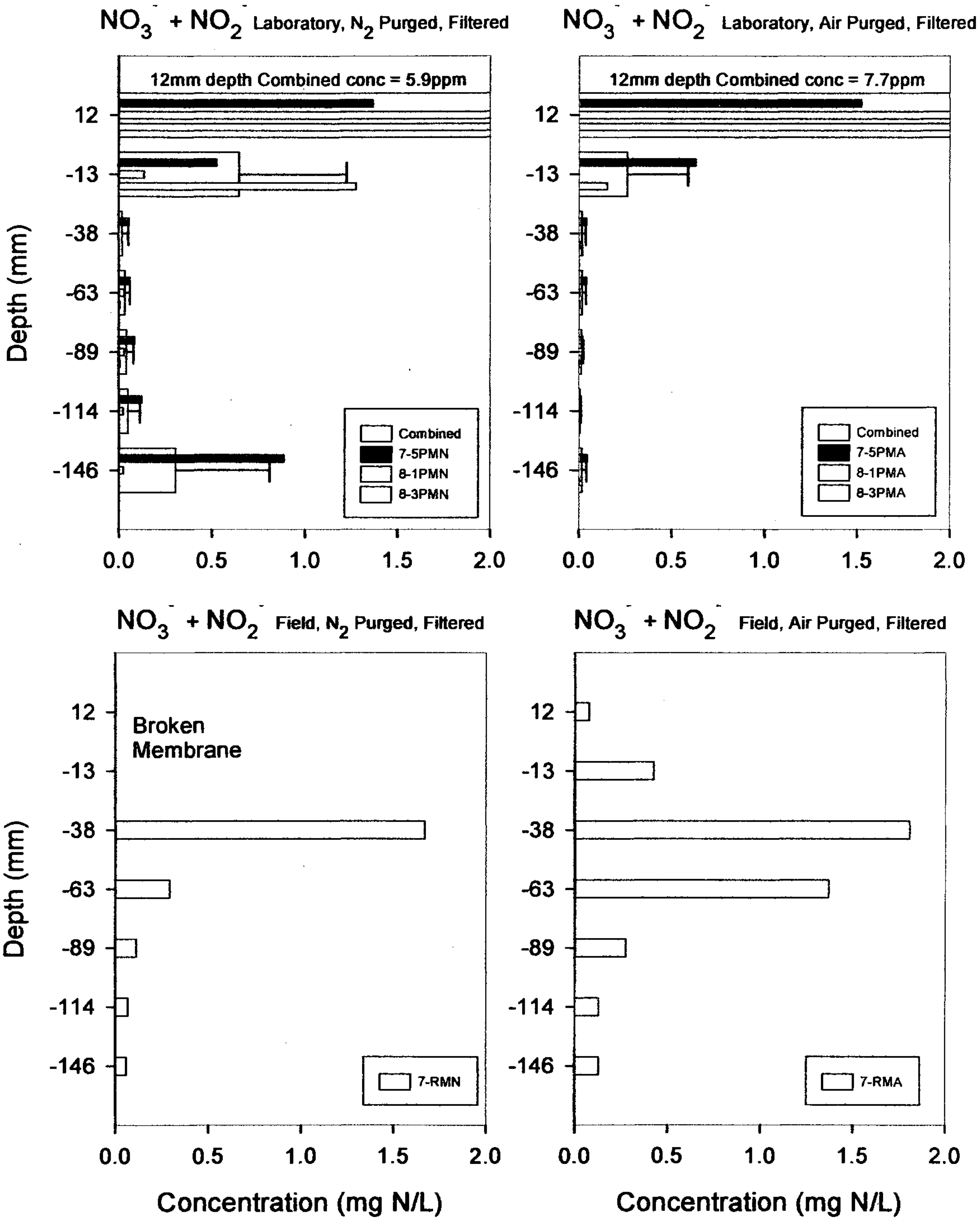


Figure 4.32: Merrimack River Nitrate + Nitrite Depth
Nitrate + nitrite concentration depth profiles of filtered peeper samples removed from the Merrimack River sediment in laboratory and field studies. The peepers used for the chart on the left were purged with nitrogen during preparation. The peepers for the chart on the right were purged with air. The thin bars on the laboratory sediment are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

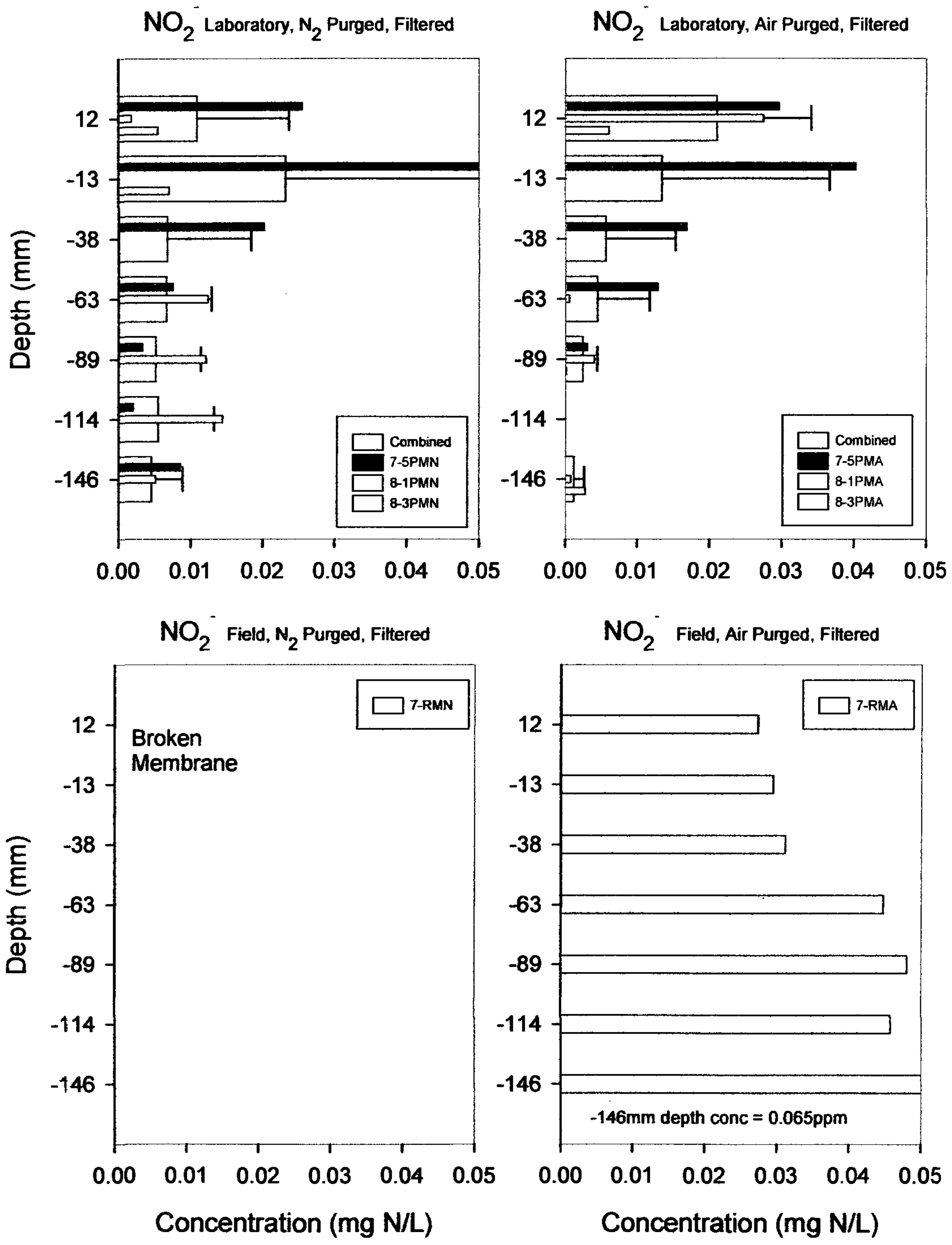


Figure 4.33: Merrimack River Nitrite Depth Profile
Nitrite concentration depth profiles of filtered peeper samples removed from the Merrimack River sediment in laboratory and field studies. The peepers used for the chart on the left were purged with nitrogen during preparation. The peepers for the chart on the right were purged with air. The thin bars on the laboratory sediment are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

Nitrate plus nitrite and nitrite depth profiles for filtered peepers in the Merrimack River can be seen in figures 4.32 and 4.33, respectively. Combined nitrate and nitrite concentrations are highest in the river water for the laboratory study at 5.9 mg N/L and 7.7 mg N/L, nitrogen and air purged peepers respectively. Nitrite alone also has the highest concentration in the river water. In the field study for nitrate plus nitrite, the highest concentration is at -38mm (figure 4.32). The field study for the nitrogen purged peeper has no nitrite in any of the chambers. A broken membrane in the top two chambers precludes examination of the river water nitrite concentration. The air purged peepers has nitrite concentrations between 0.03 mg N/L and 0.065 mg N/L throughout the entire peeper gradually increasing with depth (figure 4.33). The ratio for nitrite to nitrate plus nitrite, in the laboratory study on Merrimack River sediment, is highest at depths -38mm (≈ 0.35) and -63mm (≈ 0.24) for both purged gas types. The ratio is lowest in the river water and top chamber.

The Squamscott River laboratory studies show the highest nitrate plus nitrite concentrations in the river water and first chamber for both purge gas types (figure 4.34). The combined nitrate and nitrite concentrations in the field peepers are consistent throughout the whole peeper for both preparation purge gas types. However, the concentrations are much lower than the laboratory studies. Squamscott River nitrite concentrations in the laboratory studies are highest in the river water and top chamber (figure 4.35). The field study shows very little nitrite in the peepers. The ratio for nitrite to nitrate plus nitrite for Squamscott River laboratory pore water is greatest after the depth of -38mm.

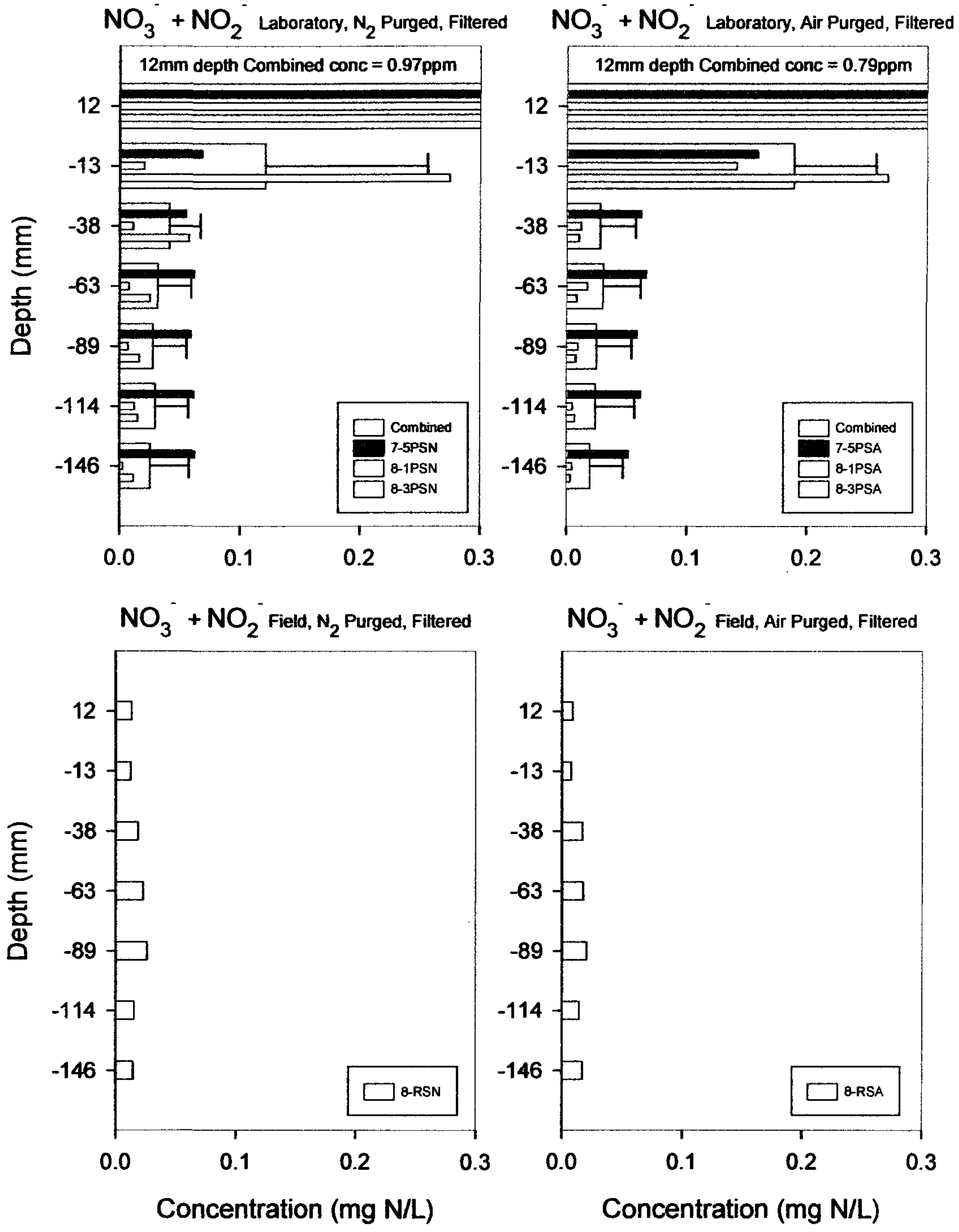


Figure 4.34: Squamscott River Nitrate + Nitrite Depth Profile

Nitrate + nitrite concentration depth profiles of filtered peeper samples removed from the Squamscott River sediment in laboratory and field studies. The peepers used for the chart on the left were purged with nitrogen during preparation. The peepers for the chart on the right were purged with air. The thin bars on the laboratory sediment are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

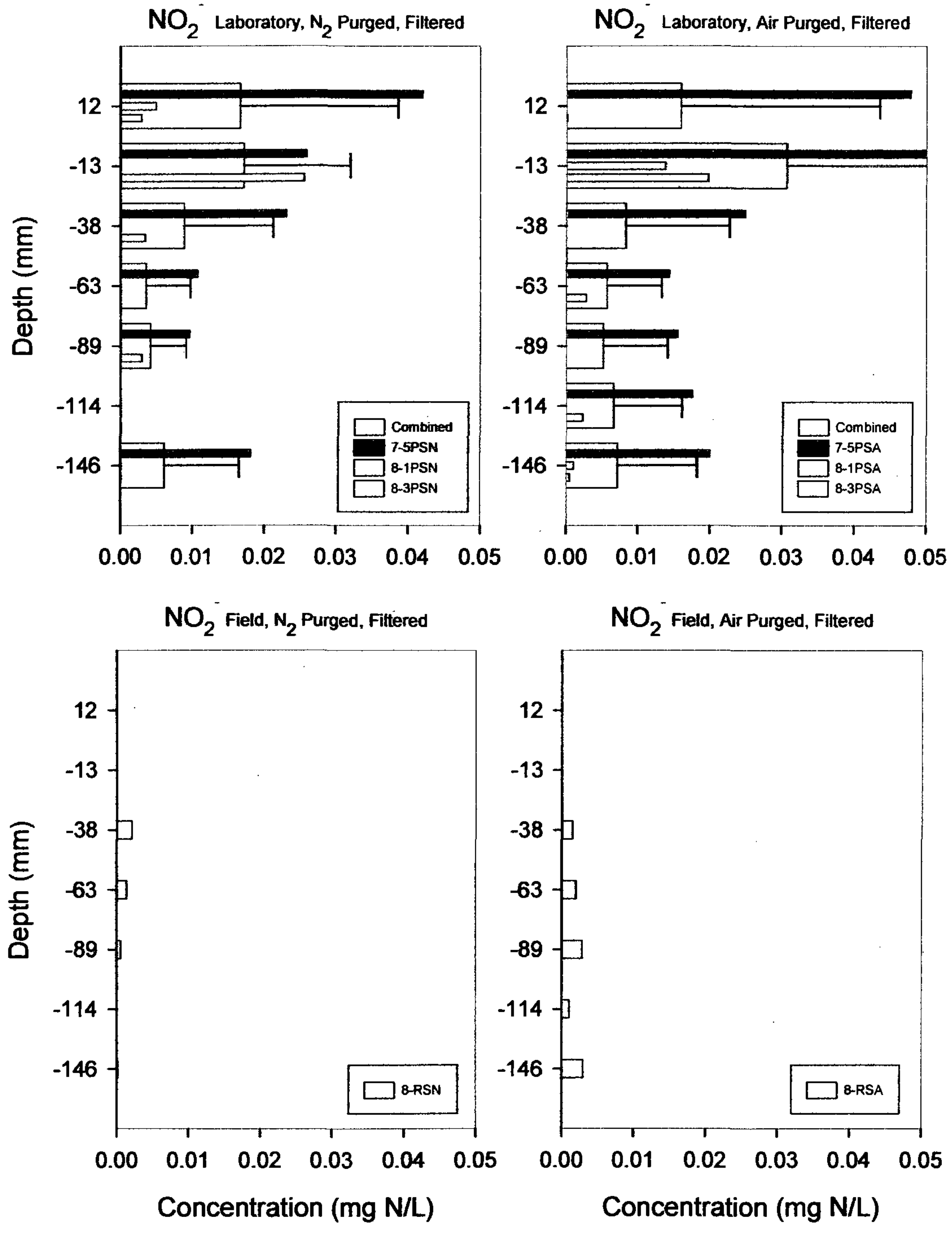


Figure 4.35: Squamscott River Nitrite Depth Profile
Nitrite concentration depth profiles of filtered peeper samples removed from the Squamscott River sediment in laboratory and field studies. The peepers used for the chart on the left were purged with nitrogen during preparation. The peepers for the chart on the right were purged with air. The thin bars on the laboratory sediment are individual peeper while the thick bar is the average of those peepers. Each depth represents two adjacent peeper cells. The exception is depth -146, which is the last three cells of the peepers.

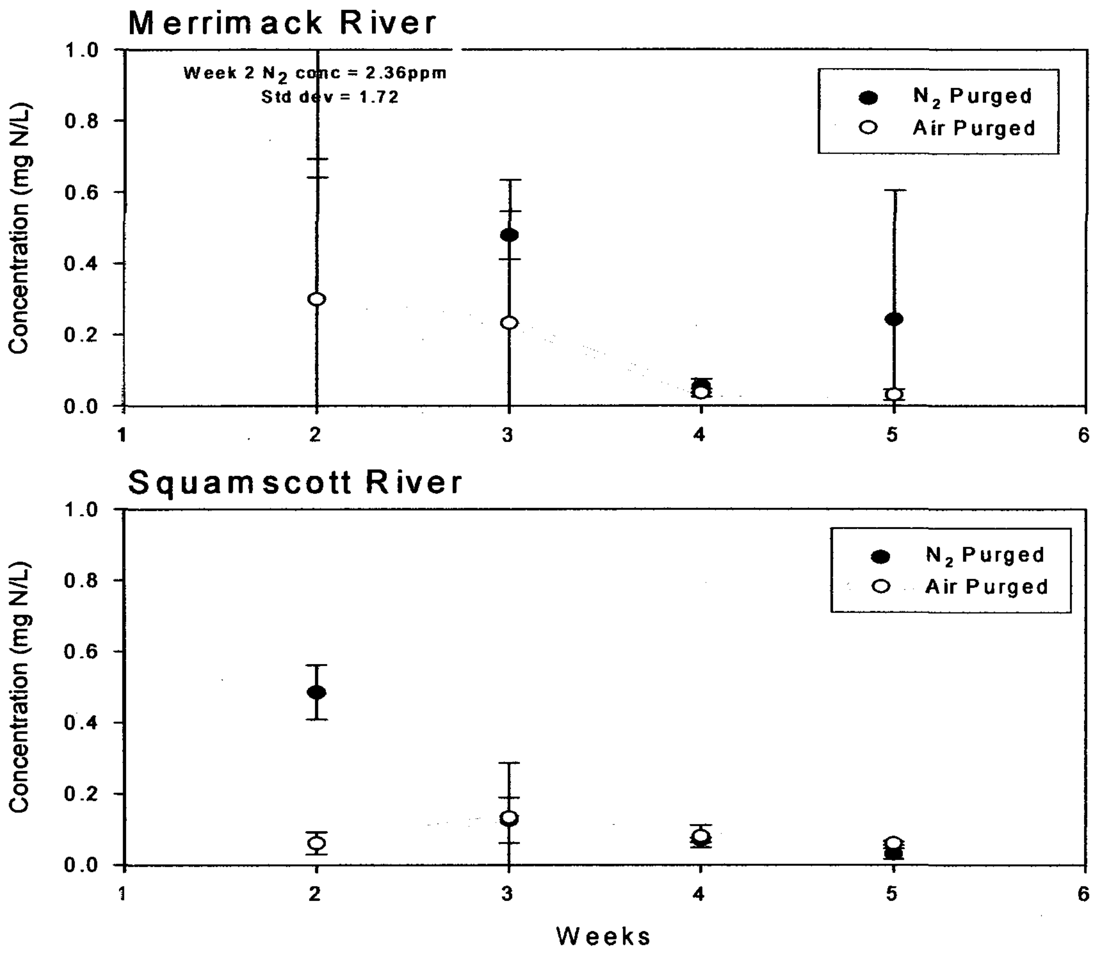


Figure 4.36: Sediment Pore Water Nitrite + Nitrate Equilibration Trend
The nitrite plus nitrate equilibration trends are from laboratory analysis of filtered peeper samples for average cell concentrations for depths 63mm to 145mm below the sediment. Analysis was performed with a colorimeter.

Data used for the trends in figures 4.36, 4.37 and 4.38 are from filtered peeper samples for average cell concentrations for depths 63mm to 145mm below the top of sediment. The nitrite plus nitrate equilibration trend for filtered peeper samples from the Merrimack and Squamscott Rivers can be seen in figure 4.36. In the Squamscott River, the trends for nitrogen and air purged peeper converge at week 3. They remain very close, slightly trending down, thereafter. The Merrimack River trends for the purge gas type converge at week

4. For the Merrimack River, nitrogen purged peeper samples increase from week 4 to 5 (figure 4.36). Nitrite plus nitrate concentrations remain relatively from week 4 to 5. The Squamscott River peepers and air purged Merrimack River peepers reach equilibration by week five. The upward trend at week five for Merrimack River nitrogen purged peepers does not allow for confirmation that equilibrium has been reached.

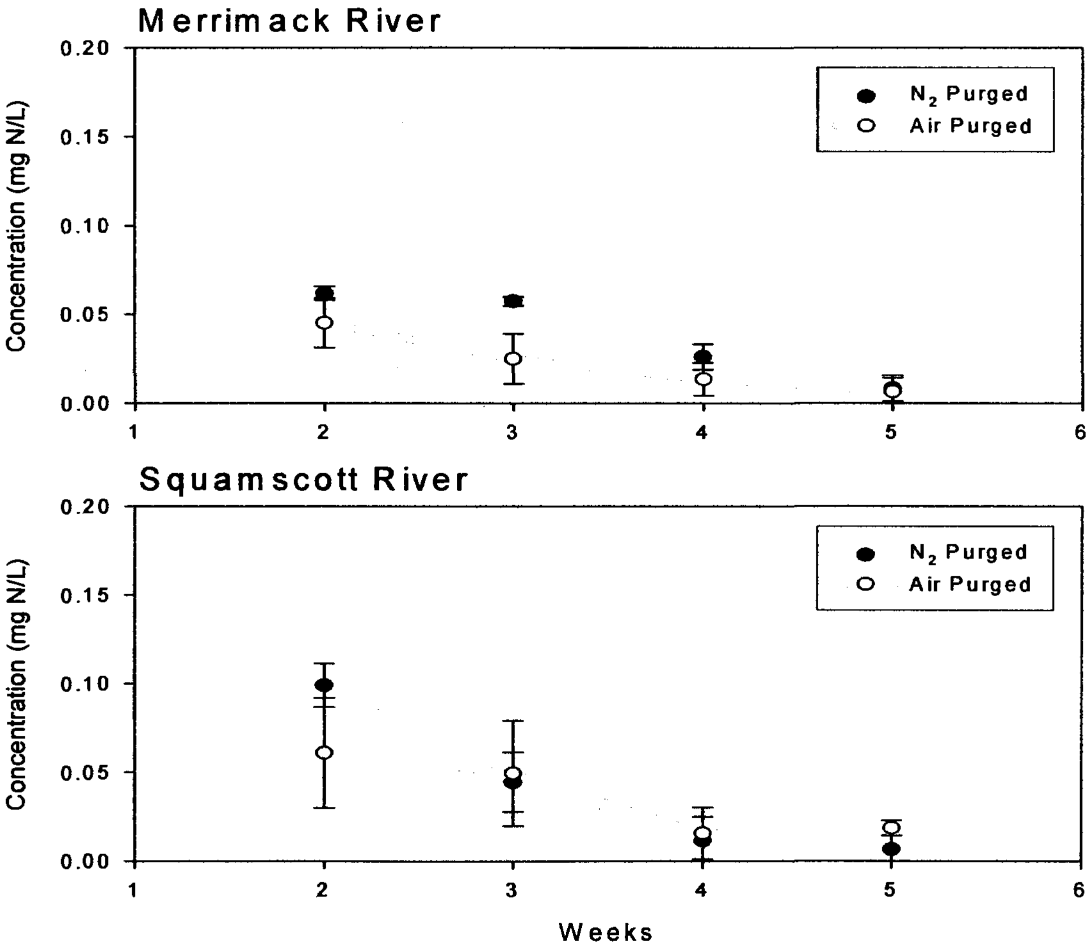


Figure 4.37: Sediment Pore Water Nitrite Equilibration Trend
The nitrate equilibration trends are from laboratory analysis of filtered peeper samples for average cell concentrations for depths 63mm to 145mm below the sediment. Analysis was performed with a colorimeter.

The nitrite concentrations for both purge gas types for the Merrimack River follow a similar downward trend, converging at week five (figure 4.37). Nitrite concentrations in the Squamscott River follow a similar downward trend as those in the Merrimack River. The Squamscott River peepers appear to reach equilibrium between weeks 4 and 5. In the Merrimack River, equilibrium can not be verified.

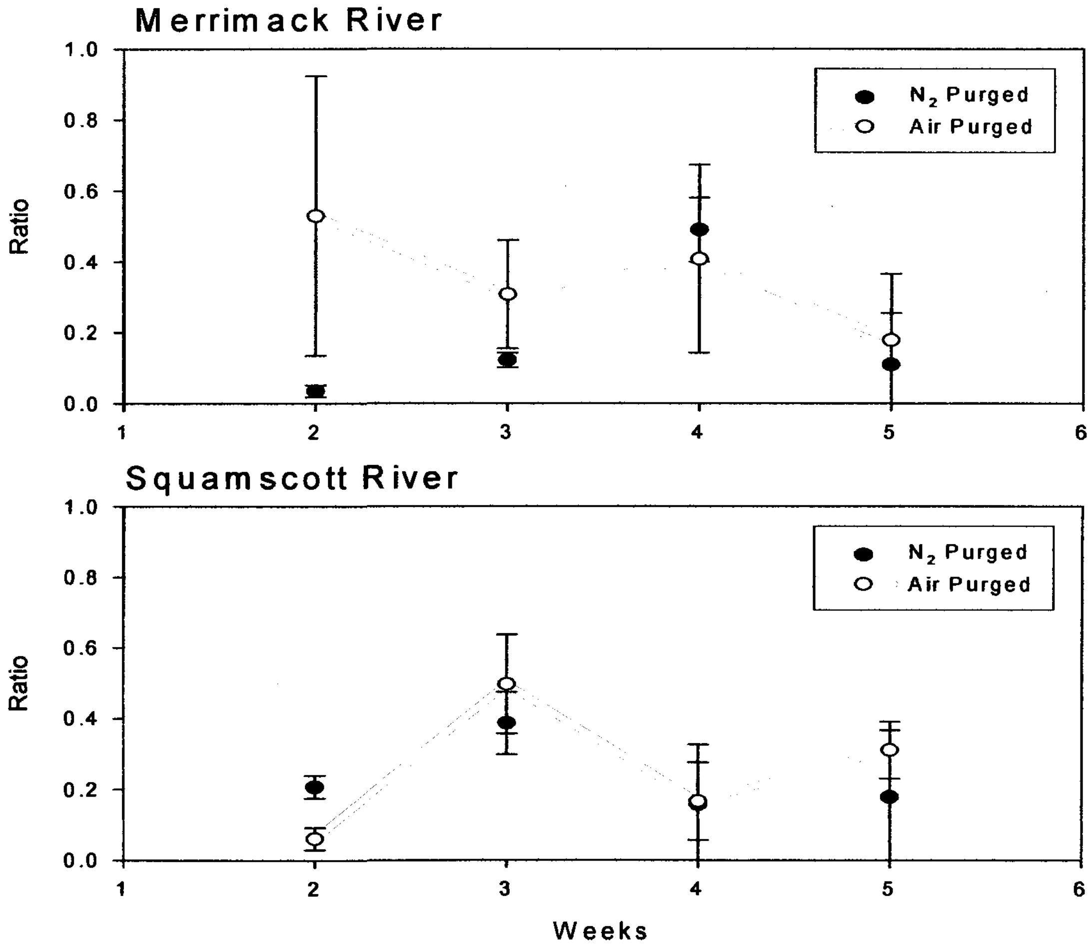


Figure 4.38: Sediment Nitrite/Nitrite + Nitrate Ratio
The nitrite/nitrate plus nitrate trends are from laboratory analysis of filtered peeper samples for average cell concentrations for depths 63mm to 145mm below the sediment. Analysis was performed with a colorimeter.

It was expected that as microbes converted nitrate to nitrite, the ratio of nitrite to nitrate plus nitrite would trend upward. The nitrite to nitrate plus nitrite equilibration trend for filtered samples from the Merrimack and Squamscott Rivers can be seen in figure 4.38. Although the data is erratic, bouncing up and down, it is relatively flat. There is no appreciable difference in the purge gas types. As a result, the ratio of nitrite to nitrate plus nitrite is not a good indicator of microbial activity.

4.2.6 Oxygen Effects On Peeper Material

Peeper material was identified as a primary source of artifacts by Carignan. He stated that oxygen leaching out of the plastic caused the redox sensitive metals to precipitate within the peeper chambers. His conclusions were based on an orange tint to polycarbonate peepers. The vertical peepers in this thesis were all made from polycarbonate. This section uses visual analysis of peepers, that were just removed from the sediment, to indicate oxygen effects from peeper material.

Carignan noted that an orange substance, identified as ferric oxide, was present on all of the peepers made from polycarbonate. Polycarbonate did have a high dissolve oxygen content (3.7 O_2 %Vol/Vol) in his studies but its half live was relatively fast (1.6 days). After five weeks or thirty-five days in anaerobic sediment, the dissolved oxygen leaching from the peepers should be negligible. If oxygen leaching from peeper material is causing artifacts, those effects should be greater in peepers removed early in the equilibration process and seen in all sediment types.

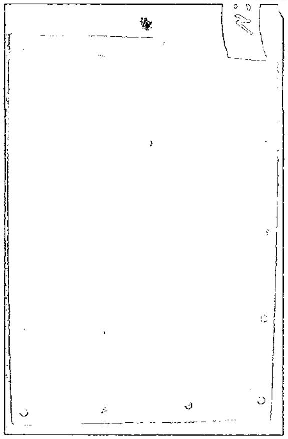
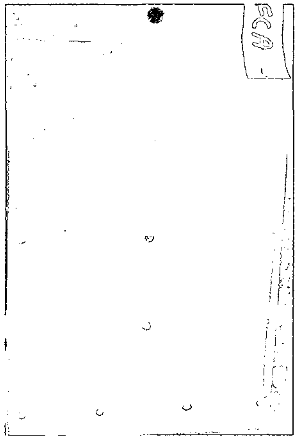
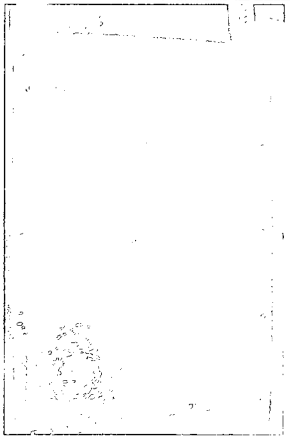
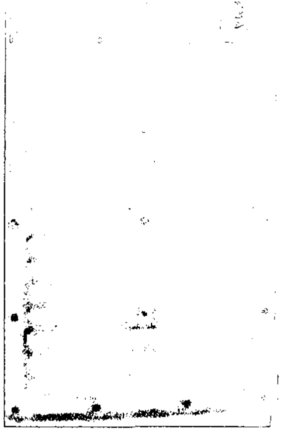
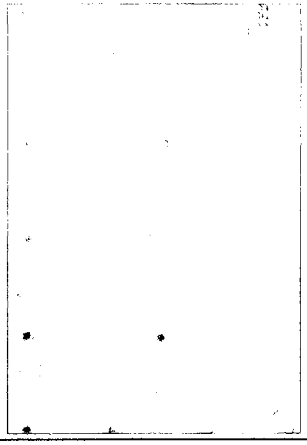
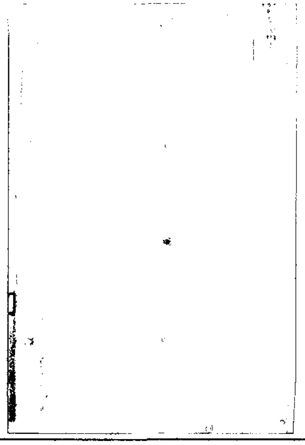
	Nitrogen Purged	Air Purged
Cocheco River		
Merrimack River		
Squamscott River		

Figure 4.39: Equilibrated Peeper Backs Prior to Sample Removal
Cocheco River field and Merrimack and Squamscott Rivers laboratory peepers removed from the sediment after four weeks. Peepers were cleaned prior to the pictures being taken. Orange tint in the Cocheco and Merrimack River peepers is iron oxide. The brown tint in the Squamscott River peepers is fine sediment particles that passed through the membrane.

In Figure 4.39 "Peepers Prior to Sample Removal", the orange color can be seen distinctly in peepers from the Cocheco and Merrimack Rivers, regardless of the type of purge gas. The Cocheco River peepers are part of the field study while the Merrimack and Squamscott River peepers are from the laboratory studies. However, the peepers from the Squamscott Rivers did not show any orange tint. The Squamscott River peepers did show a dark brown substance that appeared to be from the very fine sediment particles leaching across the membrane. Although not shown, vertical peeper used in Cottonwood Bay did not show any evidence of the orange tint. Vertical peepers used in the Anacostia River had only faint orange tint in isolated spots on the peepers. With the exception of the nitrogen purged Merrimack River peeper, the top two chambers in the peepers did not show any orange color. These were the chambers located in the water body above the sediment. The peepers in Figure 4.39 were all post-equilibration.

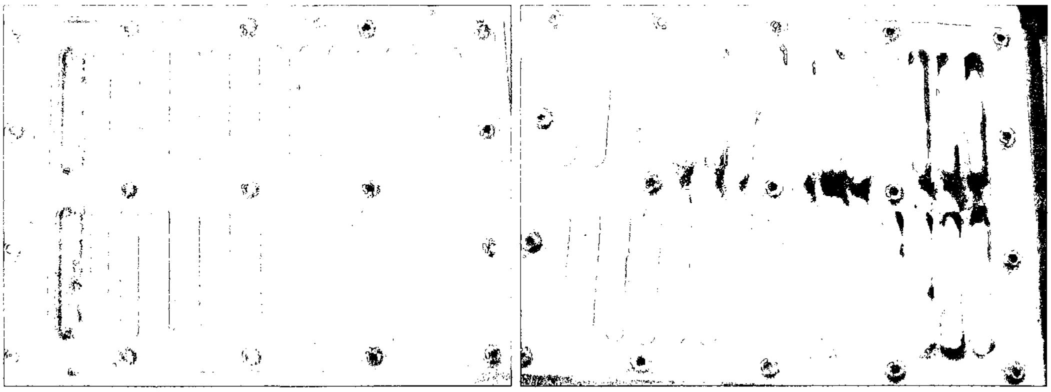


Figure 4.40: Merrimack & Squamscott Rivers Peeper Faces
Merrimack and Squamscott Rivers laboratory peepers removed from the sediment after four weeks. Peepers were cleaned prior to the pictures being taken. Orange tint on the Merrimack River peeper is iron oxide. The brown tint in the Squamscott River peeper is fine sediment particles.

Carignan also commented on that the orange color was also observed on the membranes. The peepers depicted n Figure 4.40 “Merrimack & Squamscott River Peeper Faces” are the faces of the air purged peepers from the Merrimack and Squamscott Rives seen in figure 4.39. The top of the peepers is to the left. The first two chambers of each peeper were in the water body above the sediment. The membrane covering those chambers and the next two in the Merrimack River peeper showed a hint of orange. The rest of the membrane was white. The face of the Cocheco River peeper in Figure 4.39, not shown, had a faint orange color in the membrane in the water body. The bottom chambers of that peeper were white when taken out of the sediment. The faint orange color in those chambers was attributed to the picture being taken an hour after the peeper was removed from the sediment.

Figure 4.41 is a series of pictures of the faces of Cocheco River peeper faces. The peepers were removed as part of the equilibration trend study. Each was cleaned upon removal from the sediment and the pictures were immediately taken thereafter. Since the peeper material will have the most dissolved oxygen in the initial part of equilibration, the orange tint should be more visible early in the equilibration process. Week one peepers had no color at all. Week two have a fine tint while weeks three and five had a significant orange color.

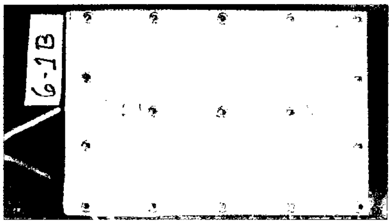
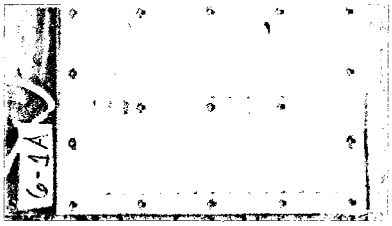
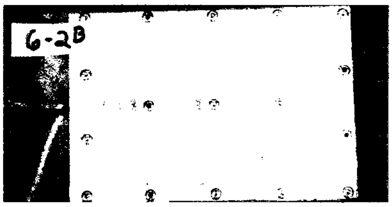
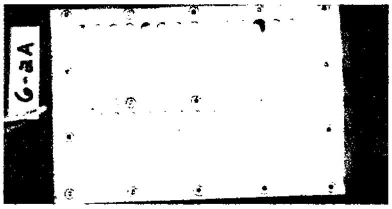
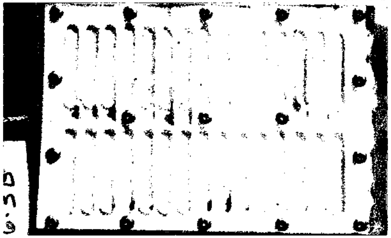
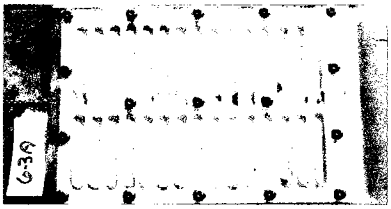
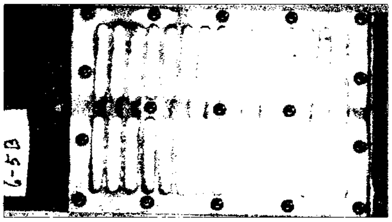
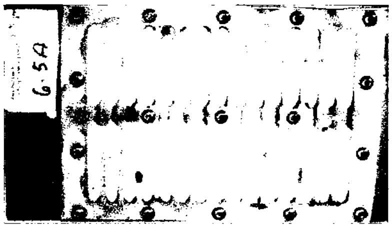
Week	Nitrogen Purged Peepers	Air Purged Peepers
1		
2		
3		
5		

Figure 4.41: Cocheco River Weekly Trend Peeper Faces
Cocheco River field peepers were removed on the indicated week and cleaned prior to pictures being taken. The orange tint on the peepers becomes darker the longer the peeper is kept in the sediment.

The weekly trend pictures of the Merrimack River peepers are seen in Figure 4.42. These peepers are from the laboratory study. They were cleaned and the pictures were taken immediately after the peepers were removed from the sediment. The trend exhibits the same phenomena as that in the Cocheco River. Though, the Merrimack River peepers have a darker orange tint earlier.

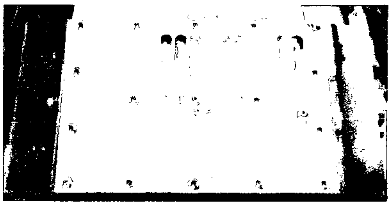
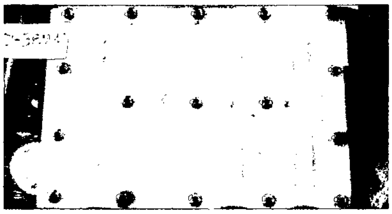
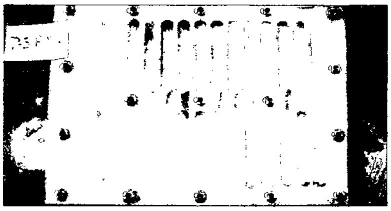
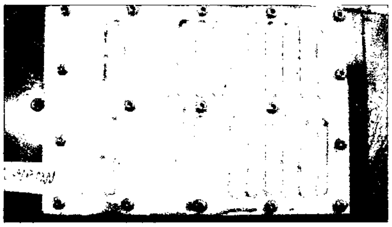
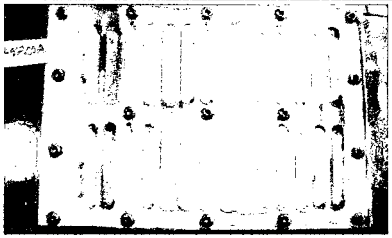
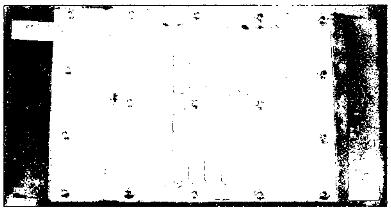
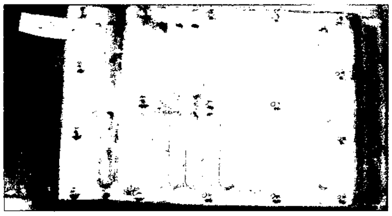
Week	Nitrogen Purged Peepers	Air Purged Peepers
2		
3		
4		
5		

Figure 4.42: Merrimack River Weekly Trend Peeper Faces
Merrimack River laboratory peepers were removed on the indicated week and cleaned prior to pictures being taken. The orange tint on the peepers becomes darker the longer the peeper is kept in the sediment.

If oxygen leaching out of the peeper material was causing sampling artifacts then the affects should be seen in all the sediment types. The fact that the Squamscott River sediment did not show any orange color indicates oxygen effects are more dependent on sediment type than peeper material. The low iron concentration, between 8ppm and 9ppm, in the Squamscott River may be a reason for not showing the color. However the Cocheco River iron concentration, between 8ppm and 18ppm, was only slightly higher and it did show orange tint. In both the Cocheco and Merrimack Rivers, the orange tint became darker the longer the peeper were in the sediment.

4.3 Evaluation of Sample Removal Techniques

4.3.1 Introduction

The removal techniques evaluated in this section are filtering options and sample removal using a nitrogen purged glove box. Filtering is used to determine if any metal precipitation within the peeper chambers affects sample concentration results. If oxygen is causing metals to precipitate within the peeper chambers then filtered samples should have lower concentrations than unfiltered ones. The glove box comparison is used to determine if atmospheric oxygen has any effects during sample removal. If atmospheric oxygen is effecting sample concentration then samples removed within the glove box should have higher metal concentrations

4.3.2 Filter Option Comparison

Filtering was competed using a syringe filter. Graphs depicting filtering/non-filtering comparisons are seen in figures 4.9, 4.18 and 4.27 on pages 65, 81 and 98, respectively. These graphs are of equilibrated peepers that are prepared with air or nitrogen purging.

In figure 4.9, “Overall Iron & Manganese Concentrations”, pore water iron and manganese concentrations are compared. Filtered samples have a higher iron concentration than unfiltered in the Merrimack River while unfiltered samples have higher iron concentration in the Cocheco River iron. In the Squamscott River, iron concentrations are equal for both filtered and unfiltered samples. Manganese concentrations in the three rivers have the same pattern as iron concentrations (figure 4.9).

Filtering options are examined in figure 4.18, “Selected Equilibrated Metal Concentrations’, for cadmium, chromium, strontium and zinc. Cadmium concentrations in the Cocheco and Squamscott Rivers are essentially equal for both filter and unfiltered samples. In the Merrimack River, filtered samples have a greater concentration than unfiltered samples. Chromium and strontium concentration are very close for filtered and unfiltered samples from all three rivers examined. Zinc concentrations are much greater in filtered samples than unfiltered ones in the Cocheco and Merrimack Rivers while they are equal in the Squamscott River (figure 4.18).

Anion concentrations are examined in figure 4.27, “Equilibrated Anion Concentrations. Chloride concentrations are equal for both filter option in the Merrimack and Squamscott Rivers. Sulfate concentrations in nitrogen purged peeper are higher for unfiltered Merrimack River samples but lower for unfiltered samples in the Squamscott River. Nitrite and nitrate plus nitrite filtered samples are higher than unfiltered ones in both the Merrimack and Squamscott Rivers (figure 4.27).

Table 4.6: Filter Option Independent t-tests

Filter and unfiltered peeper samples are compared in the t-tests. Filter option comparisons are of equilibrated concentrations of elements, Fe, Mn, Cd, Cr, Sr & Zn. Cocheco River data is from field analysis. Merrimack and Squamscott River data are from laboratory results. Concentrations used in the comparison are averages of peeper cells from 1" below the surface to the bottom of the peepers. df = degree of freedom; $t_{df,0.025}$ are from student t-test tables.

Metal	**Sediment**	**Comparison**	**df**	**t**	**Interval (ppm)**	
Fe	Cocheco	N_2	50	2.009	-4.6578	-13.9223
		Air	50	2.009	3.7244	-10.2572
	Merrimack	N_2	37	2.026	30.9375	-14.4947
		Air	38	2.024	46.4664	-0.7177
	Squamscott	N_2	24	2.064	6.1764	-5.2417
		Air	24	2.064	46.4664	-0.7177
Mn	Cocheco	N_2	50	2.009	0.3889	-3.2785
		Air	50	2.009	0.7797	-2.2571
	Merrimack	N_2	37	2.026	4.9040	-1.5188
		Air	38	2.024	9.7091	2.3205
	Squamscott	N_2	24	2.064	0.1209	-0.1525
		Air	24	2.064	0.2851	-0.1852
Cd	Cocheco	N_2	50	2.009	-0.0003	-0.0008
		Air	50	2.009	0.0002	-0.0006
	Merrimack	N_2	37	2.026	0.0014	-0.0006
		Air	38	2.024	0.0021	0.0001
	Squamscott	N_2	24	2.064	0.0004	-0.0004
		Air	24	2.064	0.0008	-0.0006
Cr	Cocheco	N_2	50	2.009	0.0012	-0.0022
		Air	50	2.009	0.0018	-0.0014
	Merrimack	N_2	37	2.026	0.0005	-0.0003
		Air	38	2.024	0.0006	-0.0005
	Squamscott	N_2	24	2.064	0.0096	-0.0065
		Air	24	2.064	0.0078	-0.0071
Sr	Cocheco	N_2	50	2.009	0.2918	-0.5149
		Air	50	2.009	0.2929	-0.4402
	Merrimack	N_2	37	2.026	0.0490	-0.0323
		Air	38	2.024	0.0772	0.0043
	Squamscott	N_2	24	2.064	0.1265	-0.1408
		Air	24	2.064	0.2267	-0.2245
Zn	Cocheco	N_2	50	2.009	0.2758	0.2359
		Air	50	2.009	0.3130	0.2113
	Merrimack	N_2	37	2.026	0.1976	0.0531
		Air	38	2.024	0.1985	0.0513
	Squamscott	N_2	24	2.064	0.0559	-0.0695
		Air	24	2.064	0.0590	-0.0482

Table 4.6, “Filter Option Independent t-tests” is an independent t-test evaluation of the filter option for equilibrated concentrations of iron, manganese, cadmium, chromium, strontium and zinc for the Cocheco, Merrimack and Squamscott Rivers. Each comparison is filter vs. unfiltered samples.

The independent t-test difference interval for filtering options for chromium concentration in all three rivers includes zero. Five of the six t-test for iron, manganese and strontium include zero in the difference interval. For cadmium, four of the six include zero (table 4.6). Zero in the t-test interval indicates there is no difference in sample concentrations whether the sample is filtered or not.

Zinc is the only metal with a significant amount of non-zero difference intervals (table 4.6). The Cocheco and Merrimack Rivers have a positive difference interval for both nitrogen and air purged peepers. In the Squamscott, both nitrogen and air purged peepers have zero in the difference interval. A positive interval indicated that filtered samples have higher concentrations.

Zero is included in the difference interval of 27 of the 36 comparisons. Seven comparisons have a positive interval while 2 have a negative. The independent t-test filter option results show no apparent difference between whether you filter the sample or not. Filtering results are another indication that oxygen has caused little or no metal precipitation within the chambers.

4.3.3 Glove Box Extraction Comparison

The nitrogen purged glove box was used for the equilibrated laboratory studies on Merrimack and Squamscott River sediments. As stated earlier, atmospheric oxygen will affect redox sensitive metal more significantly than other heavy metals.

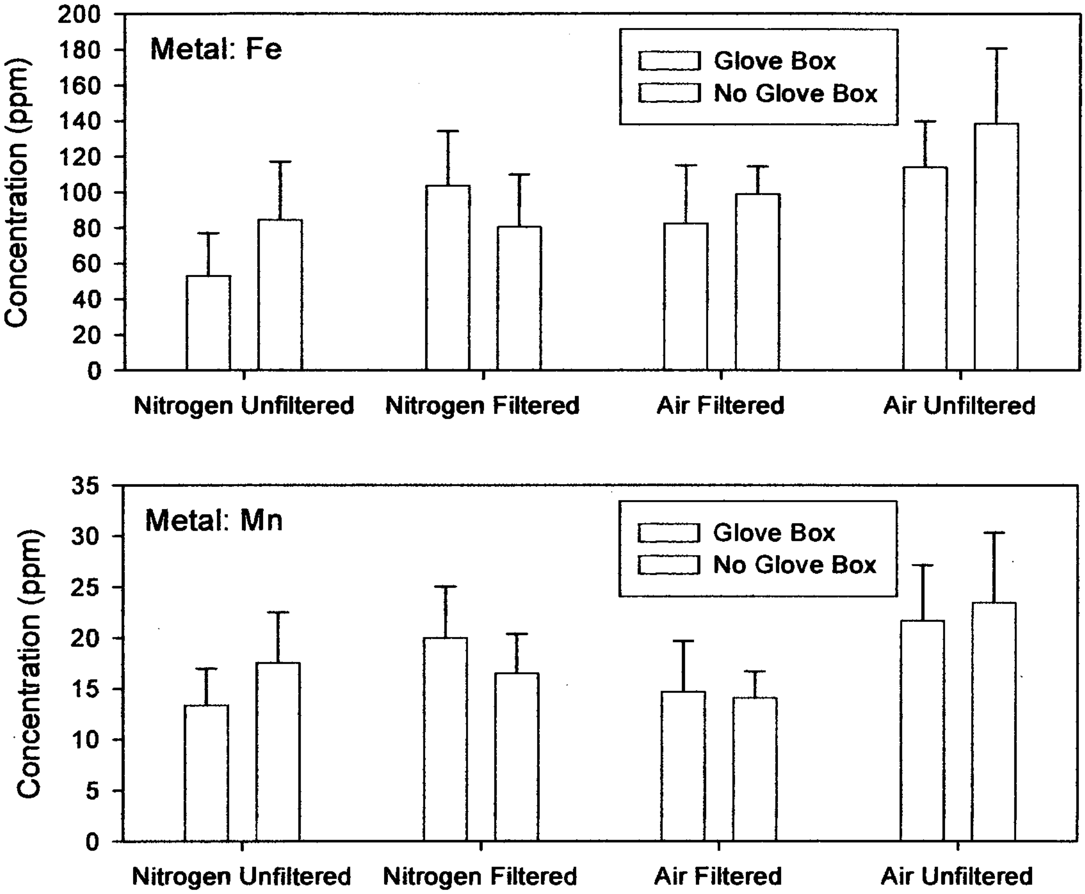


Figure 4.43: Merrimack River Glove Box Results for Redox Sensitive Metals
Merrimack River equilibrated laboratory sediment pore water peeper samples are used in the iron and manganese graphs. Each sample removal category compares samples removed with and without the use of a nitrogen purged glove box. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers.

In figures 4.43 and 4.44, iron and manganese concentrations for the Merrimack and Squamscott Rivers for glove box extraction options are compared for purge gas type and filtering option. Iron concentrations for samples removed without a glove box are higher for three categories but lower in one for the Merrimack River figure (4.43). In the Squamscott River the split is even with two categories higher for each glove box option (figure 4.44). Manganese concentrations are close to being even for the filter and purge gas options in the Squamscott River (figure 4.44). In the Merrimack River, manganese concentrations for samples removed with either glove box options are similar for air purged peepers. The results are split for nitrogen purged peepers (figure 4.43).

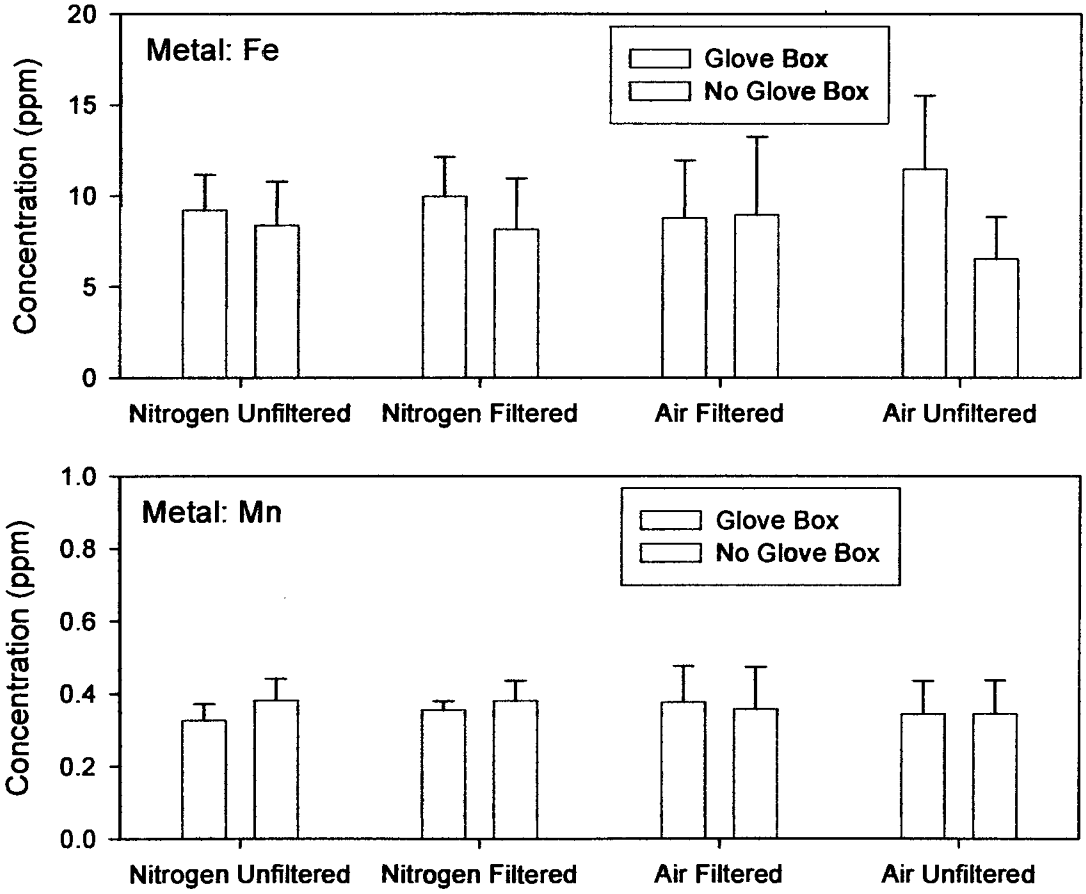


Figure 4.44: Squamscott River Glove Box Results for Redox Sensitive Metals
Squamscott River equilibrated laboratory sediment pore water peeper samples are used in the iron and manganese graphs. Each sample removal category compares samples removed with and without the use of a nitrogen purged glove box. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers.

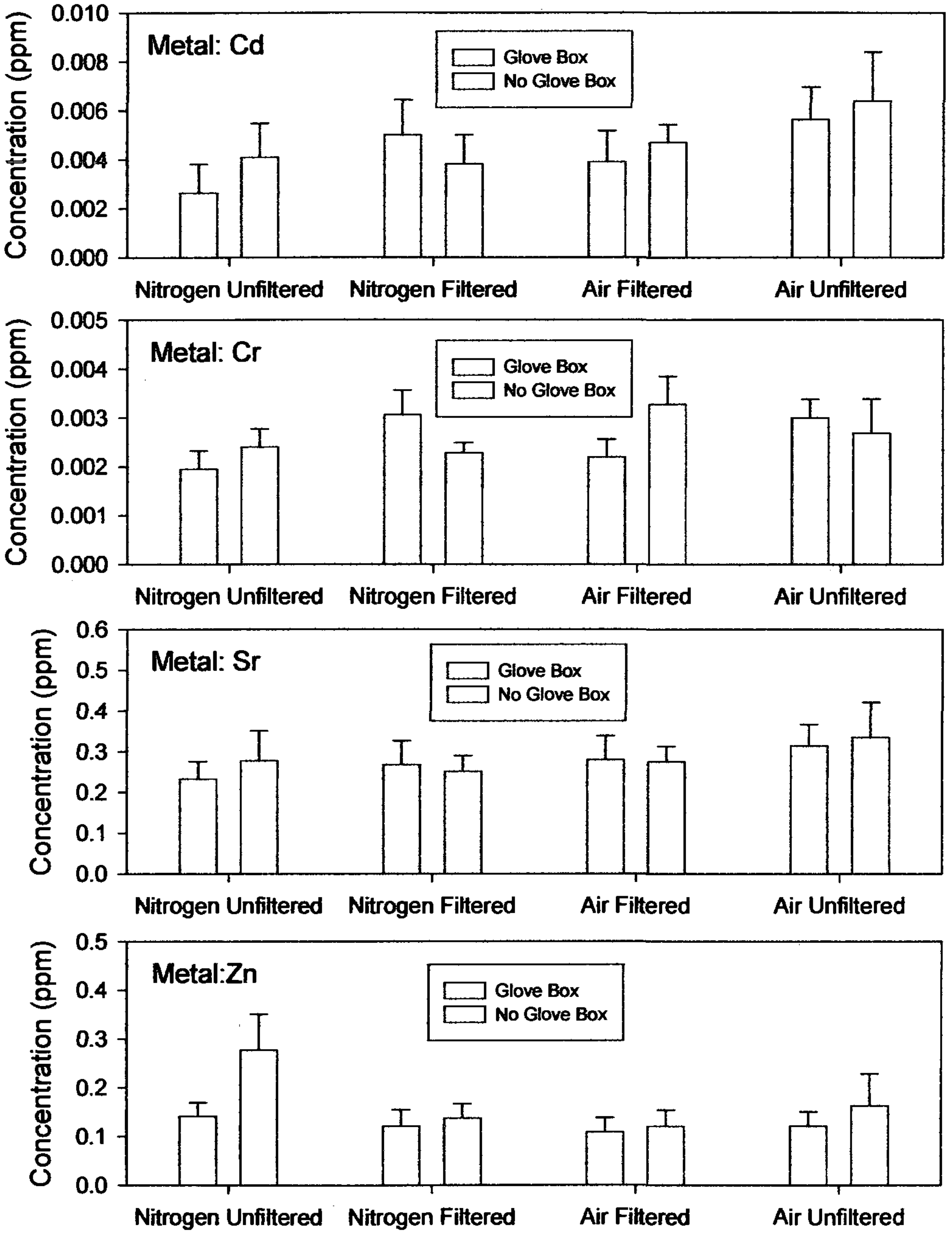


Figure 4.45: Merrimack River Glove Box Results for Selected Metals
Merrimack River equilibrated laboratory sediment pore water peeper samples are used in the Cd, Cr, Sr, and Zn graphs. Each sample removal category compares samples removed with and without the use of a nitrogen purged glove box. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers.

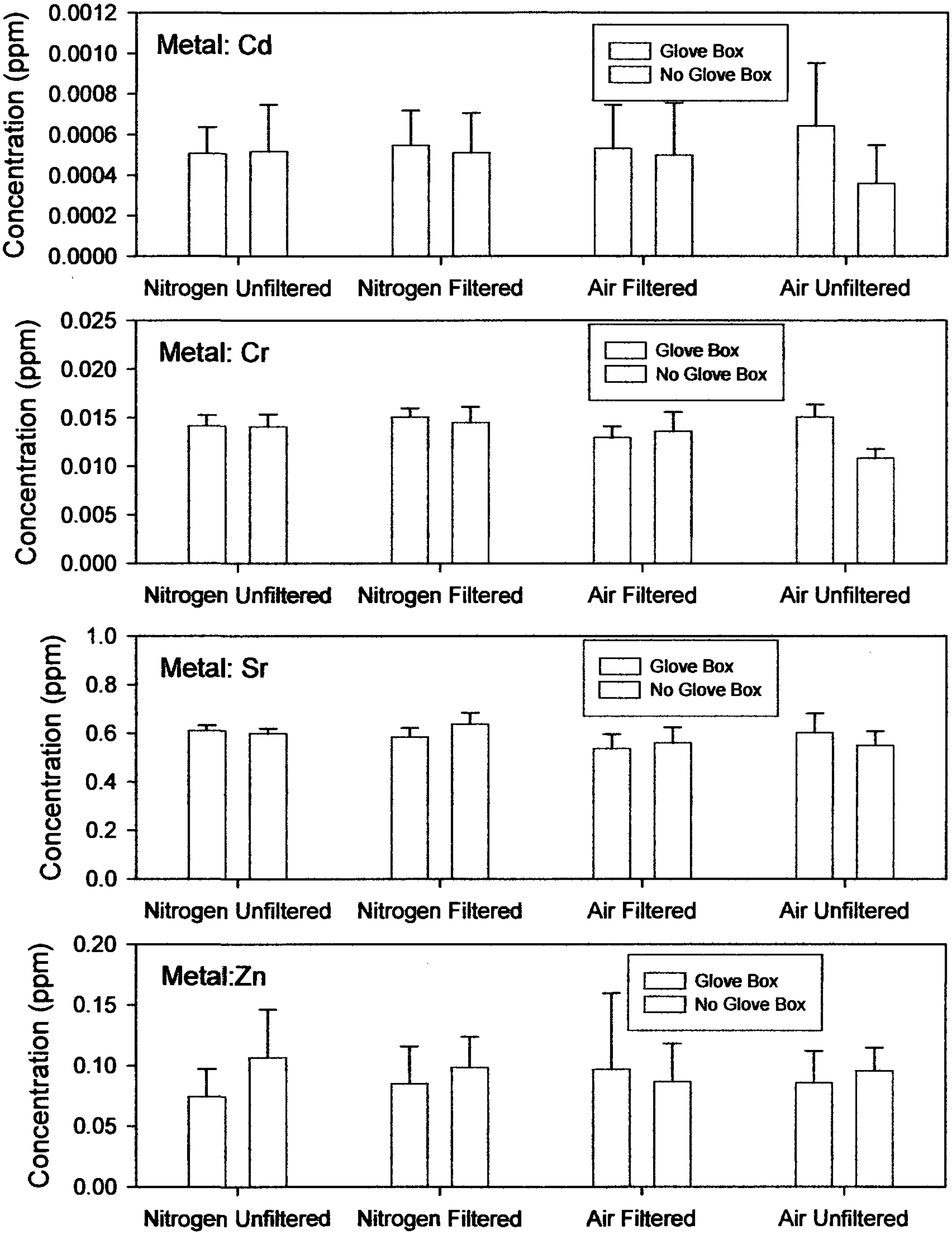


Figure 4.46: Squamscott River Glove Box Results for Selected

Squamscott River equilibrated laboratory sediment pore water peeper samples are used in the Cd, Cr, Sr, and Zn graphs. Each sample removal category compares samples removed with and without the use of a nitrogen purged glove box. Concentrations are averages of peeper cells from 1" below the surface to the bottom of the peepers.

The results for the selected heavy metals, seen in figures 4.45 and 4.46, were similar to those of the redox sensitive metals. There was no discernable trend base on whether or not the glove box was used for any of the metals or river sediment.

Table 4.7: Merrimack River Glove Box Comparison Independent t-tests

Merrimack River laboratory sediment samples removed using a glove box are compared with those without the glove box in the t-tests. Comparisons are of equilibrated concentrations of elements, Fe, Mn, Cd, Cr, Sr & Zn. Concentrations used in the comparison are averages of peeper cells from 1" below the surface to the bottom of the peepers. $t_{8,0.025}$, from student t-test tables, is 2.306.

Metal	**Comparison**	**Interval (ppm)**	
Fe	N_2 Unfiltered	10.26	-73.08
	N_2 Filtered	90.13	-44.10
	Air Unfiltered	20.71	-53.52
	Air Filtered	26.80	-75.52
Mn	N_2 Unfiltered	2.193	-10.50
	N_2 Filtered	90.13	-44.10
	Air Unfiltered	6.433	-5.231
	Air Filtered	7.281	-10.85
Cd	N_2 Unfiltered	0.000406	-0.003335
	N_2 Filtered	0.004295	-0.001951
	Air Unfiltered	0.000712	-0.002283
	Air Filtered	0.001719	-0.003241
Cr	N_2 Unfiltered	9.78E-05	-9.953E-04
	N_2 Filtered	0.002433	-0.0008749
	Air Unfiltered	-0.00038	-0.001776
	Air Filtered	0.001126	-0.0005117
Sr	N_2 Unfiltered	0.04284	-0.1326
	N_2 Filtered	0.1691	-0.1366
	Air Unfiltered	0.07706	-0.06718
	Air Filtered	0.08300	-0.1253
Zn	N_2 Unfiltered	0.05063	-0.09542
	N_2 Filtered	0.06002	-0.09148
	Air Unfiltered	0.03416	-0.05769
	Air Filtered	0.06834	-0.003630

Independent t-tests for Merrimack River peepers comparing glove box options used for sample removal can be seen in table 4.7. Twenty-three out of the twenty-four independent t-tests for the Merrimack River had zero in the difference interval. Only unfiltered air peepers for chromium had a negative interval.

Table 4.8: Squamscott River Glove Box Comparison Independent t-tests

Squamscott River laboratory sediment samples removed using a glove box are compared with those without the glove box in the t-tests. Comparisons are of equilibrated concentrations of elements, Fe, Mn, Cd, Cr, Sr & Zn. Concentrations used in the comparison are averages of peeper cells from 1" below the surface to the bottom of the peepers. $t_{8,0.025}$, from student t-test tables, is 2.306.

Metal	Comparison	Interval (ppm)	
Fe	N_2 Unfiltered	4.021	-2.379
	N_2 Filtered	5.464	-1.845
	Air Unfiltered	5.336	-5.669
	Air Filtered	9.744	0.1314
Mn	N_2 Unfiltered	0.02172	-0.1324
	N_2 Filtered	0.03805	-0.08829
	Air Unfiltered	0.1777	-0.1385
	Air Filtered	0.1331	-0.1344
Cd	N_2 Unfiltered	0.000263	-0.0002848
	N_2 Filtered	0.000306	-0.0002330
	Air Unfiltered	0.000378	-0.00031385
	Air Filtered	0.000657	-9.065E-05
Cr	N_2 Unfiltered	0.001843	-0.001694
	N_2 Filtered	0.002499	-0.001331
	Air Unfiltered	0.001735	-0.003013
	Air Filtered	0.005888	0.002651
Sr	N_2 Unfiltered	0.04174	-0.01962
	N_2 Filtered	0.007457	-0.1153
	Air Unfiltered	0.06731	-0.1138
	Air Filtered	0.1547	-0.04924
Zn	N_2 Unfiltered	0.01482	-0.07958
	N_2 Filtered	0.02741	-0.05436
	Air Unfiltered	0.08292	-0.06213
	Air Filtered	0.02344	-0.04339

Independent t-tests for Squamscott River peepers comparing glove box options used for sample removal can be seen in table 4.8. Twenty-two out of the twenty-four independent t-tests for the Squamscott River had zero in the difference interval. Only filtered air peepers for iron chromium had positive intervals.

The overwhelming t-test evidence for both rivers indicates there is no difference in metal concentrations whether or not the glove box is used. This is a strong indication that atmospheric oxygen is not a problem with timely removal of samples from peepers

4.4 Push Point Sampling Device

4.4.1 Introduction

Push point direct suction samples were extracted in conjunction with the peeper samples. Each push point sample was drawn with the sampler one inch from the face of the vertical peeper with end of the probe at a depth of five inches. Due to the sampler configuration, the extraction depth was between three and five inches. Samples were pumped into an acid washed bottle. The sample was subsequently extracted from the bottle with a syringe and, immediately put into an ICP vial. The standard procedure requires the sample to be taken after the stream cleared of all the sediment. The initial sample was taken immediately when the stream started to flow. The initial sample was full of suspended particles. The initial sample was removed from the bottle after the suspended particles sank to the bottom of the bottle. The settling time was usually five minutes. Filtering was accomplished with an attached syringe filter. Unfiltered samples all had a small amount of sediment deposited in the bottom of the ICP vials prior to analysis. The expected results were that the initial samples would be greater than the standard samples. Also, it is expected that unfiltered samples should be greater than the filtered ones. This is due to solid particles being introduced into the sample vials. The particles are subsequently dissolved when nitric acid is added as a preserving agent to the samples

4.4.2 Push Point Laboratory Sample Analysis

Laboratory samples from the Merrimack River sediment was collected from two tubs, one with nitrogen purged peeper and one with air purged peepers. The sandy sediment of the Merrimack River provided a steady stream from the peristaltic pump. The fine sediment of the Squamscott River made it very difficult to obtain a sample so no analysis was performed.

The graphs in figure 4.47 depict Merrimack River pore water metal concentrations for filtered and unfiltered samples removed using the standard extraction procedure and samples from the initially discharged pore water. There was little difference in concentration between the extraction categories for iron, manganese, cadmium and strontium. Unfiltered, standard extracted sample of zinc were lower than the other categories. Unfiltered initial concentrations of chromium were higher than the other categories (figure 4.47).

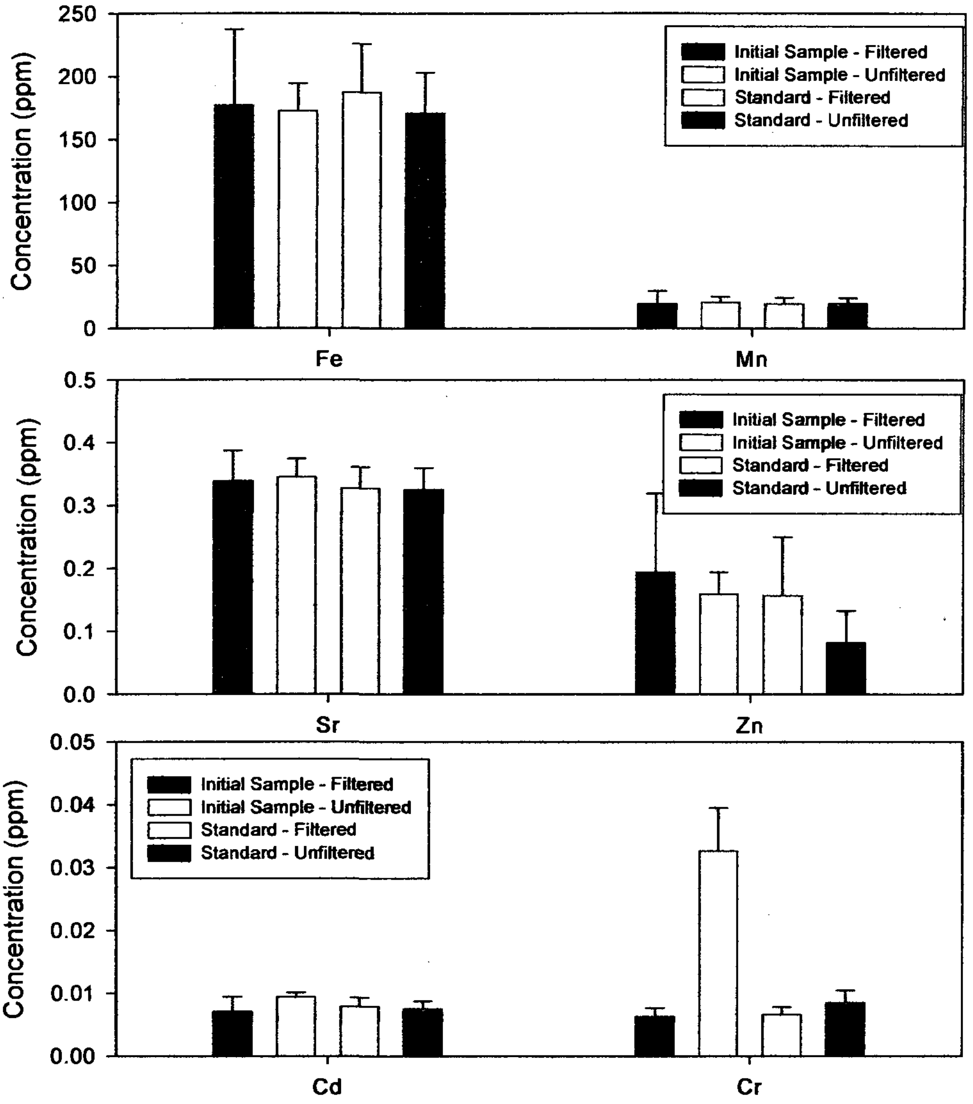


Figure 4.47: Merrimack River Laboratory Push Point Metal Analysis
Merrimack River laboratory sediment pore water concentrations of elements Fe, Mn, Cd, Cr, Sr, and Zn. Samples used in the graphs were removed with the push point end at 5" below the surface of the sediment. Samples removed using the standard removal procedure and samples immediately removed from the device are shown with the filter option.

Merrimack River sediment pore water independent t-tests shown in table 4.9 are a comparison of filtered push point samples vs. unfiltered samples for the initial and standard sampling procedures. The t-test difference interval for iron, manganese, strontium and zinc include zero for both initial and standard extracted procedures. This indicated there was no difference between filter options. Both extraction types for chromium and initial extraction for cadmium had negative difference intervals, indicating unfiltered samples had higher concentrations (table 4.9).

Table 4.9: Merrimack River Push Point Independent t-test Filtered vs. Unfiltered

Merrimack River laboratory sediment samples removed using the standard removal procedure and samples immediately removed from the device. Filtered vs. unfiltered comparisons are concentrations of elements, Fe, Mn, Cd, Cr, Sr & Zn. Samples used in the comparisons were removed with the push point end at 5" below the surface of the sediment. df = degree of freedom; $t_{df,0.025}$ are from student t-test tables

Metal	**Comparison**	**df**	**t**	**Interval (ppm)**	
Fe	Initial Sample	8	2.306	65.27	-55.97
	Standard	24	2.064	46.09	-12.86
Mn	Initial Sample	8	2.306	9.220	-11.72
	Standard	24	2.064	3.8169	-3.963
Cd	Initial Sample	8	2.306	-3.981E-05	-0.0046
	Standard	24	2.064	0.001512	-7.307E-04
Cr	Initial Sample	8	2.306	-0.01819	-0.0345
	Standard	24	2.064	-0.00061	-0.003144
Sr	Initial Sample	8	2.306	0.04922	-0.06161
	Standard	24	2.064	0.02947	-0.02593
Zn	Initial Sample	8	2.306	0.08632	-0.1559
	Standard	24	2.064	0.1559	-0.0963

The independent t-test comparisons in figure 4.10 are of the initially extracted samples vs. standard extracted samples from the Merrimack River laboratory studies. The comparisons are filtered samples all include zero in the difference interval. This indicates that when filtering, there is no discernable difference in the concentrations. Unfiltered samples of iron, manganese and strontium also include zero in the difference interval. Unfiltered samples for cadmium, chromium and zinc have a positive difference. A positive difference indicates the initially extracted samples have a higher concentration than the standard extracted ones (table 4.10).

Table 4.10: Merrimack River Push Point Independent t-test Initial Sample vs. Standard Procedure

Merrimack River laboratory sediment push point samples. Samples removed using the standard removal procedure and samples immediately removed from the device comparisons are concentrations of elements, Fe, Mn, Cd, Cr, Sr & Zn. Samples used in the comparisons were removed with the push point end at 5" below the surface of the sediment. df = degree of freedom; $t_{df,0.025}$ are from student t-test tables

Metal	**Comparison**	**df**	**t**	**Interval (ppm)**	
Fe	Filtered	18	2.101	37.61	-58.05
	Unfiltered	14	2.145	38.08	-34.59
Mn	Filtered	18	2.101	7.000	-7.051
	Unfiltered	14	2.145	6.556	-4.255
Cd	Filtered	18	2.101	0.001071	-0.002584
	Unfiltered	14	2.145	0.003333	0.0005774
Cr	Filtered	18	2.101	0.001032	-0.001586
	Unfiltered	14	2.145	0.02859	0.01975
Sr	Filtered	18	2.101	0.05181	-0.02841
	Unfiltered	14	2.145	0.05933	-0.01999
Zn	Filtered	18	2.101	0.1449	-0.07089
	Unfiltered	14	2.145	0.1337	0.02025

The Merrimack River laboratory results for the redox sensitive metals indicate there is no difference whether the initial sample or standard extraction method is used. It also does not matter if redox metal samples are filtered. The results for chromium indicate filtering option has an effect on sample concentration.

4.4.3 Push Point Field Sample Analysis

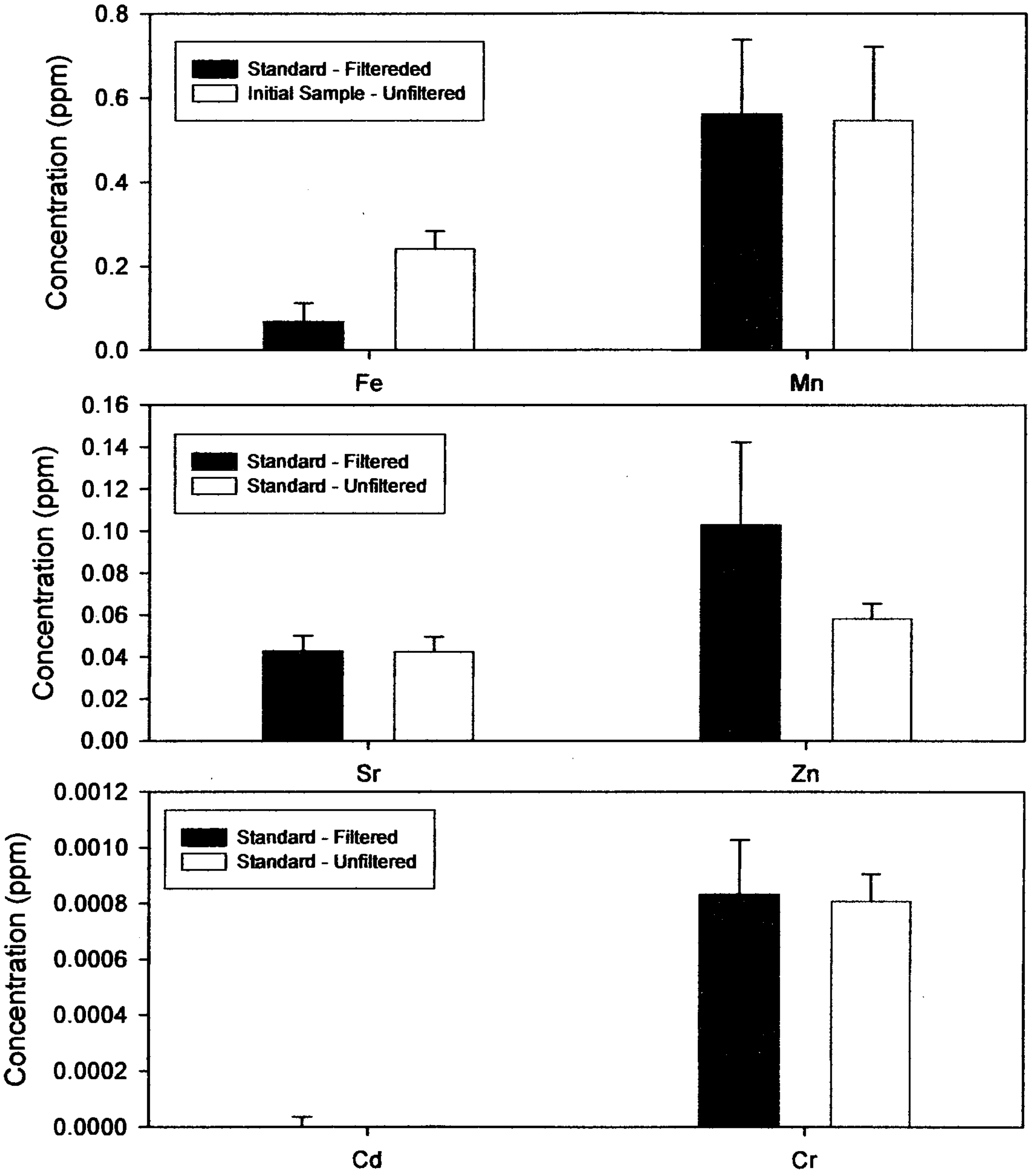


Figure 4.48: Merrimack River Field Push Point Metal Analysis
Merrimack River field sediment pore water concentrations of elements Fe, Mn, Cd, Cr, Sr, and Zn. Samples used in the graphs were removed with the push point end at 5" below the surface of the sediment. Samples removed using the standard removal procedure from the device are shown with the filter option.

Samples were obtained in the sandy sediment in the upper region of the Cocheco River but no samples could be collected from the lower clay region. Only the standard extraction method was employed. Manganese, chromium and strontium showed little difference between filtered and unfiltered samples (figure 4.48). Filtered iron and unfiltered zinc had greater concentration than their counterparts. There was very litter cadmium in the Cocheco River sediment pore water (figure 4.48).

4.4.4 Glove Box Extraction Analysis

Extraction of Merrimack River pore water was performed with the push point using a nitrogen purged glove box. Filtered and unfiltered standard extracted samples and unfiltered initially extracted samples were used to determine if atmospheric oxygen effected sampling concentrations. The push point tubing was purged with nitrogen from the glove box prior to removing samples with the push point. For non-glove box extraction, the tubing was not purged. It is expected that extraction with the glove box would eliminate any oxygen introduction in the sample. The resultant metal concentrations should be higher for samples removed with the nitrogen purged glove box as compared to those extracted with out it.

Cadmium and chromium concentration are shown in figure 4.49. The results show that cadmium concentrations are higher in all categories for extractions with out the glove box. Chromium results are mixed. The unfiltered initial samples have higher concentration in the non-glove box option while standard unfiltered samples are higher for the glove box extracted samples.

Filtered samples for chromium have similar concentrations regardless of the glove box option (figure 4.49)

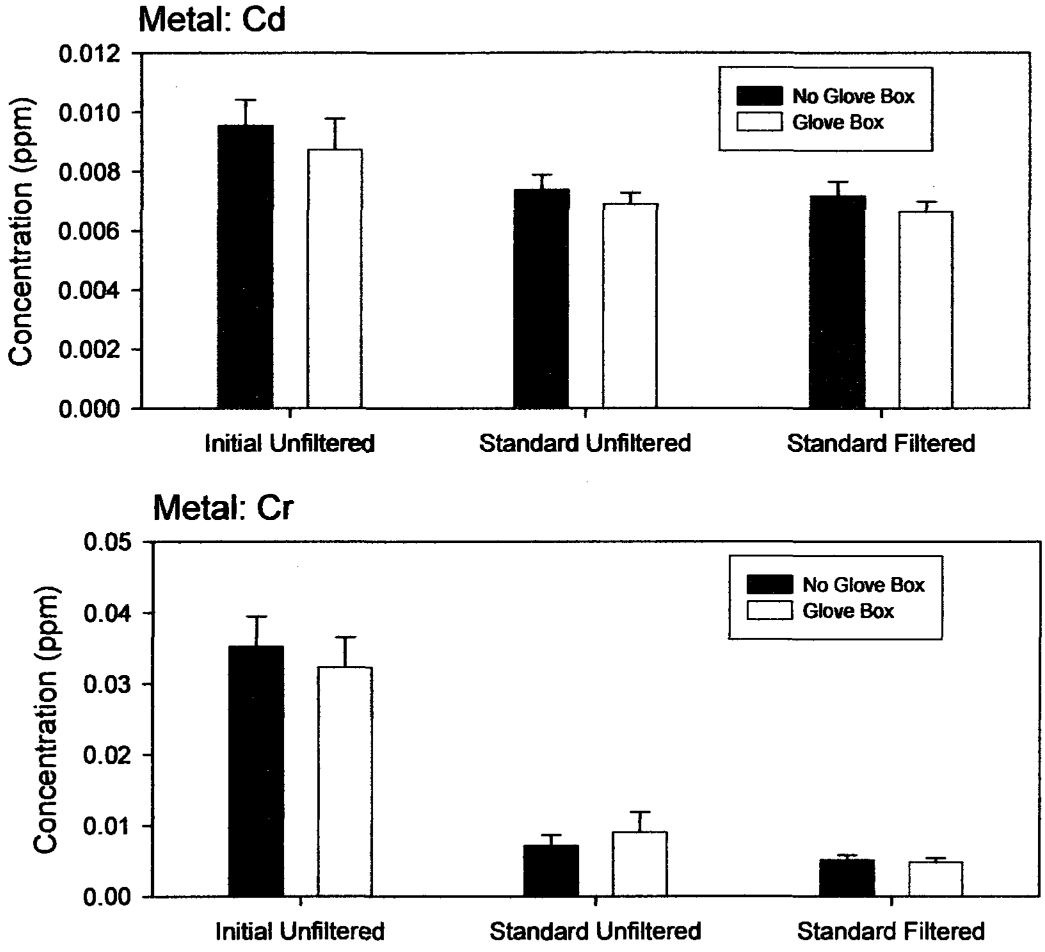


Figure 4.49: Push Point Glove Box Comparison of Cadmium and Chromium
Merrimack River laboratory sediment pore water push point samples are used in the Cd & Cr graphs. Each sample removal category compares samples removed with and without the use of a nitrogen purged glove box. Samples used in the graphs were removed with the push point end at 5" below the surface of the sediment.

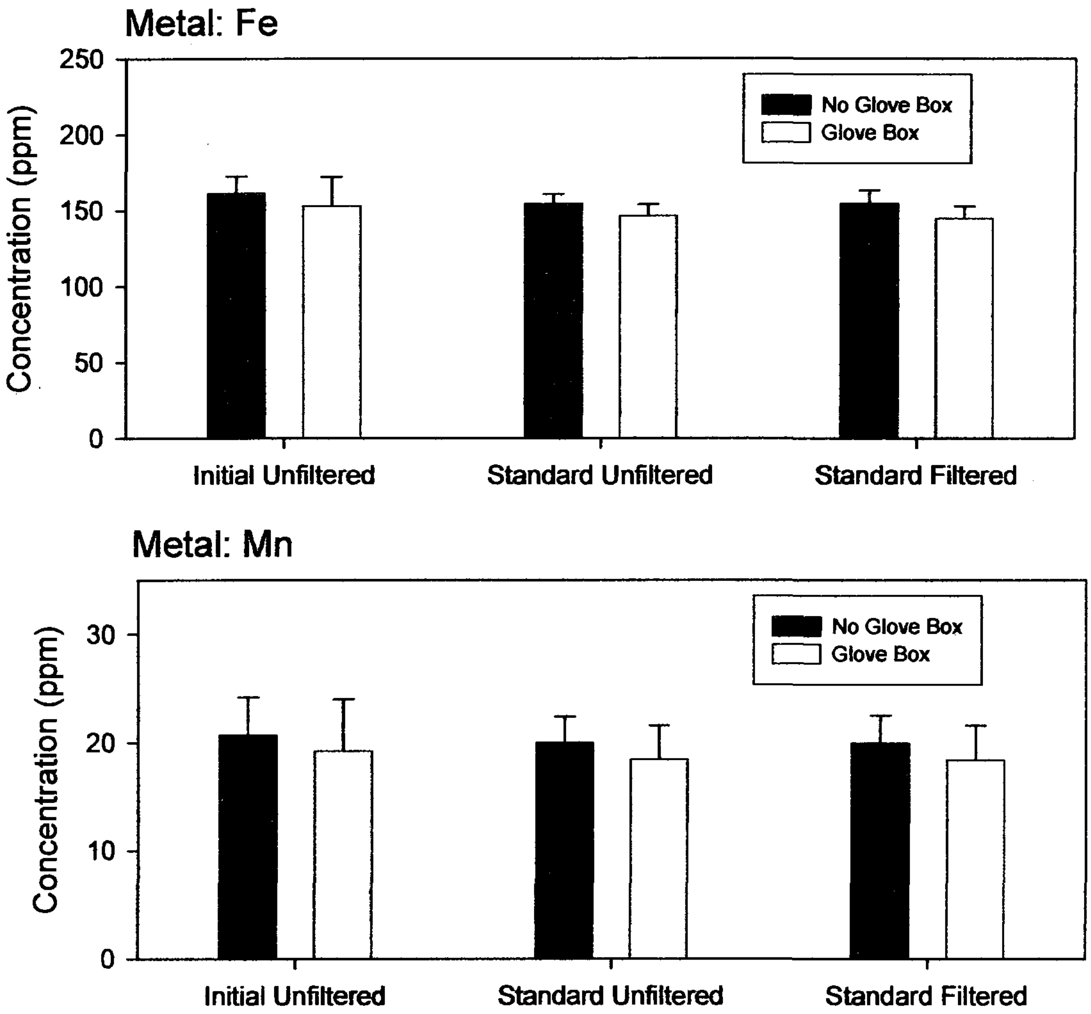


Figure 4.50: Glove Box Comparison of Iron and Magnesium
Merrimack River laboratory sediment pore water push point samples are used in the Fe & Mn graphs. Each sample removal category compares samples removed with and without the use of a nitrogen purged glove box. Samples used in the graphs were removed with the push point end at 5" below the surface of the sediment.

Iron and manganese concentration are shown in figure 4.50. The non-glove box option has slightly higher concentrations for all categories.

Strontium and zinc concentration are shown in figure 4.51. Strontium concentrations for the non-glove box option have slightly higher concentrations for all categories. The zinc results are similar to those of chromium. The unfiltered initial samples have higher concentration in the non-glove box option while standard unfiltered samples are higher for the glove box extracted samples. Filtered samples for zinc have similar concentrations regardless of the glove box option (figure 4.51)

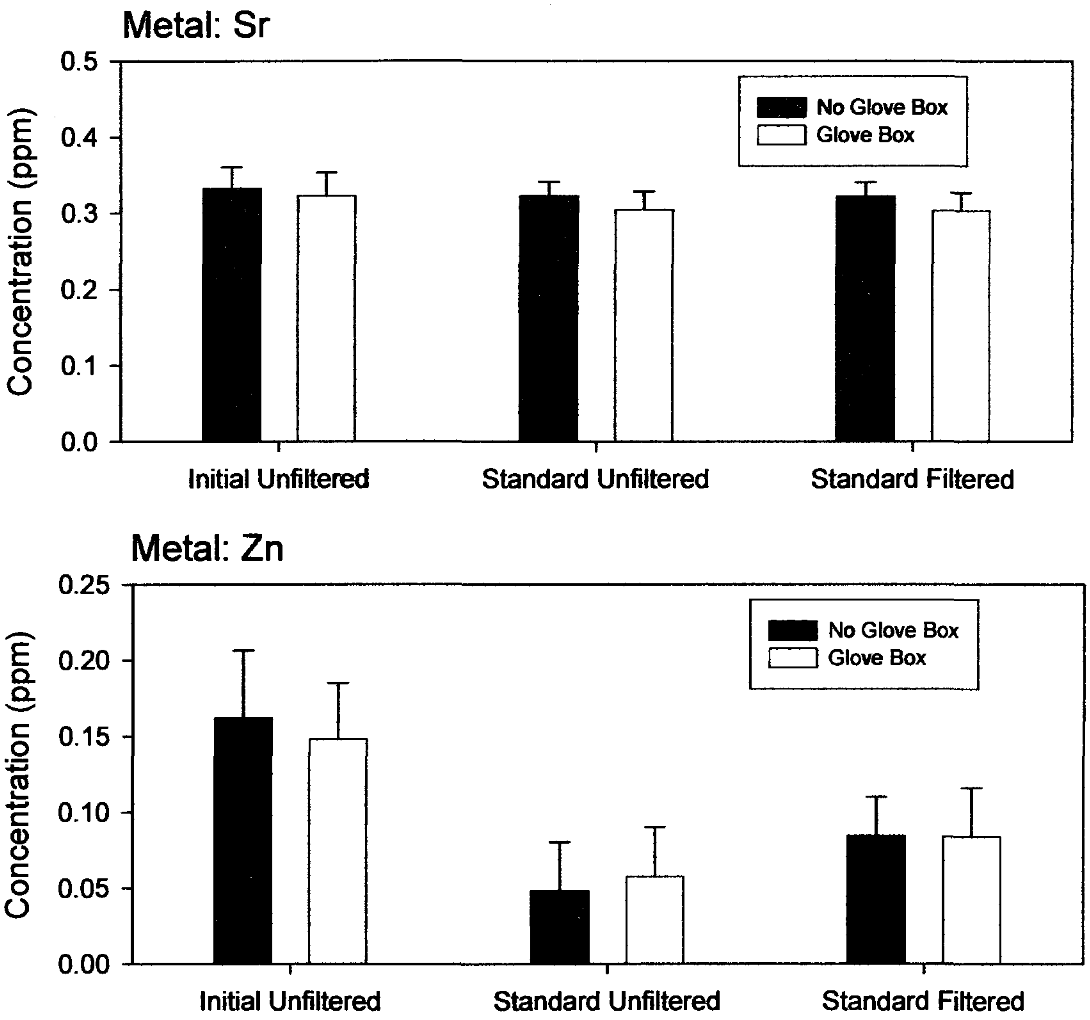


Figure 4.51: Glove Box Comparison of Strontium and Zinc
Merrimack River laboratory sediment pore water push point samples are used in the Sr & Zn graphs. Each sample removal category compares samples removed with and without the use of a nitrogen purged glove box. Samples used in the graphs were removed with the push point end at 5" below the surface of the sediment.

Table 4.11: Merrimack River Push Point Independent t-test Initial Comparison of Glove Box Extraction

Merrimack River laboratory sediment samples removed using a glove box are compared with those without the glove box in the t-tests. Comparisons are of equilibrated concentrations of elements, Fe, Mn, Cd, Cr, Sr & Zn. Samples used in the comparisons were removed with the push point end at 5" below the surface of the sediment. $t_{6,0.025}$, from student t-test tables, is 2.447.

Metal	Comparison	Interval (ppm)	
Fe	Initial Unfiltered	35.37	-18.75
	Standard Unfiltered	19.87	-3.961
	Standard Filtered	24.32	-4.278
Mn	Initial Unfiltered	8.680	-5.780
	Standard Unfiltered	6.391	-3.318
	Standard Filtered	6.564	-3.464
Cd	Initial Unfiltered	0.002467	-0.00086
	Standard Unfiltered	0.001266	-0.00028
	Standard Filtered	0.001257	-0.00019
Cr	Initial Unfiltered	0.01023	-0.00442
	Standard Unfiltered	0.002054	-0.00586
	Standard Filtered	0.001427	-0.00084
Sr	Initial Unfiltered	0.06048	-0.04096
	Standard Unfiltered	0.05477	-0.01864
	Standard Filtered	0.05512	-0.01766
Zn	Initial Unfiltered	0.08470	-0.05648
	Standard Unfiltered	0.04652	-0.06521
	Standard Filtered	0.05094	-0.04939

The independent t-test shown table 4.11 is a comparison of no glove box vs. glove box for pore water extraction with a push point sampler. The results were part of the laboratory test of Merrimack River sediment. All of the difference intervals include zero. The prevailing evidence is that there is no difference wither the nitrogen purged glove box is used or not.

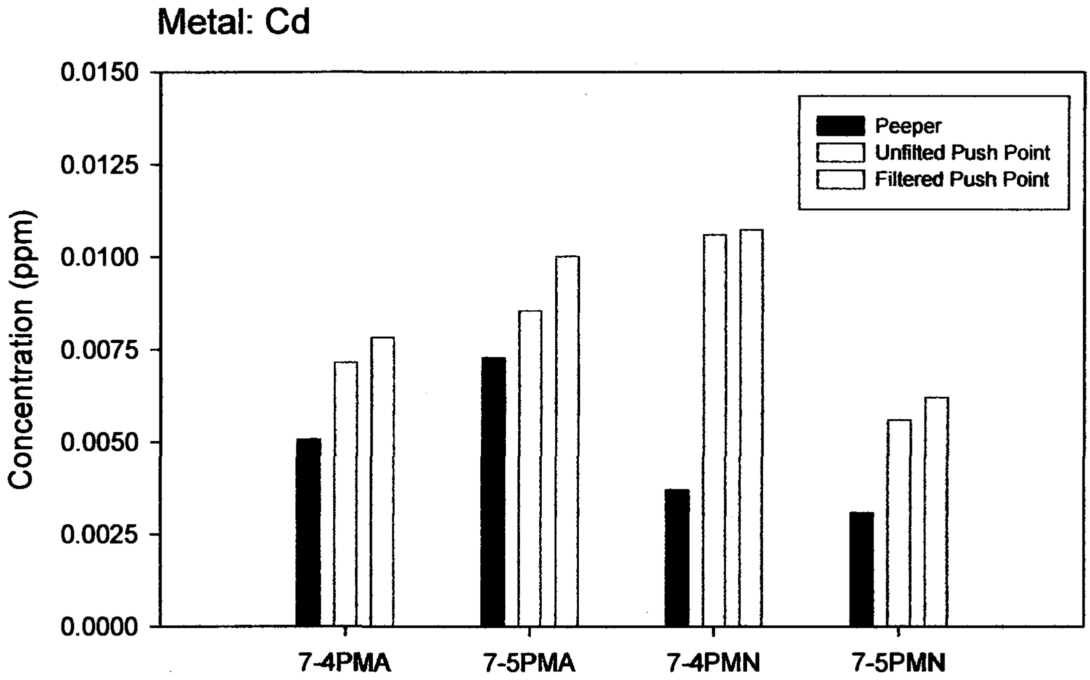
4.5 Device Comparison

4.5.1 Introduction

Peeper and push point pore water samplers are compared in this section. The purpose of the device comparison is to give researchers a reference point for metal concentrations of samples removed with the devices. Merrimack River sediment, used in the laboratory experiments, is used for the comparison. Unfiltered peeper samples with be compared with the filtered and unfiltered standard push point extracted samples. Push point samples were taken 1" in front of the peeper face with the probe 5" below the sediment surface. The peepers used in the comparisons have all reached equilibration. Peeper concentrations are an average of cell concentrations 1" below the surface to the bottom of the peeper.

4.5.2 Evaluation

Graphs seen in figures 4.52, 4.53 and 4.54 compare metal concentrations of specific peepers with the corresponding push point sample extractions. Both filtered and unfiltered push point samples of cadmium and chromium concentrations are higher than those extracted with the peepers (figure 4.52). For iron, filtered and unfiltered push point sample are higher than the peeper sample concentrations (figure 4.53). For manganese, two peeper have higher concentrations than either filtering option for the push points. One of the other peepers has a lower manganese concentration. The fourth comparison has approximately equal manganese concentrations for both devices (figure 4.53).



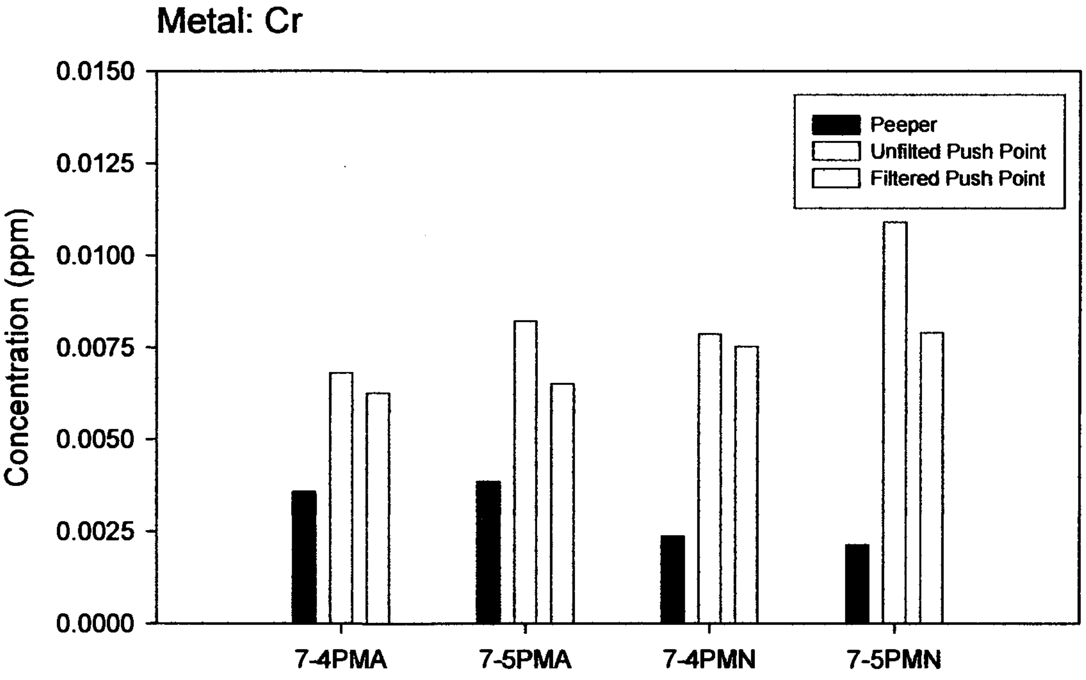


Figure 4.52: Device Comparison of Cadmium and Chromium
Merrimack River laboratory sediment samples are used for comparing peepers with push point sampling devices. Comparisons are of elements Cd & Cr. Peeper samples used in the comparison are averages of cells from 1" below the surface to the bottom of the peepers. Push Point samples used in the comparisons were removed with its end at 5" below the surface of the sediment.

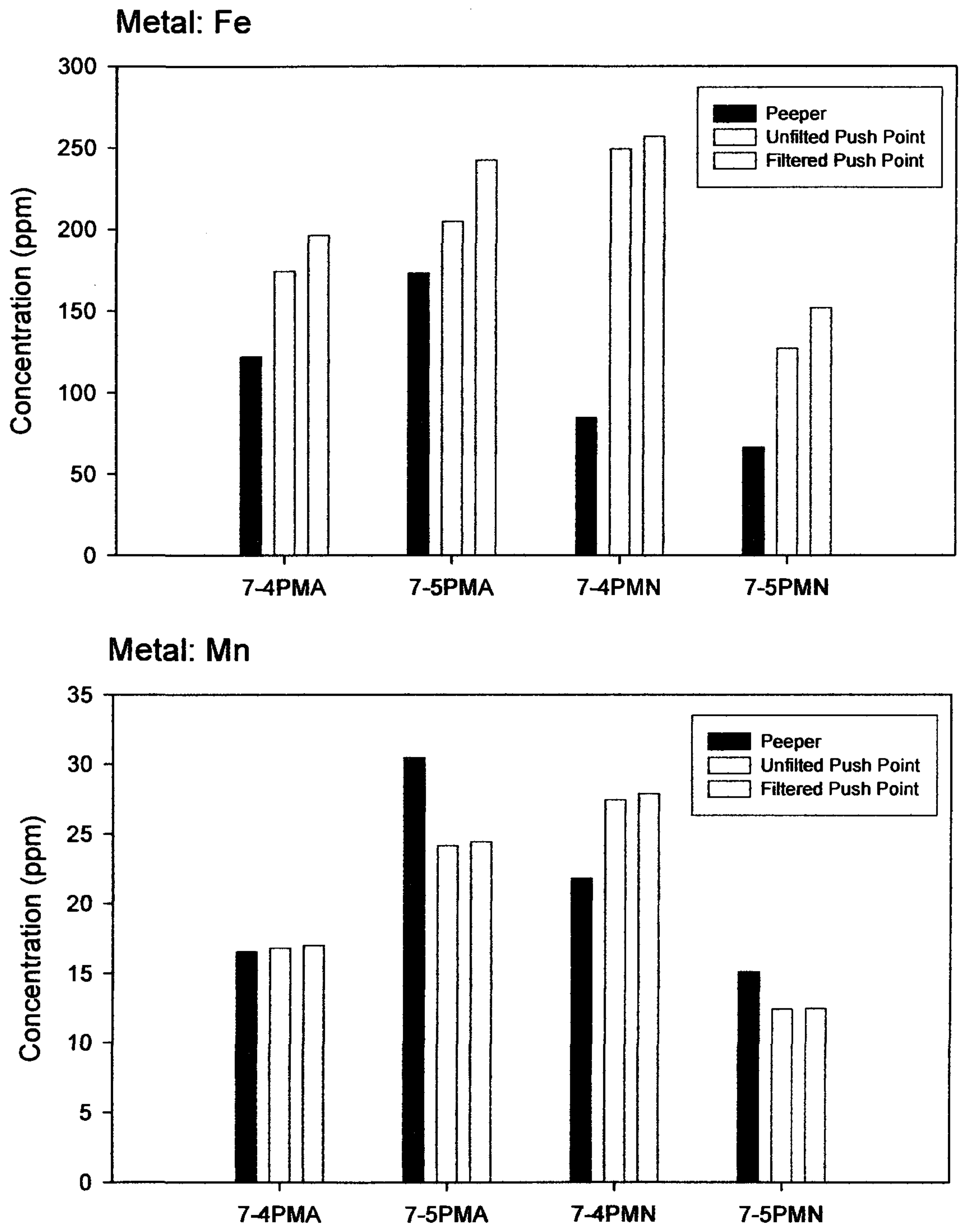
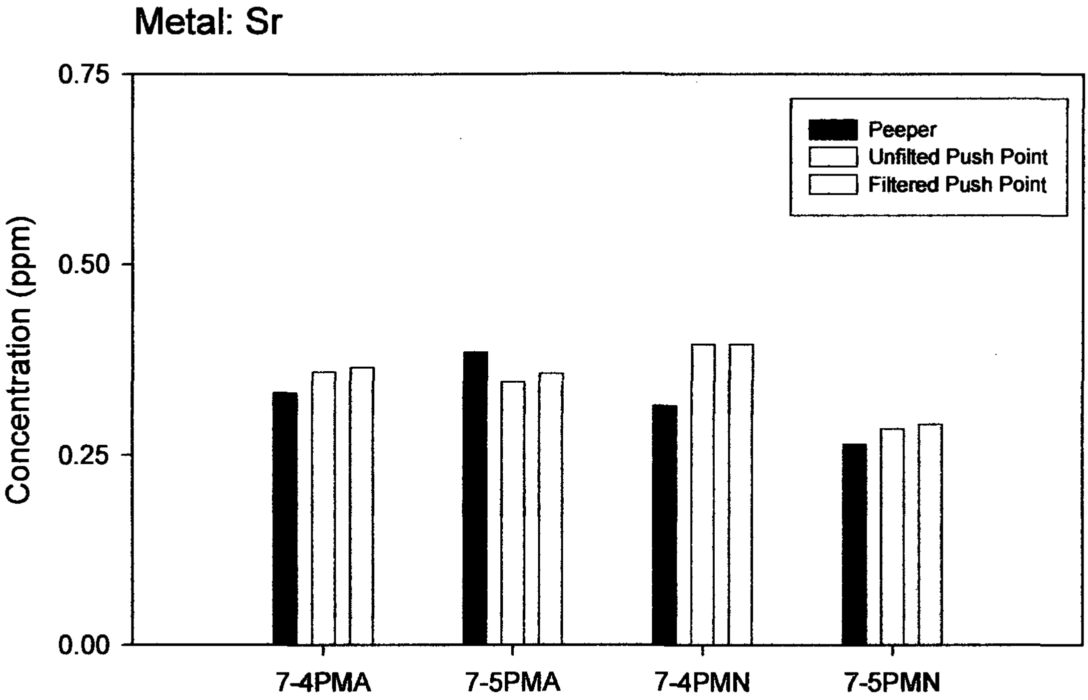


Figure 4.53: Device Comparison of Iron and Manganese
Merrimack River laboratory sediment samples are used for comparing peepers with push point sampling devices. Comparisons are of elements Fe & Mn. Peeper samples used in the comparison are averages of cells from 1" below the surface to the bottom of the peepers. Push Point samples used in the comparisons were removed with its end at 5" below the surface of the sediment.



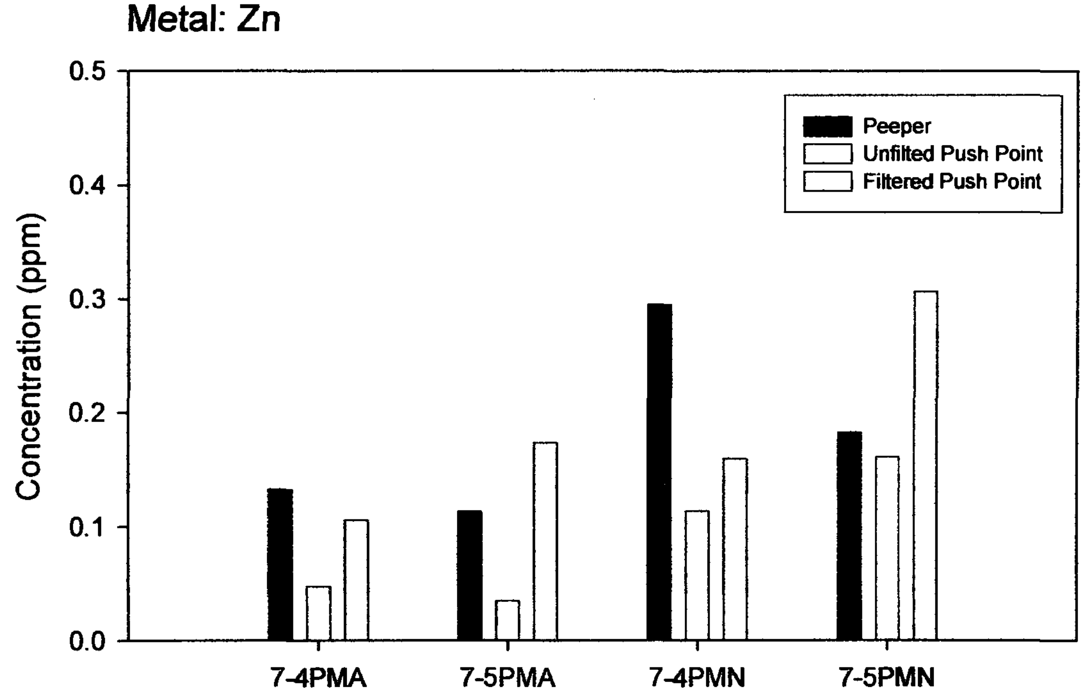


Figure 4.54: Device Comparison of Strontium and Zinc
Merrimack River laboratory sediment samples are used for comparing peepers with push point sampling devices. Comparisons are of elements Sr & Zn. Peeper samples used in the comparison are averages of cells from 1" below the surface to the bottom of the peepers. Push Point samples used in the comparisons were removed with its end at 5" below the surface of the sediment.

Three of the four peeper and push point device comparisons for strontium have higher concentration in the push points, regardless of filtering option (figure 4.54). In the fourth comparison, the peeper has the higher strontium concentration. All of the unfiltered push point samples have lower zinc concentrations than the filtered push point and peeper samples (figure 4.54). Comparisons of the filtered push point and peeper are split, two each, for which device has the higher zinc concentration (figure 4.54).

The paired t-test was used to compare peepers with the different push point filtering options is shown in table 4.12. The average difference between the devices and the t-test difference interval is included in the table. The average difference and difference interval are calculated by subtracting push point metal concentration values from corresponding peeper sample concentrations. As a result, a negative difference indicates push point metal concentrations are higher than the peeper's.

The average difference for iron concentration is -77ppm and -100ppm with a concentration spread of all devices from 66ppm to 260ppm (table 4.12). The iron concentration t-test difference interval for unfiltered push point includes zero. For the filtered samples from the filtered push point device, the difference interval is negative.

For a scale of 12ppm to 28ppm, the average difference of manganese concentrations is 0.77ppm and 0.53 for unfiltered and filtered push point devices, respectively. Zero is included in the t-test difference interval for both push point filtering options.

Table 4.12: Paired t-test for Device Comparisons of Peeper and Push Point Samples

Merrimack River laboratory sediment samples are used for comparing peepers with push point sampling devices. Comparisons are of elements, Fe, Mn, Cd, Cr, Sr & Zn. Peeper samples used in the comparison are averages of cells from 1" below the surface to the bottom of the peepers. Push Point samples used in the comparisons were removed with its end at 5" below the surface of the sediment. $T_{3,0.025}$, from student t-test tables, is 3.182.

Metal	Comparison	Average Difference (ppm)	Interval (ppm)	
Fe	Unfiltered Push Point	-77.345	-171.9	17.1702
	Filtered Push Point	-100.414	-177.5	-23.34
Mn	Unfiltered Push Point	0.768791	-7.240	8.777
	Filtered Push Point	0.531016	-7.640	8.702
Cd	Unfiltered Push Point	-0.00319	-0.0072	0.000826
	Filtered Push Point	-0.00391	-0.00723	-0.00059
Cr	Unfiltered Push Point	-0.00546	-0.00926	-0.00166
	Filtered Push Point	-0.00406	-0.00665	-0.00148
Sr	Unfiltered Push Point	-0.02228	-0.09957	0.05501
	Filtered Push Point	-0.02789	-0.09829	0.04251
Zn	Unfiltered Push Point	0.09163	-0.01381	0.1971
	Filtered Push Point	-0.00547	-0.1843	0.1734

The comparison of cadmium concentrations has an average difference of -0.003ppm and -0.004ppm with a scale of 0.003ppm to 0.01ppm for unfiltered and filtered push point devices, respectively (table 4.12). Zero is included in the t-test difference interval for unfiltered push point cadmium concentrations The t-test difference interval for filtered push point cadmium concentration is negative (table 4.12).

The t-test difference intervals for comparisons of chromium concentrations are negative for both push point filtering options (table 4.12). The averaged difference of the chromium concentrations is -0.005ppm for unfiltered push point samples and -0.004ppm for filtered push point samples with concentrations between 0.002ppm to 0.01ppm (table 4.12).

For strontium concentration between 0.28ppm to 0.39ppm, the average concentration difference is -0.02ppm and -0.03ppm for unfiltered and filtered push point devices, respectively (table 4.12). Zero is included in the t-test difference interval for both push point filtering options (table 4.12).

For zinc concentration between 0.05ppm to 0.3ppm, the average concentration difference is 0.09ppm and -0.005ppm for unfiltered and filtered push point devices, respectively (table 4.12). Zero is included in the t-test difference interval for both push point filtering options (table 4.12).

Differences in sample concentration between peepers and push points devices are dependant on the metal being sampled. For example, there is no apparent difference in sampling device for strontium or zinc while the push point device yield higher concentrations of chromium.

CHAPTER 5

CONCLUSIONS & RECOMMENDATION

5.1 Introduction

The primary purpose of this thesis is to determine the best method for using peepers for sediment sampling in the intertidal zone. Since Carignan stated that preparation and sample removal was the key to quality results, they were the focus of this study. It should be noted that Carignan completed his experiments in fresh water at the bottom of the lakes and those perform here were in the brackish water of an estuary. The push point direct sampler was examined with the results compared to those of the peeper. This device allows the researcher to acquire sample in a timely manner. Each of the following sections will discuss the conclusions, followed by recommendation for best use of the devices.

5.2 Peepers

5.2.1 Peeper Preparation

The results of samples analyzed for redox sensitive metals, selected metal and anion were examined. The affects of oxygen in the makeup water was evaluated by comparing peepers prepared with by purging air or nitrogen into the peeper keeper water. Oxygen introduction into the sampling devices was expected to cause metal precipitation that would result in lower reported concentrations.

Analysis of redox sensitive metals iron and manganese indicated oxygen was not a problem. In the Merrimack River sediment, air purged peeper had a slightly higher iron concentration. This is strong evidence that oxygen introduced into the sediment by the sampling devices in not causing artifacts. The other sediments indicated there was no difference in iron concentration based on gas purge type. The t-tests verified the results. Manganese analysis also indicated there was no real difference between the gas purge types. The equilibration trends indicated equilibrium was reached between four and six weeks.

The selected heavy metals analyzed showed similar results to those of the redox sensitive metals. The trends showed equilibration was in the same time period and oxygen introduction did not appear to be a problem.

Anion analysis followed the same pattern as the metals with oxygen tending not to be a problem. Nitrogen purging introduced nitrates into the makeup bath. Nitrite trends used in this study were not a good indication of microbial activity. However, the laboratory tubs did release gas during peeper insertion which is an indicator of microbial activity.

As preparation is a time consuming ordeal, it is recommended that the peepers be prepared in the laboratory. Since oxygen does not present a problem, it is recommended that removal of oxygen in the makeup water is not required. However, care should be taken not to introduce air bubbles in the peeper chambers during assembly. For field excursions that require travel, the prepared peepers should be sealed in the peeper keeper. The peeper keeper should be shipped in a custom, reusable, sealable shipping container. Upon arrival at the sampling site, the keeper should not be removed from the shipping container until just prior to sampling. Leaving the shipping container behind, the keepers should be used to transport the peepers from the staging area to the sampling site. Peepers should be removed from the keeper and inserted immediately.

5.2.2 Peeper Material

Orange tint was evident on peepers based on sediment type. Sandy or loose sediment had the orange tint. Sediment with fine, closely packed particle did not have any orange tint. Also, peepers that were continually covered by water (not in the intertidal zone) did not exhibit the orange tint. Based on the experimental design, oxygen effects in peeper material was included in the preparation studies. The results indicate oxygen in the material does not affect sampling concentrations. It should be noted that the horizontal peepers made from acrylic did not show an orange tint in any of the sediment. It should be noted that those peepers were above the aerobic/anaerobic interface.

Polycarbonate was originally used to provide durability in the cobble, clay sediment in the Cocheco River. Since orange tint did not form on acrylic peepers in that sediment, it is recommended that any future peepers be made from acrylic.

5.2.3 Sample Removal

Most of the studies performed in this thesis included a syringe filter option. The results indicated that it did not matter whether the sample was filtered or not. The nitrogen purged glove box study also indicated it was not needed to extract a reliable sample. The best practice is to remove the sample immediately after the peeper is removed from the sediment. A disposable syringe should be used to extract the sample. The extracted sample should be immediately put into a vial. The samples should be preserved in a timely manner.

5.3 Push Point Sampler

The push point sampling device yields a sample with a minimum of effort and training but it is only effective in loose, sandy sediment. The results indicate that nitrogen purged glove box or other oxygen limiting device is not needed for sample removal. Unfiltered samples had only a slightly higher concentration than filtered ones. However, unfiltered samples left particles in the bottom of ICP tubes. It is, therefore, recommended that samples be filtered during the extraction procedure. The best practice calls for the sample to be deposited into a clean beaker or bottle directly from the push point device. The sample should be drawn immediately from this container with a syringe with attached filter, and then deposited into an ICP vial. The equilibration trends indicated equilibrium was reached between four and six weeks.

5.4 Device Comparison

Using peepers and push points in conjunction is a useful research tool. Preliminary results can be obtained with the push point at the first visit to a sediment sampling site. Samples are easily extracted with the push point and multiple areas at a site can be evaluated quickly. The preliminary findings can be used to identify "hot spots" that peepers can be used to sample at a later date.

The prevailing evidence is that push point yields a higher concentration of certain metals than those obtained with peepers. However, the difference is not so great that it does not preclude using the devices together as part of the overall sampling plan.

The flexibility of peeper designs allows it to be modified to accommodate sampling in a variety of circumstances and sediment types. The device can yield a depth profile and is effective for evaluating caps. This makes the peeper the primary sampling tool for heavy metals in pore water analysis. The limitations of push point make it a secondary sampling tool. Using the push point for geotextile reactive mat evaluation is not recommended.

CHAPTER 6

FUTURE RESEARCH

6.1 Porewater Flow

This thesis was designed to evaluate sampling devices to evaluate the effectiveness geotextile reactive caps. The majority of the field studies were conducted in the intertidal zone in estuaries. The field sediment had flow from ground water below and tidal influences from above. Each of these sources has significantly different constituents and characteristics. The flow will actively *recharge* the pore water adjacent to the peeper membrane. The laboratory portion of the studies also used the sediment from the intertidal zone. At least an inch layer of water was kept above the sediment during the equilibration time. The pore water was stagnant and the only recharging came from diffusion.

An experiment should be designed to study the effects of the tidal flow. It should examine whether there is a correlation between equilibration and tidal influences. The laboratory study should incorporate a pumping station that can add fresh water from below the sediment or brackish water from the top. Comparing the different effects will give a better understanding of how the tidal changes impact the performance of the peepers.

6.2 Intertidal vs. Deep River Water

Carignan performed his studies at the bottom of lakes while the majority of experiments in this thesis were performed in the intertidal zone. There were enough differences in the experimental design that a direct comparison between the methods was subjective. The flow of the water above the sediment in lakes is limited compared to the flow in rivers. The water at the bottom of a lake is anaerobic while that in the river may not be. The experiment should be designed so samples can be compared at varying depths from the intertidal zone to the middle of a river.

6.3 Equilibration

The design of the equilibration studies in thesis made it difficult to determine the precise equilibration time. There was an expected difference between field and laboratory studies. The range for the field studies was between zero and three weeks, depending on the metal. For the laboratory experiments it was between three and five weeks with the possibility of a greater than five week equilibration time. The regression line analysis requires a minimum of three data points but many more to be statistically accurate. More data points should be in the kinetically active zone of each experiment type. For example in future field studies, peepers should be removed after day one or two and continue on two or three day cycle through at least week 3. In the laboratory experiments, a similar interval should be used starting after week two.

LIST OF REFERENCES

Adolphson, P. (1995). Determining Toxicity of "Naturally" Occurring Contaminants Under the Washington State Department of Ecology's Sediment Management Standards, Washington Department of Ecology.

Allen, H. E. (1995). Metal Contaminated Aquatic Sediments, Ann Arbor Press.

Anderson, J. (2005). Appendix C: DEQ Characterization of Potential Upland Contaminant Sources, Oregon's Department of Environmental Quality (DEQ).

Ankley, G. T. T., N.A.; Di Toro, D.M.; Hansen, D.J.; Mahony, J.D.; Berry, W.J.; Swartz, R.C.; Hoke, R.A.; Garrison, A.W.; Herbert E. Allen, H.E.; Zarba, C.S. (1994). "Assessing potential bioavailability of metals in sediments: A proposed approach." Environmental Management 18(3): 331-337.

Barth, R. (2006). Interview.

Berg, P., Risgaard-Petersen, N., & Rysgaard, S. (1998). "Interpretation of Measured Concentration Profiles in Sediment Pore Water." Limnology and Oceanography 43(7): 1500-1510.

Berger, W. (2006). Guide to Membrane References, Diffusion Sampler Database Web Site.

Berthouex, P. M., Brown, L. C. (2002), Statics for Environmental Engineers, Lewis Publishers

Bokuniewicz, H. J., Kamlet, K.S., Bohlen, W.F., Grassle, J.F., Hayes, D.F., Hunt, J.R., Lee, D.G., McConnell, K.E., Pavlou, S.P., Peddicord, R.K., Shelley, P., Thiboudeaux, L.J., Wenzel, J.G., Young, L.Y. (1997). Contaminated Sediments in Ports and Waterways: Cleanup Strategies and Technologies, National Academy Press.

Brita Sundelin, B. E., A-K. (2001). "Mobility and Bioavilability of Trace Metals in Sulfidic Coastal Sediments." Environmental Toxicology and Chemistry 20(4): 748-756.

Buchman, M. F. (1999). NOAA SQRT: Screening Quick Reference Tables, NOAA.

Bufflap, S. E. A., H.E. (1995). "Sediment pore water collection methods for trace metal analysis: A review." Water Research 29(1): 165-177.

Carignan, R. (1984). "Interstitial Water Sampling by Dialysis:

Methodological Notes." Limnology and Oceanography 29(3): 667-670.

Carignan, R. N., J. O. (1985). "Trace metal deposition and mobility in the sediments of two lakes near Sudbury, Ontario." Geochimica et Cosmochimica Acta 49(8): 1753-1764.

Carignan, R. R., F.; Tessier, A. (1985). "Sediment porewater sampling for metal analysis: A comparison of techniques." Geochimica et Cosmochimica Acta 49(11): 2493-2497.

Carignan, R. S.-P., S.; Gachter R. (1994). "Use of Diffusion Samplers in Oligotrophic Lake Sediments: Effects of Free Oxygen in Sampler Material." Limnology and Oceanography 39(2): 468-474.

Chapman, P. M., Wangb, A.F., Germanoc, J.D. & Batleyd, G. (2002). "Viewpoint: Pore water testing and analysis: the good, the bad, and the ugly." Marine Pollution Bulletin 44(5): 359-366.

Clark, R. B. (2001). Marine Pollution, Oxford University Press.

DiToro, D. M. (2001). Sediment Flux Modeling.

EPA (2007). Groundwater to Surface Water Contamination Migration Monitoring: Trident Probe and UltraSeep Meter.

EPA (2008). Contaminated Sediment in Water, EPA.

Howes, B. L., Darcey, J.W.H. & Wakeham, S.G. (1984). "Effects of sampling technique on measurements of porewater constituents in salt marsh sediments." Limnology and Oceanography 30(1): 221-227.

Huerta-Diaz, M. A. R.-D., I.; Sañudo-Wilhelmy, S.A. ;Flegal, A.R. (2007). "Comparative distributions of size fractionated metals in pore waters sampled by in situ dialysis and whole-core sediment squeezing: Implications for diffusive flux calculations." Applied Geochemistry 29(11): 2509-2525.

L.M.Rauch (2006). Treatment of Dioxin/Furan and PCN Contaminated Sediments with Palladized Magnesium. Civil Engineering. Durham, NH, University of New Hampshire: 95.

Liu, W. W., Z.; Wen, X.; Tang, H. (1999). "The Application of Preliminary Sediment Quality Criteria to Metal Contamination in the Le An River." Environmental Pollution 109(3): 355-366.

Long, E. R., Morgan, L. G. (1990). The Potential for Biological Effects of Sediments-Sorbed Contaminants Tested in the National Status and Trends Program, NOAA.

Lorah, M. (2006). Interview.
Mudroch, A., Azcue, J.M. (1995). Manual of Aquatic Sediment Sampling.

NOAA (2006). Sediment Quality Guidelines (ERL/ERM).

Rickley (2004). Modified Hesslein In-Situ Pore Water Sampler. R. H. Company.

Romano, E., Ausili A., Zharova N., Magno M.C., Pavoni B., Gabellini M. (2004). "Marine sediment contamination of an industrial site at Port of

Bagnoli, Gulf of Naples, Southern Italy." Marine Pollution Bulletin 49(5-6): 487-495.

Rostron, D. M., Subsea Survey (2001). Procedural Guideline No. 3-10 Sampling marine benthos using suction samplers, Marine Monitoring Handbook.

Stanley, J. D., Carlsonb, R.W., Van Beekc, G., Jorstadd, T.F., & Landaue, E.A. (2007). "Alexandria, Egypt, before Alexander the Great: A multidisciplinary approach yields rich discoveries." Geological Society of America 17(8): 4-10.

Zirbser, K. H., R.; Stahl, L.; Tate, B.; Diamond, J.; Burton, A.; Johns, M.;Scott, J. (2001). EPA: Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual.