Best Practices User's Guide

Standardizing Sediment Porewater Passive Samplers for Inorganic Constituents of Concern
ESTCP ER20-5261

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Acronyms and Abbreviations

°C	degrees Celsius
µg	microgram(s)
µg/L	micrograms per liter
µm	micrometer
AVS	acid volatile sulfide
Cfree	concentration of freely dissolved contaminants
cm	centimeters
DGT	diffusive gradient in thin film
ESTCP	Environmental Security Technology Certification Program
FAQ	frequently asked question
F	design factor
GPS	Global Positioning System
HDPE	high density polyethylene
LDPE	low density polyethylene
mg/L	milligram(s) per liter
mL	milliliters
mm	millimeter
ND	nondetect (no detection above the method detection limit)
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
PP	polypropylene
PTFE	Polytetrafluoroethylene
QA	quality assurance
QC	quality control
SEM	simultaneously extracted metals
SOP	standard operating procedure
USEPA	United States Environmental Protection Agency

1. INTRODUCTION

1.1 Introduction to Peepers

Sediment porewater dialysis passive samplers, also known as “peepers,” were developed more than 45 years ago (Figure 1-1; Hesslein, 1976) as a potential approach to circumvent challenges associated with other methods of sampling inorganic chemicals in sediment. Peepers are inert containers with a small volume of purified water (“peeper water”) capped with a semipermeable membrane. Deploying a peeper consists of inserting it into the sediment or water, where it is left for a period of a few days to a few weeks. During this time, passive sampling is achieved via the principle of diffusion, as the enclosed volume of peeper water equilibrates with the surrounding aquatic matrix via transport of inorganics through the peeper’s semipermeable membrane. After an equilibration period, the peeper is retrieved, and the peeper water is transferred to a storage container and analyzed for inorganics in the same manner as a typical surface water sample. The result obtained from the analysis is then reported as a concentration in water (i.e., milligram inorganic per liter of water [mg/L]).

Figure 1-1: General Hesslein (1976) Peeper design (42 peeper chambers), from the United States Geological Survey (https://www.usgs.gov/media/images/peeper-samplers).

Despite being in use for over four decades, there is no standard guidance for peepers, and uncertainties remain regarding peeper field methodology, equilibration dynamics, and device materials, hindering the use of peepers for routine applications at sediment sites under regulatory oversight.

1.2 Goals and Overall Approaches for This Project

Geosyntec Consultants, SiREM, Texas Tech University, and the United States Navy's Naval Information Warfare Center initiated a 3-year research effort to address the lack of standard guidance for using peepers to evaluate metal availability in sediment and water. Funded by the United States Department of Defense's Environmental Security Technology Certification Program (ESTCP, project number ER20-5261[1]), the project's overall objective was to enhance the standardization of, and confidence in, peeper usage for passive sampling of inorganic constituents— especially for the target metals[2] that were the focus of our evaluation.

To support this project's goals, three main tasks were conducted:

1. **Literature Review:** A detailed literature review was conducted on passive inorganics sampling in sediment, examining past and present best practices for peeper preparation, deployment, retrieval, and data analysis. The comprehensive review included over 85 peer-reviewed and grey literature documents from the last 45 on the subject of applying peepers to measure freely dissolved inorganics in sediment porewater. In an effort toward standardization, the review also identified several key technical aspects where additional work would be beneficial to promote the routine application of peepers to aid decision-making at contaminated sediment sites under regulatory oversight.
    - The literature review (Risacher et al., 2021) is attached to this document as Appendix A. The review was also published in a peer-reviewed journal in 2023 (Risacher et al., 2023a).
2. **Laboratory Experiments:** A series of seven laboratory experiments was conducted over a period of 17 months to validate the best practices for peeper usage, specifically addressing methods for end-users to be able to prepare, ship, store, process, and preserve peeper samplers. The methods validated in the laboratory studies were informed and improved by using the data gaps identified in the literature review.
    - The laboratory experiments are summarized in a laboratory report (Conder et al., 2023), which is attached to this document as Appendix B.
3. **Field Demonstration:** To demonstrate the methods and standardization developed in the laboratory experiments, a field demonstration was performed in which peepers were deployed in surface sediment and surface water at Naval Base San Diego, San Diego, California, in October 2022. Detailed methods, logistical details, and recommendations for planning and executing successful peeper investigations were provided using examples and lessons learned from the field demonstration.

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[1] Project details can be found at https://serdp-estcp.org/projects/details/db871313-fbc0-4432-b536-40c64af3627f.

[2] The inorganics targeted in this project ("Target Metals") are cadmium, chromium, copper, nickel, lead, zinc, and total mercury, because they are common chemicals of concern in contaminated sediment. Iron and manganese were also evaluated in several aspects of the project. The approaches evaluated in this document are also generally applicable to many other inorganic analytes.

- The field demonstration is detailed in a report (Risacher et al., 2023b), which is attached to this document as Appendix C.

As a result of these primary efforts, additional resources produced by this project include the following:

1. **Peeper Preparation Standard Operating Procedure:** A detailed standard operating procedure (SOP) was created to provide step-by-step instructions for preparing peepers using the methods validated in this project.
    - The peeper preparation SOP is attached to this document as Appendix D.
2. **Peeper Deployment, Retrieval, and Processing Standard Operating Procedure:** A detailed SOP was created to provide step-by-step instructions for deploying, retrieving, and processing peepers at field sites using the methods validated in this project.
    - The deployment, retrieval, and processing SOP is attached to this document as Appendix E.
3. **Peeper Pre-equilibrium Calculation Spreadsheets:** For the use of pre-equilibrium methods evaluated in the laboratory experiments and field demonstration, Excel spreadsheets were created to facilitate calculations.
    - The spreadsheets are attached to this document as Appendix F, which is provided as an Excel file attached to this document (as a PDF).

1.3 Goals and Overview of this Document

The resources developed in the literature, laboratory, and field efforts in this project are detailed in Appendices A through C. In the hopes of disseminating these results to Department of Defense staff, regulatory agencies, and other industry practitioners such as environmental consultants and commercial analytical laboratories that support sediment investigations, the remainder of this document features an overview of the best practices identified in our project. The goal of the document is to present these best practices in a user-friendly guide that enables end-users to successfully prepare, deploy, and retrieve peepers, as well as interpret and use peeper data in a decision-making context at sediment sites under regulatory oversight.

The remainder of this document is organized as best-practice answers to frequently asked questions (FAQs) for investigators wanting to measure metal availability in sediment and water, and is organized via the following sections:

- **Section 2, Best-practice Answers to FAQs,** provides answers to common questions about evaluating metal availability in sediment and water using peepers:
    - 2.1 Why measure metal availability in sediment?
    - 2.2 What is a peeper, and how does it measure metal availability?
    - 2.3 Are there other abiotic tools to measure metal availability?
    - 2.4 Where can peepers be obtained?
    - 2.5 How are peepers prepared?
    - 2.6 Do peepers sample colloidal or other sorbed metals from sediment?

  - 2.7 Do peepers and peeper water need to be deoxygenated prior to deployment in sediment?
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- **Section 3, References,** provides a list of references cited in the document.
- **Appendix A:** Literature Review.
- **Appendix B:** Laboratory Experiments Report
- **Appendix C:** Field Demonstration Report
- **Appendix D:** Peeper Preparation SOP
- **Appendix E:** Peeper Deployment, Retrieval, and Processing SOP
- **Appendix F:** Peeper Pre-equilibrium Calculation Spreadsheets (provided as Excel file attachment to PDF)

2. BEST-PRACTICE ANSWERS TO FREQUENTLY ASKED QUESTIONS

2.1 Why measure metal availability in sediment?

Contaminated sediments are a major environmental concern, and aquatic sediment contaminated with inorganic constituents, primarily metals and metalloids, represents significant challenges at many sites. Biologically available inorganics in sediment can be characterized by measurements that attempt to quantify the concentration of freely dissolved contaminants (Cfree) in sediment and sediment porewater (Conder et al., 2015; Cleveland et al., 2017). This approach represents an advantage over measuring the total extractable concentrations of inorganics in bulk sediment (United States Environmental Protection Agency [USEPA], 2005), which can overestimate the portion of biologically available inorganics in sediment (Peijnenburg et al., 2014). Cfree measurements can provide a superior quantitative understanding of metals in sediment (compared to bulk analysis of metals in sediment) that is particularly useful in filling a variety of data gaps typical of sediment site investigations, such as environmental fate, availability, nature and extent, ecological and human health risks, and remedial performance.

Why measure metal availability in sediment?

- Measuring metal availability allows a better quantitative understanding of fate, risks, and remediation performance.

2.2 What is a peeper, and how does it measure metal availability?

Sediment porewater dialysis passive samplers, also known as "peepers," were developed more than 45 years ago (Hesslein, 1976) as a potential approach[3] to circumvent the problems associated with other methods of sampling inorganic chemicals in sediment (i.e., overestimation of bioavailable concentrations of inorganics). Peepers (Figure 2-1) are inert containers with a small volume (1–100 milliliters [mL]) of purified water ("peeper water") capped with a semipermeable membrane. Peepers usually feature a protective cap or structure that secures the membrane to the peeper.

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[3] Other methods to evaluate metal bioavailability in sediment are discussed in Section 2.3.

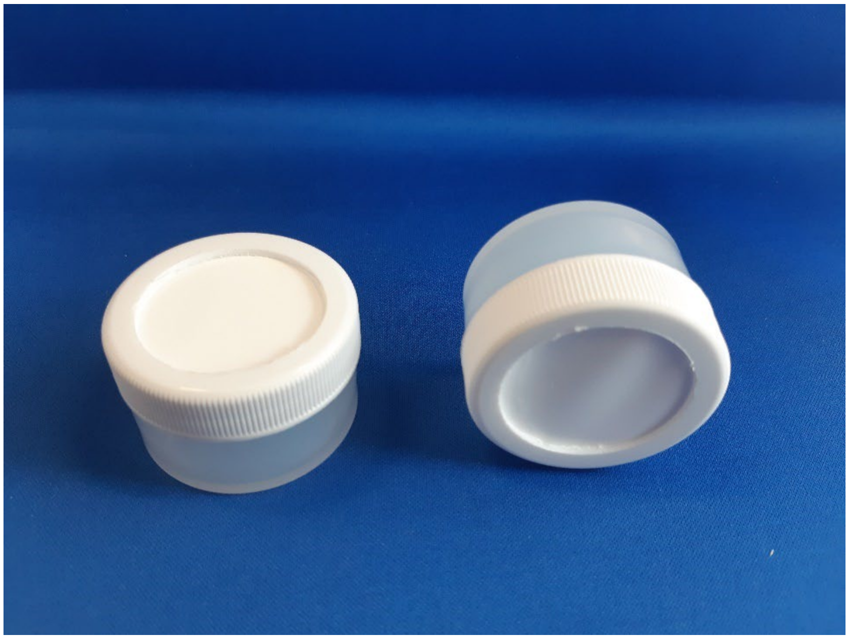


Figure 2-1: Photographs of the peeper design selected for the laboratory experiment and field demonstration (SiREM), showing the peeper vial and membrane surface. The peeper vial contains 15 mL of peeper water.

Peepers function by allowing a small water compartment to chemically equilibrate with sediment porewater via passive diffusion through a semipermeable membrane (Risacher et al., 2023a), as shown in Figure 2-2.

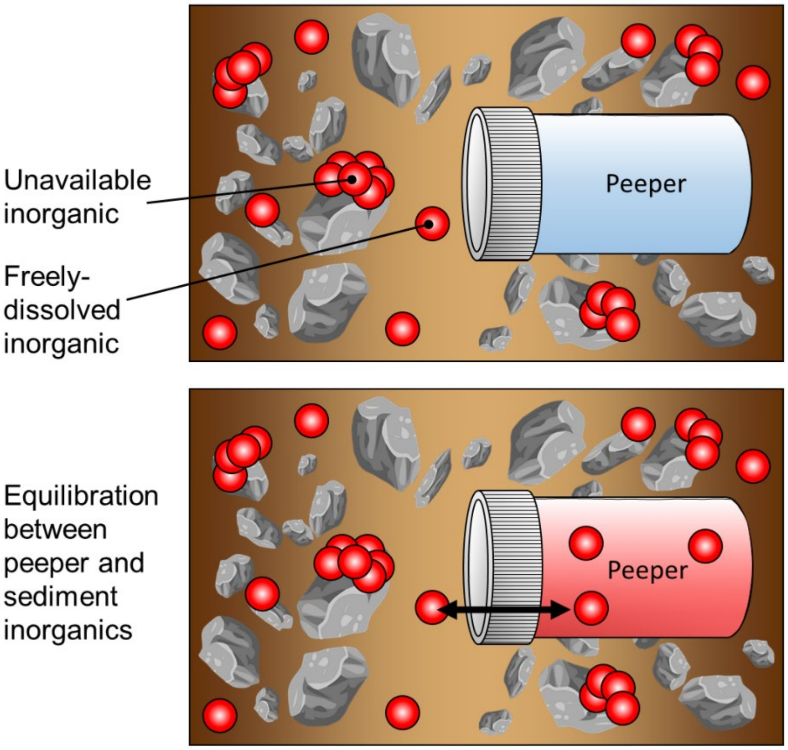


Figure 2-2: Conceptual illustration of peeper passive sampling in a sediment matrix, showing peeper immediately after deployment (top) and after equilibration between the porewater and peeper chamber water (bottom).

The water inside the peeper is deionized, creating a concentration gradient that facilitates diffusion of inorganic chemicals through the membrane into the solution within the peeper. Peepers are usually deployed via insertion into surface sediment by divers and waders, or from a vessel. After an equilibration period (several days to several weeks), the concentration inside the peeper will approach the concentration in the sediment porewater. After retrieval, the peeper water is transferred to a storage container, which usually contains a preservative (e.g., nitric acid for metals). Following shipment to an analytical laboratory, the liquid water sample is analyzed for inorganics in the same manner as a typical surface water sample. The result obtained from the analysis is then reported as a concentration in water (i.e., milligram inorganic per liter of water [mg/L]).

Over the last 45 years, peepers have been used for a variety of scientific applications and in regulatory investigations at Superfund and state-regulated sediment sites. As detailed in Appendix A and Risacher et al. (2023a), over 85 documents involving peepers were included in the literature review of past peeper applications and research.

What is a peeper, and how does it measure metal availability?

- Peepers are simple tools that sample metals in sediment and water through diffusion.
- Peepers provide data as a concentration in water (i.e., mg/L).
- Peepers have been in use to measure inorganic availability for more than four decades.

2.3 Are there other abiotic tools to measure metal availability?

Measuring metal availability in sediment can be achieved by measuring the concentration of metals in aquatic organisms exposed to sediment, often via bioaccumulation exposures using standard laboratory organisms exposed to field sediment samples, or via collecting wild benthic organisms from sediment. However, bioaccumulation testing or organism collecting are not always practical, effective, possible, and/or efficient for many investigations.

A variety of abiotic approaches for measuring metal availability can offer an alternative to biological approaches, including the following:

- **Mechanical sediment porewater analysis** (Figure 2-3) usually consists of collecting large volumes of bulk sediment, which are then mechanically squeezed, or centrifuged, to produce a supernatant liquid (porewater) that is filtered to extract the water for analysis (Gruzalski et al., 2016). Porewater can also be mechanically collected through suction. The mechanical extraction process poses challenges due to the heterogeneity of sediments, high reactivity of some inorganic analytes, and chemical and physical disturbances of the sediments. These factors can cause the concentration of dissolved inorganics obtained from analyzing a mechanically extracted sample to deviate from the concentration of available metals in sediment porewater (Peijnenburg et al., 2014). For example, it is widely recognized that sampling disturbances can affect redox conditions (Teasdale et al., 1995; Schroeder et al., 2020), which can lead to under- or over-representing

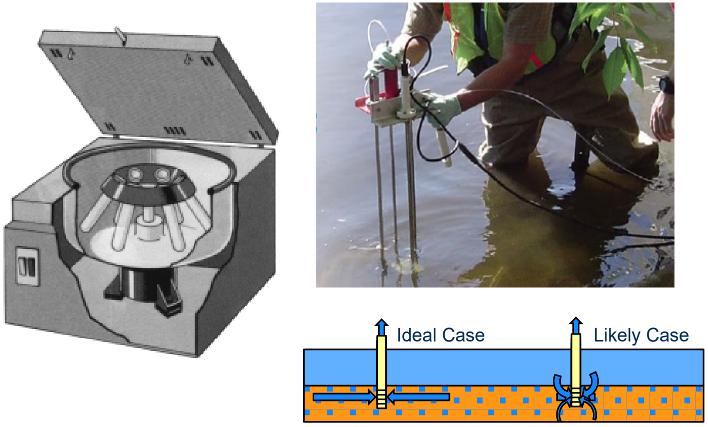


Figure 2-3: Mechanical porewater sampling via centrifugation (left) and porewater suction (right).

inorganic chemical concentrations relative to the true dissolved phase concentration in the sediment porewater (Wise, 2009; Gruzalski et al., 2016).

- **Analysis of acid volatile sulfide and simultaneously extracted metals (AVS/SEM)** in bulk sediment is often used to evaluate metal availability in sediment. This approach has been used for nearly 20 years to evaluate metal toxicity in sediments (USEPA, 2005). This measurement evaluates bioavailability of divalent metals (cadmium, copper, lead, nickel, and zinc) via a weak acid extraction of a bulk sediment sample (i.e., SEM measurement). Along with measuring and normalizing a chelating agent (AVS), the approach can provide a quantitative value of available divalent metals. Sample-specific AVS/SEM values can be compared to a conservative threshold that, if exceeded, may indicate the need for additional toxicity testing or evaluation due to the potential for toxicity (USEPA, 2005). This approach has the advantage of simple procedures in the field (e.g., collecting a bulk sediment sample), relatively simple data evaluation (USEPA, 2005; DeForest et al., 2022), and a relatively high acceptance and familiarity among regulatory stakeholders. However, the AVS/SEM approach is primarily limited to cadmium, copper, lead, nickel, and zinc, and the quantitative estimate produced by the analysis is primarily limited to evaluating the need for aquatic toxicity testing, rather than more broad data *uses* in nature and extent evaluation or fate modeling.
- **Diffusive Gradient in Thin Film (DGT)** passive samplers (Figure 2-4) offer the minimal disturbance and time-integrative advantages of peepers (Cleveland et al., 2017). DGTs technically measure flux (i.e., microgram of metal per square meter per hour). A measured flux value provided by a DGT can be converted to a concentration in water (e.g., microgram per liter) using modeling, and in this manner, DGT data can be related to concentration-based criteria for water quality or used for efforts to understand human/environmental risk and contaminant fate. Applying DGTs often requires modeling to convert the concentration measured in the DGT to fluxes, then to porewater concentrations or Cfree. Additionally, special care must be taken when inserting and retrieving DGTs from sediment due to the delicate nature of the adsorbent films used in DGTs. In contrast to peeper water, which can be analyzed by any commercial laboratory offering standard analysis of inorganics in water, there are fewer commercial analytical laboratories that will analyze DGTs, though costs for the DGTs themselves are less expensive than or similar in cost compared to most peeper designs.

Figure 2-4: Examples of DGTs.

The comparison of abiotic tools that can measure metal availability is limited; however, it is generally recognized that mechanical sediment porewater analysis may have the most drawbacks. As a result of the complications with mechanical porewater sampling for inorganics, passive sampling approaches for inorganics are generally preferred, as they are assumed to have a low impact on the surrounding geochemistry of sediment and sediment porewater and enable a more accurate measurement of Cfree (USEPA, 2005; Cleveland et al., 2017). Direct comparisons of porewater samples obtained from mechanical extraction methods and porewater in peepers have generally indicated peepers are more accurate in terms of predicting metal availability in sediment. For example, Judd et al. (2022) suggested that metal concentrations collected from peepers, combined with other parameters (e.g., major ions, pH), can more accurately reflect inorganic availability to organisms compared to mechanically generated samples obtained via centrifugation. A recent study used a multi-metal biotic ligand model assessment of peeper data to demonstrate the value of peeper porewater-based evaluations, along with sediment chemistry, in understanding toxicity observed in bioassay studies (Santore et al., 2022).

As detailed in Appendix B, this project compared the results and logistics for peepers and DGTs at a field site. The evaluation was limited to deploying peepers and DGTs in surface water, just above the sediment-water interface. In general, for metals consistently detected in surface water (copper, manganese, and zinc) by both methods, peeper and DGT data were statistically different, with average Cfree values differing by a factor of 2 to 6. Additional study may be needed to refine the differences in DGT and peeper measurements, although it is notable that these very different techniques were within an approximate agreement factor of 5. More research would be beneficial to evaluate the comparison between peepers, DGTs, and AVS/SEM.

Research Opportunity

Comparing the performance and results of commonly applied peeper, AVS/SEM, and DGT tools.

Are there other abiotic tools to measure metal availability?

- In addition to peepers, other tools are available to measure metal availability, including mechanical porewater extraction from sediment, AVS/SEM analysis of sediment samples, and passive sampling using DGTs.
- AVS/SEM, peepers, and DGTs are currently recognized as the best tools for measuring metal availability, although more research to compare the performance of these tools would be beneficial.

2.4 Where can peepers be obtained?

Peepers are generally available from commercial service providers, commercial analytical labs, academic researchers, and government researchers.

A standard Hesslein acrylic peeper frame can be purchased online from several sources, such as Performance Results Plus Inc. (https://prph2o.com/hesslein-in-situ-pore-water-sampler-1/). These devices must be assembled with peeper water and a membrane before deployment, usually under controlled conditions in an environmental or chemical analysis laboratory. Commercial analytical chemical laboratories, commercial consulting laboratories, and other government or academic laboratories may be able to assist in constructing peepers.

Several academic and government researchers actively involved in sediment research can produce peepers and provide deployment, retrieval, and analysis support. For example, Dr. Andrew Jackson (Texas Tech University) has provided High Resolution Passive Profiler peeper sampling support for several projects. The High Resolution Passive Profiler was developed with support from ESTCP (project ER-201734), and more information is available here: https://serdp-estcp.org/projects/details/f773f67f-194d-4f73-b7a5-7a794ef1ea45. The United States Geological Survey has also been involved in peeper research and may be able to provide devices (https://www.usgs.gov/media/images/passive-metal-samplers-peepers).

Several commercial service providers can produce peepers and provide deployment, retrieval, and analysis support. For example, the peepers used in this study were obtained from SiREM (https://www.siremlab.com/), a commercial service provider of passive samplers.

When obtaining peepers for use at a site, it is recommended to discuss the following with the peeper supplier to make sure the peepers and services offered will meet the needs of the investigation:

- Design details and specifications of the peepers
- The availability of standard operating procedures for peeper preparation, deployment, retrieval, and processing
- The deployment time for peepers and the use of tracers in the peeper to verify equilibration or allow pre-equilibrium deployments
- Chemical analysis approaches for the peeper water, especially if standard USEPA SW-846 methods are to be used and the accreditation of the analytical laboratory
- Typical schedules for preparation, shipment, and analysis of peepers

Where can peepers be obtained?

- Peepers are available from commercial service providers and research laboratories in academia and government.

2.5 How are peepers prepared?

Peepers (Figure 2-5) are inert containers with a small volume of deionized water ("peeper water") capped with a semipermeable membrane.

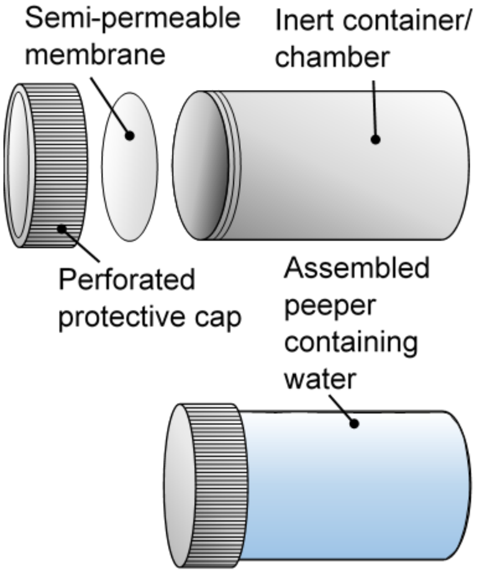


Figure 2-5: Example peeper construction showing (top, left to right) the peeper cap (optional), peeper membrane, and peeper chamber, and an assembled peeper containing peeper water (bottom).

A detailed SOP reflecting the final recommendations and best practices for peeper preparation is provided in Appendix D. The general approaches provided in the peeper preparation SOP are specific to the peeper design used in this project (Figure 2-1), but they are applicable to the wide variety of peeper designs described in Risacher et al. (2023a) and Appendix A.

Generally, the steps involved in peeper preparation include the following:

1. **Specify the Optimal Peeper Design:** Materials needed include a peeper chamber that will hold a volume of deionized water secured by a membrane. Peeper chamber material, peeper chamber volume, and membrane type are critical considerations in peeper design and preparation.

   It is important that the chamber is inert with regards to the analytes of interest (i.e., peeper chamber materials will not appreciably sorb the analytes from the sediment or surface water in which it is deployed). As shown below in Figure 2-6, our literature review indicated a wide variety of materials are available (acrylic, high density polyethylene [HDPE], low density polyethylene [LDPE], polytetrafluoroethylene [PTFE], polyvinyl chloride [PVC], polypropylene [PP], and chlorinated polyvinyl chloride). The best candidate materials from our review suggests a polymer ideal for trace metal analysis of water samples (i.e., LDPE, HDPE, polycarbonate, PP, or PTFE) as a standard peeper material.

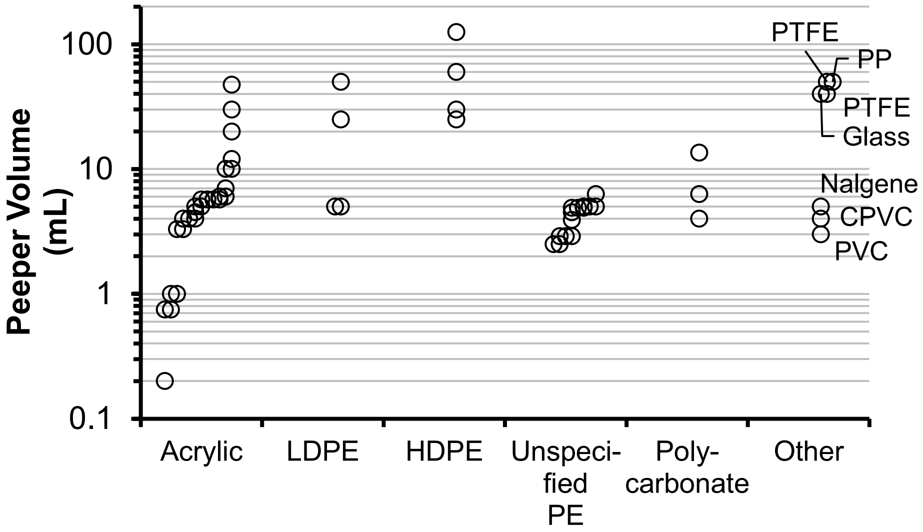


Figure 2-6: Peeper chamber volume by peeper material type. Labels next to each symbol represent the peeper water volume (mL) and material type (for the peepers in the "Other" category). The figure is on a logarithmic scale.

Volume is also a critical issue. As shown in Figure 2-6, peepers can be designed with a wide variety of volumes (e.g., 0.1-100 mL). A complex aspect of peeper design is the balance between the peeper chamber volume and the shape of the peeper in terms of the area of the peeper membrane relative to the peeper chamber volume, referred to as the design factor (F), where F = volume (mL) ÷ diffusion area (square centimeters [cm^2] or the specific surface area). Larger chamber volumes allow for broader analyte scopes and/or lower detection limits, especially for commercial analytical laboratories that follow standard USEPA SW-846 methods, which often specify 50 to 100 mL or more of water per sample. Large chamber volumes can be offset by higher specific surface areas for the membrane of the peeper, which results in a smaller F value. Smaller F values allow for faster equilibration with porewater and, therefore, shorter deployment times. For example, the 15-mL peeper used in this project (Figure 2-1) featured an F factor of 2.8 mL/cm^2, and equilibration in water or field sediment was generally reached in approximately 10 to 14 days (see Appendix B and Appendix C). A larger volume 60-mL peeper with approximately the same membrane surface area featured a higher F value (8.0 mL/cm^2) and required a longer time period (approximately 21 to 28 days) to achieve a similar level of equilibration as the 15-mL peeper.

A third key aspect of peeper design is the peeper membrane. A variety of materials with pore size diameters of approximately 0.2- to 1-micrometer (µm) have been used as peeper membranes (Figure 2-7). Polysulfone and polyethersulfone are similar in performance and are the most commonly used membrane types, and have also been used for most recent studies because of their chemical inertness and resistance to biofouling (Risacher et al., 2023a; Appendix A). A 0.45-µm pore size polyethersulfone membrane was used in this project, as indicated in the SOP (Appendix D). A 0.45-µm pore diameter polysulfone membrane is a reasonable material to use for typical peeper evaluations, given the widespread use of the 0.45-µm pore size in typical environmental sampling applications that evaluate "dissolved" chemicals in aqueous samples, as well as in common methods that rely on 0.45-µm filters to obtain an aqueous sample that represents "dissolved" metals.

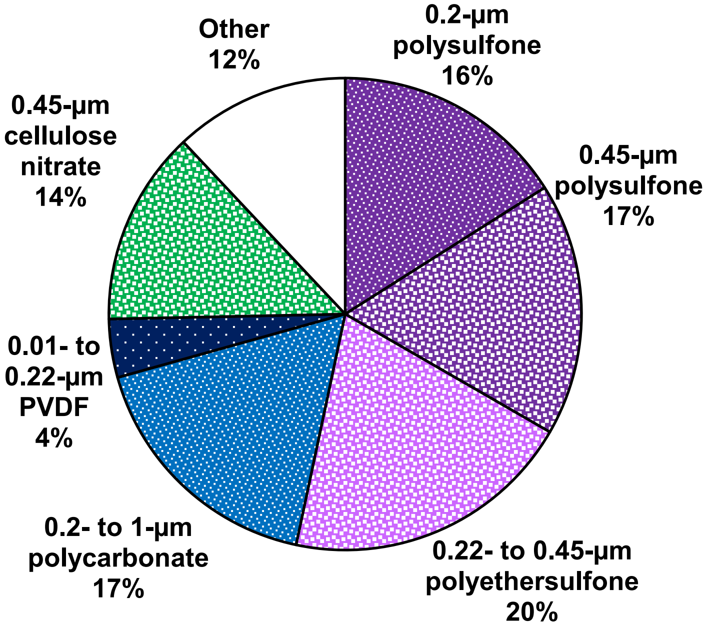


Figure 2-7: Peeper membrane type for the 75 studies reporting membrane details. Values reflect the percentage of studies using peepers with the specified membrane type.

2. **Prepare the Peeper Device:** This step generally consists of preliminary work needed to prepare the device. It can involve several efforts, including cutting or drilling access holes in a cap for a peeper adapted from a commercially available container (Appendix D), cutting the membrane to fit the peeper vial opening, and preparing additional support materials, such as frames, to insert peepers or mesh guards to protect peeper membranes in coarse sediments, gravels, and shell hash (Figure 2-8).

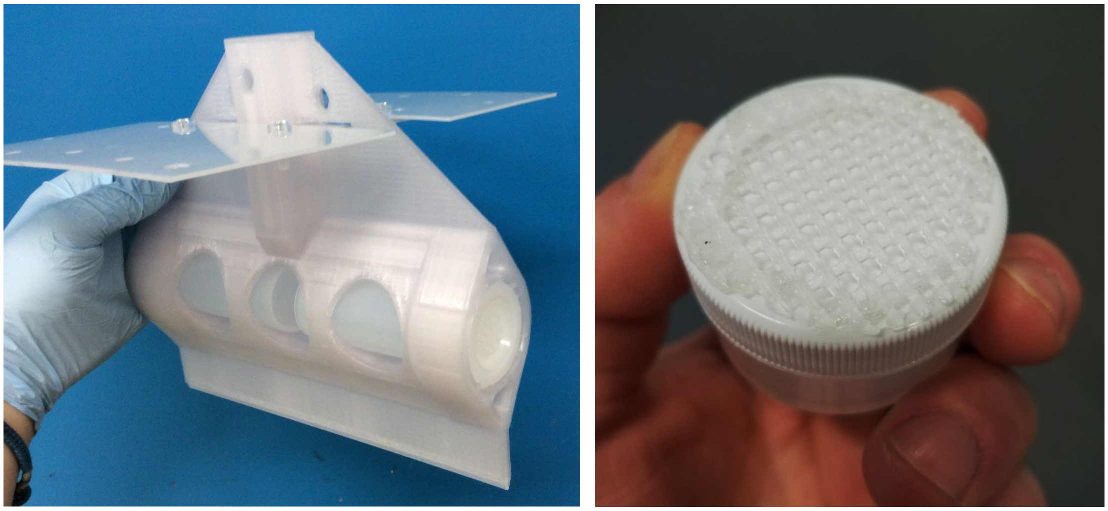


Figure 2-8: Example of ancillary design materials applied to peepers, including a support frame (left) and a peeper with a protective mesh cover to protect peeper membranes in gravel sediment (right).

3. **Clean the Peeper Device:** This step generally consists of preparation work needed to clean the peeper before filling it with water and proceeding with final assembly. At minimum, it usually involves washing the peeper with a standard laboratory detergent, followed by multiple rinses. For trace metal analysis, multiple soakings in weak acid, followed by rinsing with deionized water is standard practice, as indicated in the SOP for the peeper design used in this study (Appendix D).
4. **Prepare the Peeper Water:** This step consists of filling the peepers with the water which will equilibrate with the sediment porewater. The water needs to be ultrapure trace metal grade and can be from a laboratory supplier or a laboratory grade purification system (e.g., Millipore or equivalent). A reverse tracer can be added to the peeper water during this step, which may be used to evaluate the amount of equilibration attained by the peeper during its deployment in sediment or water. As shown in our laboratory and field work (Appendix B and Appendix C), lithium bromide at a concentration of 100 mg/L for freshwater deployments, or a concentration of 1000 mg/L for seawater deployments, was considered optimal. Lithium was demonstrated to be an appropriate tracer as shown in our experiments, because it can be measured in the same sample by the same analytical method as other metals that are commonly analyzed. Once the peeper water is prepared, peepers can be filled with the water using a pipette. Care must be taken to completely fill them without any air left in the container once the membrane is added. Peeper water doesn't need to be deoxygenated, as shown in our experiments (Appendix B).
5. **Peeper Preservation for Shipping:** For this step, peepers are packaged to be shipped to the field site. Peepers can be stored in Mylar bags to prevent them from drying or getting contaminated or damaged during transport. Peepers should be stored flat in the Mylar bags and stacked in a hard plastic chest cooler. Empty spaces can be filled with packing material such as bubble wrap to prevent the peepers from moving during transport.

6. **Additional Preparation Tips:** Begin peeper preparation (ideally) at least 2–3 weeks in advance of deployment to account for potential material delays or shipping delays. We recommend ordering at least 5-10% more peepers than required for deployment; this will provide extra peepers in case of damage that may occur during shipping, handling, deployment, and allow additional flexibility in the field.

How are peepers prepared?

- Peepers are chambers comprised of inert material (e.g., HDPE, PTFE) capped with a semipermeable polyethersulfone or polysulfone membrane.
- In terms of preparation steps, peepers are thoroughly cleaned, filled with ultrapure deionized water (with or without a tracer), stored in an airtight container, and shipped in a protective container to the site.
- An example SOP for peeper preparation is available in Appendix D.

2.6 Do peepers sample colloidal or other sorbed metals from sediment?

Peepers generally feature a semipermeable membrane that allows ions to diffuse into (and out of) the peeper water from the surrounding sediment or water matrix. A common membrane used for peepers is a polyethersulfone or polysulfone membrane with a 0.45-µm pore size. It is possible that metals bound to colloids, which have sizes in the 0.001- to 1-µm size range (Buffle et al., 2007), could pass through this membrane, entering the peeper water. The metals bound to such solids would not generally be considered freely dissolved, and the entry of colloids through the peeper membrane could overestimate Cfree. Carignan et al. (1985) noted that metals results for sediment-deployed peepers with 0.45-µm membranes were identical to results from peepers with a much finer 0.03-µm pore size membrane. In that example, a pore size of 0.45-µm was reasonable for limiting the entry of particulate and/or colloid-bound inorganics.

More research on the effect of colloidal-bound metals and their ability to diffuse into peepers would be helpful; however, the uncertainty regarding the effects of colloids on environmental sampler analysis is not limited to peepers. Surface water samples that are to be analyzed for “dissolved” metals are generally processed via filtration through a 0.45-µm filter. Thus, using a 0.45-µm membrane for peepers is consistent with this operational definition of “dissolved” by regulatory organizations (e.g., USEPA, 1996). Because of this consistency, peeper results can be compared to risk-based criteria typically using measurements of dissolved analytes in water samples that have been filtered using a 0.45-µm membrane.

Research Opportunity

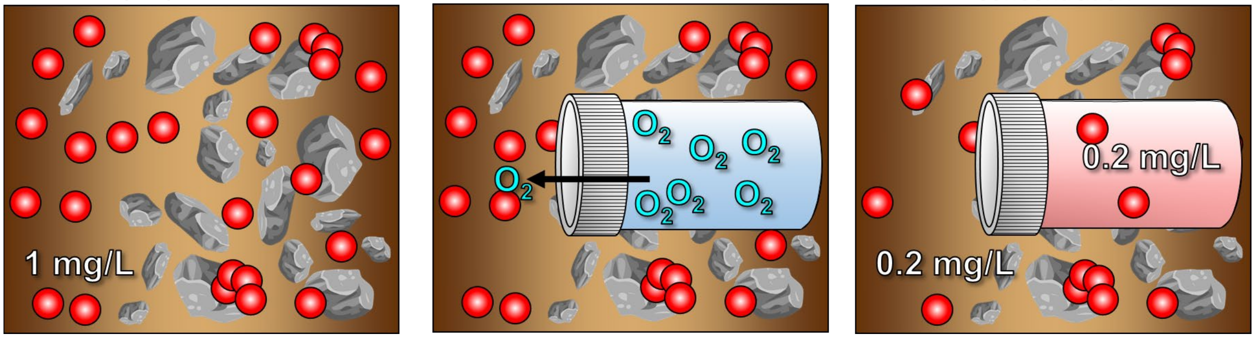
Assessing the effects of colloid-bound metals (or other sorbed phases) on peeper results.

Do peepers sample colloidal or other sorbed metals from sediment?

- Limited research does not indicate colloids or particulate-bound metals affect peeper results, although more research would be helpful.
- Analytes that can pass through a 0.45-µm peeper membrane are generally considered "dissolved" since 0.45-µm membranes are used to filter water to be analyzed for "dissolved" analytes under typical regulatory methods.

2.7 Do peepers and peeper water need to be deoxygenated prior to deployment in sediment?

Deionized water used to fill peepers generally contains dissolved oxygen unless it is specifically deoxygenated. As discussed in Risacher et al. (2023a) and Appendix A, a common assumption is that the presence of dissolved oxygen in peeper water prior to deployment could alter redox conditions in the sediment in which it is deployed, potentially affecting the availability of redox-sensitive metals. Oxygen contamination from peepers was first highlighted by Carignan (1985), who observed a solid precipitate in the peeper water within peepers deployed in anoxic sediment. This issue was attributed to oxygen in the peeper material and peeper water, causing precipitation of redox sensitive species. The introduction of oxygen from the peeper and/or peeper water could also result in changes to redox conditions adjacent to the peeper that could cause changes in concentrations of freely available metals (Figure 2-9).


freely-dissolved concentration 1 mg/L prior to peeper addition

oxygen (O_2) leaves peeper/peeper water during equilibration with porewater, resulting in changes to redox conditions that lowers porewater metal availability

freely-dissolved concentration lowered to 0.2 mg/L after equilibration, underestimating original freely-dissolved concentration

Figure 2-9: Example of hypothetical oxygen contamination from a deployed peeper changing redox conditions and concentrations of freely dissolved metals in a sediment. This phenomenon was not found to affect peeper results in this project (Appendix B).

To protect against the potential effects of oxygen contamination when deploying in sediment (which is often anoxic or hypoxic), investigators often deoxygenate the peeper water and peepers via sparging with inert gases (e.g., argon, nitrogen) prior to deployment. This complicated, labor-intensive process presents additional health and safety issues for laboratory peeper preparation technicians and potentially exposes peeper water to inadvertent contamination. Maintaining or conducting deoxygenation of the peepers in the field often adds the considerable logistical headache of shipping and handling dangerous and heavy cylinders of inert gases.

In this project, laboratory experiments were conducted to compare the concentration of the target metals in peepers prepared with and without deoxygenation when deployed in sediment (Appendix B). As shown in Figure 2-10, 14-day deployment metals results for peepers deployed in sediment indicated no significant differences ($P > 0.05$) between peepers that had been deoxygenated versus peepers that remained oxygenated. Thus, the small amount of oxygen present in the peeper water (approximately 0.5 mg), plus the small amount that may have been present within the solid peeper material (PP), did not appear to influence dissolved oxygen in the surface sediment to a level that affected metals geochemistry and peeper results over the 14-day deployment period.

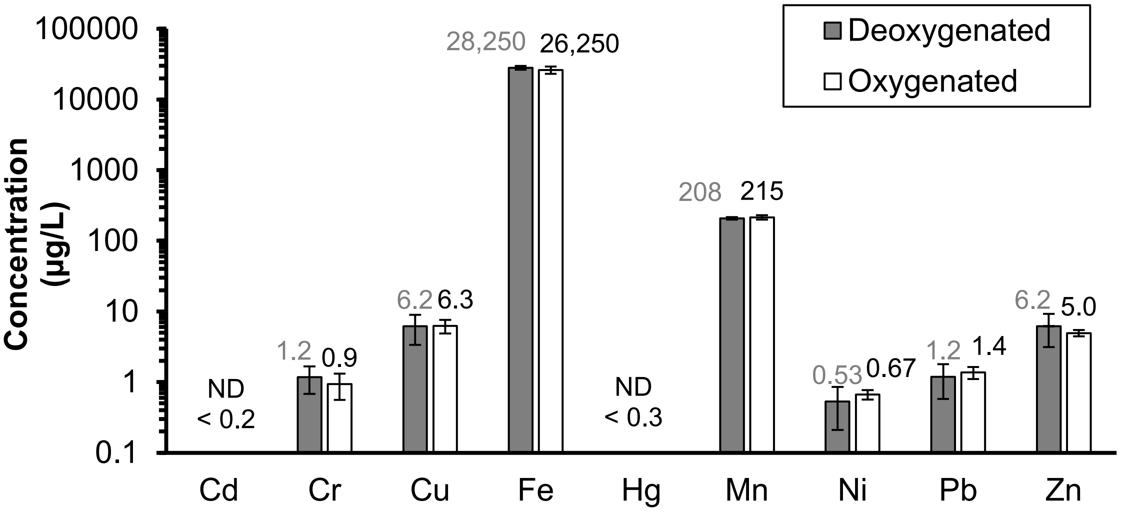


Figure 2-10: Mean concentrations (standard deviation) of metals in standard sediment-deployed peeper waters for peepers that were either oxygenated or deoxygenated prior to deployment. Data is not shown for mercury or cadmium due to the high number of nondetect (ND) results.

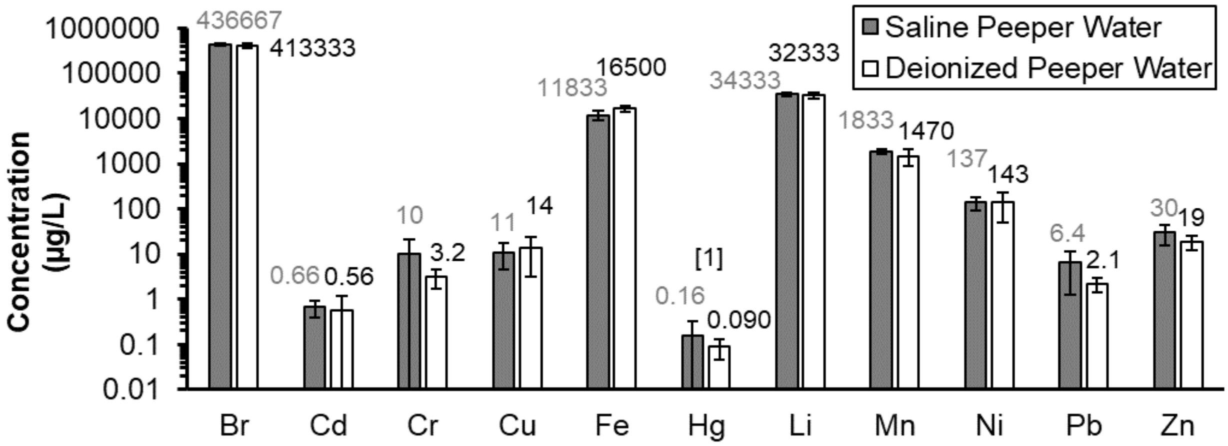
Do peepers and peeper water need to be deoxygenated prior to deployment in sediment?

- Peepers do not need to be deoxygenated during construction, transport, or deployment.
- The amount of oxygen present in the peeper is minimal and does not impact sediment peeper results for redox-sensitive metals.

2.8 Does the peeper water salinity need to be the same as the salinity of the water or sediment in which it is to be deployed?

Peepers are typically filled with deionized water that is devoid of detectable concentrations of analytes, even when deployed in marine sediments (Risacher et al., 2023a; Appendix A). Differences in salinity between deionized peeper water and external saline water when a peeper is first deployed in water or a saline sediment have been hypothesized to result in density gradients that could affect diffusive processes during peeper sampling.

In this project, laboratory experiments were conducted to test the impact of initial peeper water salinity on diffusion speeds and overall results for peepers deployed in marine sediment. Some of the peepers were prepared using ultrapure deionized water, while others were prepared with water containing 35 grams per liter of trace-metal grade sodium chloride (to match general marine salinity levels) instead of deionized water. As shown in Figure 2-11, 14-day deployment results for the peepers indicated no significant differences ($P > 0.05$) between peepers prepared using the standard approach (i.e., filled with deionized water) and peepers prepared with saline water.



[1]: Unable to statistically compare due to high proportion (≥ 50%) of ND results.

Figure 2-11: Average concentrations of metals and tracers in peepers prepared with deionized water and saline water, as deployed in standard spiked sediment for 14 days.

Does the peeper water salinity need to be the same as the salinity of the water or sediment in which it is to be deployed?

- Peepers should be prepared with deionized water, even for peepers that will be deployed in marine sediment or water.

2.9 How are peepers deployed in sediment or water?

Peepers can be successfully deployed at an aquatic site in a variety of scenarios:

- **Surface water:** Peepers can be deployed in surface water via a variety of approaches, including attachment to in-water structures (piers, docks, stationary vessels) or a weighted buoy line.
- **Surface sediment:** Peepers can be deployed in surface sediment (e.g., upper 0 to 30 cm) through inserting into surface sediment by SCUBA divers, wading personnel, or from a vessel using a mechanical device (e.g., peeper attached to a push pole or device suspended into the water using a line). It is generally recommended to house peepers in a support frame (Figure 2-8, left) so that the peeper can maintain position in the surface sediment during the deployment. The frame also allows attachment points for ground marker lines or buoy lines to mark peeper position so that it can be located and retrieved following deployment. The frame provides additional protection to the peeper, especially the membrane, which can be punctured if not handled carefully. Additional protection for the

membrane can be added to the end of the peeper (Figure 2-8, right) if the sediment is expected to be particularly coarse (e.g., angular gravels, shell hash).

- **Subsurface sediment:** Peepers can be deployed in subsurface sediment beyond depths of 30 cm. Deployment in deeper sediments requires a more customized support frame and deployment techniques.
- **Stormwater:** Peepers can be deployed to measure Cfree in stormwater located in stormwater infrastructure. It is important that the peeper membrane remain submerged in water for the duration of the deployment, as peepers exposed to air will slowly dry out, which will impair the diffusion sampling process. Peepers deployed in stormwater infrastructure should be attached or mounted to a weight or device that keeps them submerged in stormwater. If high-flow velocity or debris is expected, additional protection for the peeper membrane is recommended (Figure 2-8, right).

An example SOP for peeper deployment is available in Appendix E, and a video depicting the process is available at this link: https://vimeo.com/809180171/c276c1873a.

Generally, the steps involved in peeper deployment include the following:

1. **Shipping, Inspection, and Storage of the Peepers:** Peepers should be shipped to a secure location where they can be stored at room temperature (or refrigerated) at least a few days or 1 week in advance of the field deployment. It is highly recommended to verify the number and conditions of peepers and any support materials (frames, line, weights, buoys) necessary for the deployment.
2. **Peeper Assembly:** Peepers should be removed from storage just prior to insertion into their pre-assembled support frames or other attachment devices.
3. **Peeper Deployment:** Peepers should be deployed as quickly as possible, and the location at which peepers are deployed should be clearly recorded with an accurate Global Positioning System (GPS) device with a resolution of 2 meters or less. The peeper should be clearly marked with a surface marker buoy, stake, or, more commonly, an underwater ground line. The ground line consists of a length of line attached to the peeper that is 10 to 15 meters in length. At the other end of the line, a small anchor (sandbag) is present. The anchor can be placed by a SCUBA diver or from the vessel approximately 10 to 15 meters from the passive sampler, such that the ground line extends along the sediment surface from the sampler location to the anchor. Snagging or locating the ground line facilitates recovery of the peeper during retrieval. It is also recommended to assume that less than 100% of the peepers deployed at a field site will be recovered; thus, most investigations will deploy approximately 10% to 30% more peepers than required.

Appendix C details a demonstration of peeper deployment techniques in the field and offers information on field logistics, including rates of peeper station deployments in a typical field day, staffing needs for deployment, and other information useful to those that wish to plan a peeper field investigation.

How are peepers deployed in sediment or water?

- Peepers can be deployed in sediment, water, and stormwater via a variety of methods (wading, from a vessel, using SCUBA divers, etc.).
- Appendix C provides examples of a peeper field deployment, including a how-to peeper deployment video.
- An example SOP for peeper deployment is available in Appendix E.

2.10 How long are peepers left to equilibrate in sediment and water?

Passive sampling with peepers relies on the passive diffusion of ions to achieve equilibrium between the sediment porewater (or surface water) and the peeper water. Sampling and analyzing a peeper before achieving equilibrium will provide an underestimation of the true Cfree value; thus, it is best to measure and report the Cfree value at equilibrium.

Achieving equilibrium can take several days or weeks, and the speed of the equilibration process is not always predictable, as it can vary depending on matrix- and site-specific conditions. As detailed in Appendix A and shown in Figure 2-12. A wide variety of deployment times for peepers of varying volumes (and F factors) have been used. In some cases, achieving equilibrium was assumed and not necessarily verified with measurements.

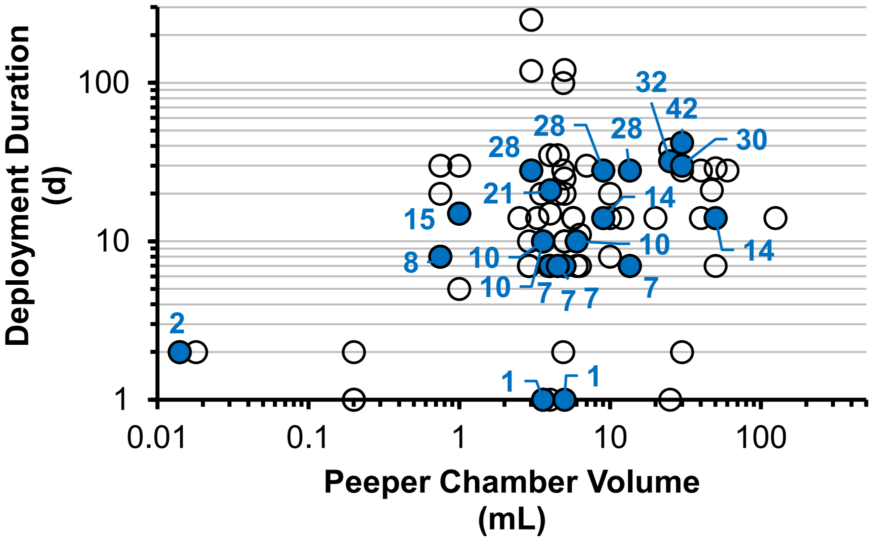


Figure 2-12: Deployment duration versus peeper chamber volume. The figure is on a logarithmic scale. Blue-filled symbols indicate peepers that were confirmed to be at equilibrium at the deployment time indicated by the blue label (note that equilibration may have been reached prior to the deployment time). Hollow symbols represent peepers that were not at equilibration or instances in which equilibration status was not confirmed.

It is recommended that the percentage of equilibrium attained by a peeper sampler should be measured when deploying peepers (Risacher et al., 2023a). Although one can evaluate the equilibrium concentration of an analyte in a sediment by evaluating analyte results for peepers deployed for multiple time periods (i.e., a time series), this is often impractical for typical field investigations, as it would require several mobilizations to the site to retrieve samplers at multiple events. Alternately, one can use a reverse tracer (referred to as a performance reference compound when used with organic compound passive sampling) to evaluate the percentage of equilibrium reached by a passive sampler. For example, a reverse tracer can be added to the peeper water at a concentration of 100 mg/L. After deployment in sediment, if the concentration of the reverse tracer is determined to be 50 mg/L, one can infer that the peeper has reached 50% of equilibration.

Using a reverse tracer also enables the possibility of deploying the peeper for a time period that is less than that needed for equilibration, referred to as "pre-equilibrium sampling," which was explored in work by Thomas and Arthur (2010) as detailed in Risacher et al. (2023a) and Appendix A. Pre-equilibrium sampling approaches usually rely on data from the tracer to infer the degree of equilibration attained by an analyte of interest diffusing into the peeper from the sediment or surface water. For example, continuing from the example mentioned above, if a reverse tracer was measured in a sampler before and after deployment and found to be at 50% of equilibration, one could multiply the concentration of an analyte that had diffused into the peeper by 2 in order to estimate the concentration that analyte would have reached if the peeper had been deployed for a time period sufficient to reach equilibrium (assuming the tracer and analyte diffuse at the same rate).

As shown in our laboratory and field work (Appendix B and Appendix C), lithium bromide at a concentration of 100 mg/L for freshwater deployments, or a concentration of 1,000 mg/L for seawater deployments, was considered optimal adding a tracer to peeper water. Lithium was demonstrated to be an appropriate tracer as shown in our project, because it can be measured in the same sample and by using the same method as other metals that are commonly analyzed. Detailed information on the calculations needed for pre-equilibrium sample data processing and interpretation is provided in Appendix B, and an example calculation sheet is provided as an Excel file attachment to this document as Appendix F (i.e., Excel file attached to this PDF file).

The pre-equilibrium approach for peepers has not been fully validated and demonstrated in sediment. A time series experiment in the laboratory using peepers deployed in metal-spiked water (Appendix B) confirmed that the uptake of metals and elimination of the tracer met expectations and assumptions regarding kinetics. For example, Figure 2-13 depicts the uptake of copper by the peeper and simultaneous elimination of the lithium tracer from the peeper. At 9 days, the concentration of copper in the peeper was at approximately 90% of the equilibrium concentration attained in latter measurements—a concentration that was approximate to the concentration in the water in which the peeper was deployed.

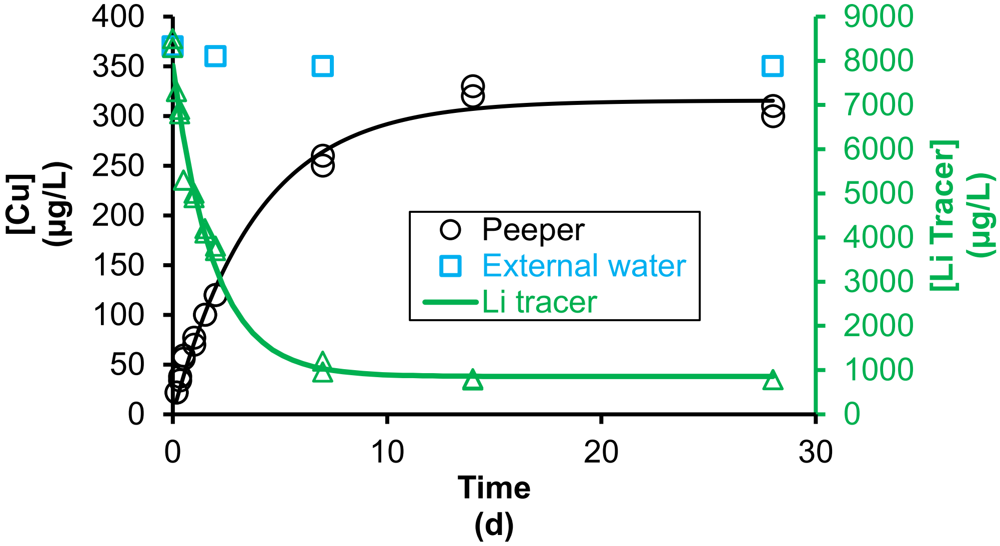


Figure 2-13: Copper uptake (black) by and lithium tracer elimination (green) from a peeper deployed in copper-spiked water. Solid lines depict nonlinear models applied to the copper and lithium data. Blue boxes indicate measured values of copper in the copper-spiked water in which the peeper was deployed.

The relationship shown in Figure 2-13 supported using analyte and tracer data from peepers sampled before equilibrium to predict the concentration at equilibrium. In general, for the metals evaluated in the experiment, data from peepers obtained before equilibration were reasonably accurate in predicting concentrations achieved at equilibrium (Appendix B). For example, as shown in Figure 2-14, the equilibrium-corrected value estimated by using the pre-equilibrium approach was a factor of 0.6 to 1.2 of the copper concentration in the water in which the peeper was deployed. Thus, equilibrium-corrected values were within 40% of measured values. For metals in the study, equilibrium-corrected concentrations of target metals were generally within 20% of measured values between days 2 and 7, when a sufficient proportion of equilibration had been reached according to the lithium tracer (i.e., tracer at 50% to 75% equilibrium).

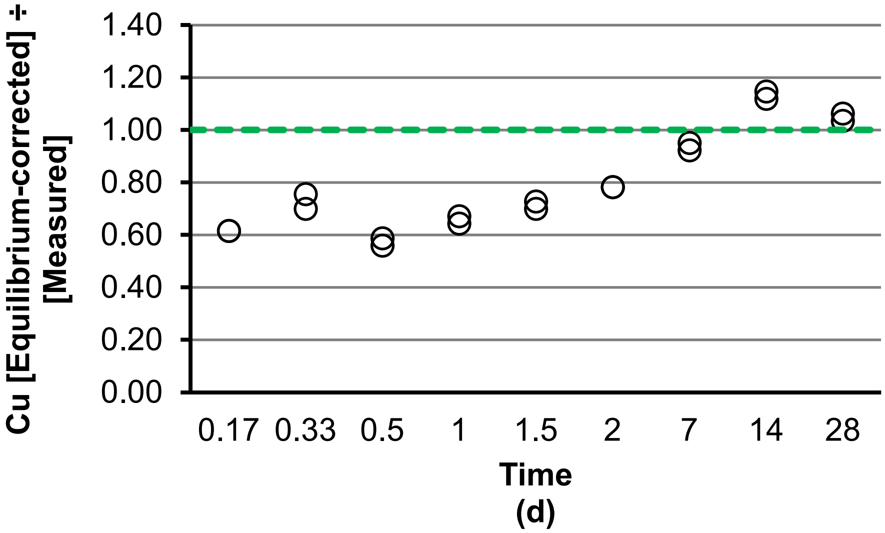


Figure 2-14: Model-predicted equilibrium concentrations of copper for each peeper sample (deployed in copper-spiked water for various time periods) divided by the average measured concentration of copper in the water in which peepers were deployed. The dotted green line indicates perfect agreement (i.e., a value of 1) between the model-predicted equilibrium concentration in the peeper and the average measured concentration of the water.

The uptake experiment for water was also conducted in sediment twice with a spiked, standard sediment and an additional sediment (Appendix B). Unfortunately, the evaluation of the pre-equilibrium sampling approach could not be fully evaluated in sediment because of limitations of the laboratory sediment system, which may have been due to a lack of geochemical stability that prevented equilibrium from being established over the course of the time series. For a robust evaluation of the pre-equilibrium approach in sediment, it is recommended that a time series be conducted in a field sediment with relatively stable hydrodynamic conditions that would likely meet the assumption of Cfree equilibrium in the sediment to which the peepers would be exposed.

Research Opportunity

A field study involving a peeper time series would be most robust for evaluating the pre-equilibrium approach for sediment.

Although the sediment mesocosms were not considered to provide a thorough assessment of the pre-equilibrium approach in sediment, the water deployment data (Figures 2-13 and 2-14) provided a basic proof of concept for the efficacy of the pre-equilibrium approach to predict equilibrium concentrations in peepers using data from peepers sampled before equilibrium. Additionally, the field study conducted in this project was useful in understanding sampling kinetics and tracer application in field sediment. In field sediments, equilibration appears to occur more quickly than in stagnant laboratory sediments tested in this experiment. For example, equilibration of lithium tracer averaged 87% to more than 99% for peepers deployed in surface sediment and water, respectively, in a 10-day San Diego Bay field deployment (Appendix C). In contrast, lithium equilibration at 14 days in the laboratory experiments was lower, from approximately 50% to 70%.

Until the pre-equilibrium approach can be further evaluated in sediment, we recommend that a tracer (e.g., lithium) should be used with peepers so that, at minimum, the percentage of equilibrium obtained by a peeper can be explicitly quantified. For deployments in sediment, we recommend the following approaches for using a peeper spiked with a lithium tracer[4]:

1. **Deploy the peeper in sediment for approximately 4 to 7 days** and apply the pre-equilibrium sampling approach (detailed in Appendix B and provided as calculation spreadsheets in Appendix F). In this case, the lithium tracer will be approximately 50% to 75% equilibrated in field sediment. At this level of equilibration, it is hypothesized that Cfree for the slowest diffusing metals (e.g., chromium) would only be at approximately 30% to 60% equilibration. In the worst-case scenario, the pre-equilibrium sampling approach could overestimate equilibrium Cfree by as much as 2 to 3 times. A 4-to-7-day deployment in surface water would likely be sufficient to reach equilibrium (based on kinetics observed in laboratory and field work in this project) without needing to apply the pre-equilibrium sampling approach.
2. **Deploy the peeper in sediment for approximately 10 to 14 days.** In this case, lithium will be approximately 85% to 95% equilibrated in field sediment. Application of the pre-equilibrium sampling approach (detailed in Appendix B and provided as calculation

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[4] The time periods and percentages of equilibration noted below are specific to the general design of the peeper used in this project (15-mL volume, F Factor of 2.8 milliliters per cm^2) for measuring typical inorganic analytes (metals) via a peeper sediment deployment. Peepers with higher F Factors would be expected to require longer deployments to achieve similar levels of equilibration and measurement certainties. Shorter deployment periods could be used for surface water deployments.

spreadsheets in Appendix F) is not likely needed but could be considered. At this level of equilibration, it is hypothesized that Cfree for the slowest diffusing metals (e.g., chromium) would only be at approximately 70% to 80% equilibration. In the worst-case scenario, the pre-equilibrium sampling approach could overestimate equilibrium Cfree by as much as 1.2 to 1.5 times (i.e., 20% to 50% difference) according to worst-case assumptions. This range of uncertainty is relatively reasonable for many sediment data quality objectives.

3. **Deploy the peeper in sediment for approximately 21 days or longer.** In this case, lithium will be more than 99% equilibrated in field sediment. Application of the pre-equilibrium sampling approach is not needed because analytes at this level of equilibration would be at concentrations that are within approximately 10% or less of equilibrium.

How long are peepers left to equilibrate in sediment and water?

- A period of days to weeks is needed for peepers in sediment or water to reach equilibrium, depending on the design of the peeper and the characteristics of the sampled media. For the 15-mL peeper design used in this project, approximately 10 to 21 days are needed for most analytes to achieve equilibrium in sediment and 4 to 7 days are needed for most analytes to achieve equilibrium in surface water.
- Pre-equilibrium sampling approaches that use tracers added to peepers can allow the use of deployment periods shorter than that required to achieve equilibrium. These approaches are not fully validated for sediment and are best applied when the peepers are at least 50% to 75% equilibrated according to the tracer, which occurs in a time period of at least 4 to 7 days in sediment for the 15-mL peepers used in this project. A spreadsheet that enables the user to process peeper data using the pre-equilibrium is provided in Appendix F (i.e., Excel file attached to this PDF file).

2.11 Does biofouling affect peepers?

It is possible for algae and other organisms to attach to and grow on passive samplers deployed in aquatic ecosystems, forming a biofilm. In the worst cases, a biofilm can represent a barrier that can impede analytes from diffusing into a peeper, especially if the biofilm forms upon the peeper membrane.

Fortunately, based on this project team's experience and review of the literature (Appendix A), peepers deployed in sediment for up to 4 weeks have not been found to be affected by biofilm formation on the membrane. Peepers deployed in surface water are more subject to biofilm formation because biofilm-forming biota tend to be more active in the water column compared to sediment. During the 10-day field demonstration in this project (Appendix C), biofilm was not observed in peepers deployed in surface sediment or surface water.

Overall, biofilm formation should not be an issue for typical peeper deployment periods. In cases in which a biofilm forms, the biofilm will impede equilibration. If a tracer is present in the peeper, the level of equilibration can be quantified and evaluated with respect to the amount of biofilm present. The ability to quantify equilibrium using tracers presents another advantage to using tracers in peepers, even when the deployment period is expected to be sufficient to achieve equilibrium.

Does biofouling affect peepers?

- Given the relatively short deployment times for measuring inorganic Cfree using peepers, it is unlikely that biofilms will affect peeper sampling.
- Biofilms were not observed in peepers deployed in surface water and surface sediment peepers in this project, and there no reports from the literature noting this issue.
- In the event a biofilm could form on a peeper, time to equilibrium will slow, and this can be quantified and accounted for via the use of a tracer.

2.12 How are peepers retrieved from sediment or water?

Peepers can be successfully retrieved at an aquatic site in a variety of methods, depending on the site and how the peepers were deployed. Appendix C provides concrete examples of peeper retrieval methods at the field demonstration site. An example SOP for peeper retrieval is available in Appendix E, and a video depicting the process is available at this link: https://vimeo.com/811073634/303edf2693. Retrieving peepers from surface water is generally more straightforward than from sediment. Lessons learned and general recommendations specific to retrieval of peepers from surface sediment (which can also apply to peeper surface water deployments) include the following:

- **Accurate position measurement is a must.** Retrieving peepers from sediment depends heavily on accurate GPS measurements of locations at which peepers were deployed. It is recommended that a GPS instrument with an uncertainty level of 2 meters of less should be used. Ideally, the same GPS instrument should be used for both deployment and retrieval.
- **SCUBA divers are a typical approach for retrieval**. In general, the use of SCUBA divers is a tried-and-tested approach for retrieval from sediment. When using divers for recovery, the support vessel will usually navigate to a station at which a peeper has been deployed. When on station, a member of the vessel crew will drop a weighted buoy line at the station to mark the approximate location of the peeper. When the vessel is safely anchored or positioned, a diver will enter the water and navigate to the anchor line and begin a circular search pattern to locate the device. As noted in Section 2.9, placing a marker or ground line will greatly improve the efficiency of a successful retrieval. This is especially important for low visibility conditions, as the diver will primarily locate the marker, ground line, or

peeper by touch. Once the peeper is removed from the sediment, the peeper should be placed in a protective bag or returned to the vessel immediately (Figure 2-15).

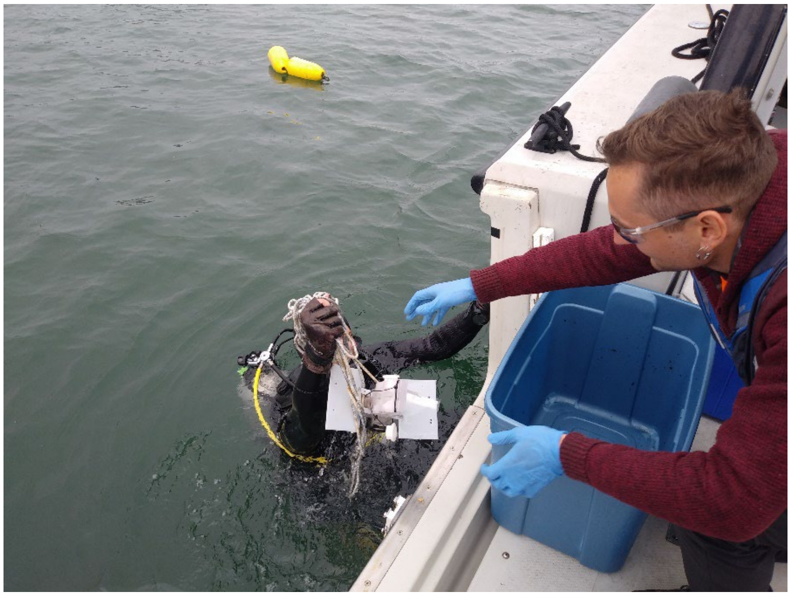

Figure 2-15: A SCUBA diver handing a retrieved peeper device to the vessel. The peeper location is shown in the background (yellow floats attached to the buoy line).

- **Grappling hooks offer a retrieval approach that avoids the use of SCUBA divers**. Retrieving sediment-deployed peepers can be accomplished from the vessel without the use of SCUBA divers. For this approach, a long (10-to-15-meter) ground line must be laid out from the peeper location during deployment (Section 2.9). Once the vessel navigates to a station at which a peeper has been deployed, a grappling hook at the end of a line can be dragged along the sediment surface such that it snags the ground line, allowing the peeper to be brought to the vessel.

- **Recovery rates are less than 100%.** It is recommended to assume that less than 100% of the peepers deployed at a field will be retrieved and available to be successfully processed into samples for analysis. For example, in the field effort in this project (Appendix C), approximately 80% of the peepers deployed were able to be analyzed. Some peepers were lost or compromised via damage or particle contamination (Figure 2-16). In general, success rate also decreases as deployment times increase. Most investigations will deploy approximately 10% to 30% more peepers than required for the investigation.

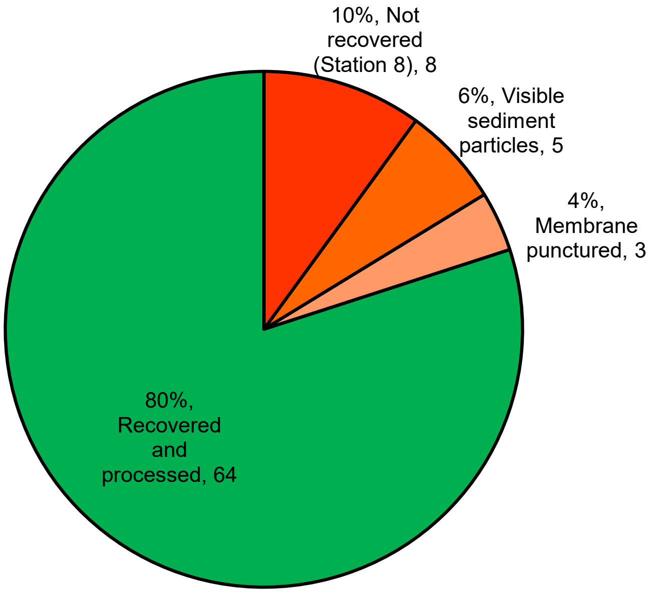

Figure 2-16: Recovery summary of the 80 peepers that were deployed in surface water and sediment at the 10 field stations (Appendix C).

- **Peepers should be stored or processed as soon as possible after removal from sediment or surface water**. As detailed in Appendix B, laboratory experiments with peepers containing low dissolved oxygen (i.e., similar to peepers deployed in anoxic sediment) accumulate oxygen when exposed to the atmosphere (Figure 2-17). Oxygen entry into the peeper can potentially affect sample results, so it is best to avoid oxygen contamination by placing peepers in storage as soon as possible after removing them from sediment, ideally within 10 to 30 minutes.

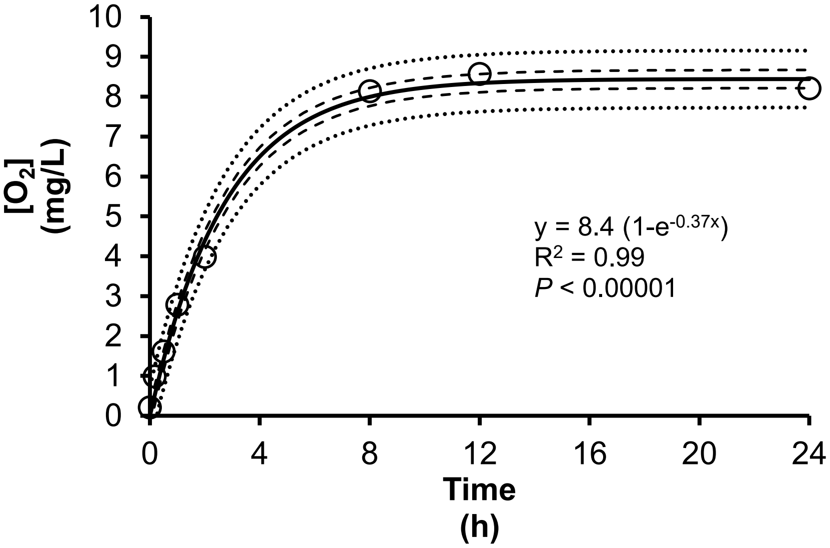

Figure 2-17: Concentration of oxygen in deoxygenated peepers left exposed to the ambient atmosphere.

- Unless peepers are processed immediately (which usually consists of transfer to a storage vessel containing a preservative), our laboratory work (Appendix B) indicated that the best approach for sample preservation was to place the peepers in a small, airtight zipseal Mylar bag containing 2 to 3 "500-cc" oxygen absorber/oxygen muncher packets (Figure 2-18). Prior to storage, any damaged peepers (Figure 2-19) can be noted as such and discarded from inclusion in the sample storage container. Consistent with standard approaches for storage of water samples for chemical analysis, peepers should be kept in a protected container, away from light, and cold (e.g., 4 degrees Celsius [°C]).

Figure 2-18: A "500-cc" oxygen absorbent "oxy muncher" packet (left) and blue zipseal bags for storing peepers (right).

Figure 2-19: A damaged peeper (torn peeper membrane).

- Retrieving peeper frames can likely achieve rates of 10 stations per day when divers are used, or higher rates (10 to 20 stations per day) when diverless techniques are optimally employed. These rates are highly dependent on field staff, site conditions, station arrangement, transit times, deployment approaches, and other site-specific factors. It is recommended that time on the water at the investigation site should be limited to allow 1 to 2 hours of onshore work at the end of the field day for processing the retrieved peepers. Retrieval of peepers is most optimal with at least two field staff.

Appendix C details peeper retrieval techniques in the field and offers information on field logistics, including rates of peeper station retrievals in a typical field day, staffing needs for retrieval, and other information useful to those who wish to plan a peeper field investigation. Peeper processing is discussed in Section 2.13.

How are peepers retrieved from sediment or water?

- Peepers can be retrieved using SCUBA divers, a grappling hook, or other methods.
- Appendix C provides examples of peeper field retrieval, including a how-to peeper retrieval video.
- An example SOP for peeper retrieval is available in Appendix E.

2.13 When and how do you process retrieved peepers?

To process peepers, the peeper water needs to be removed from the peeper and placed into storage containers that will be shipped to the laboratory for analysis (Figure 2-20). Consult the analytical laboratory for the best recommendations for the analyte(s) of interest for container material and any preservatives that should be added. An example SOP for peeper processing is available in Appendix E, and a video depicting the process is available at this link: https://vimeo.com/811328715/aea3073540.

Figure 2-20: Peeper processing.

Processing should occur within 10 to 30 minutes of retrieving peepers from the sediment (if processed immediately) or within approximately 8 hours if the peepers are preserved using Mylar bags and oxygen absorbing packets. Laboratory studies with sediment-exposed peepers conducted as a part of this project (Appendix B) found that longer storage times do not affect sample results for most metals, but results for one metal, cadmium, suggested a detectable difference in results among storage times (Figure 2-21). The recommendation to process peepers within 8 hours of collection is based on this observation for cadmium; however, additional research to confirm this observation and evaluate storage time effects with other metals would be beneficial.

Research Opportunity

Additional evaluation of the potential effects of storage time and conditions (and potential mechanisms involved) on peeper Cfree results.

Additionally, cadmium was the only metal to indicate a statistically detectable difference between Cfree results of a peeper that was processed immediately versus a peeper that was simply placed in a Mylar zipseal bag and stored for 14 days (Figure 2-21). Based on this observation, it is recommended that two to three "500-cc" oxygen-absorbing "oxy muncher" packets (Figure 2-18) should be included in the storage bag for the 8 hours between peeper retrieval and peeper processing. Given that oxygen muncher packets are inexpensive (< $0.20 per packet), widely available, and easy to work with, this approach is easily adapted during peeper investigations.

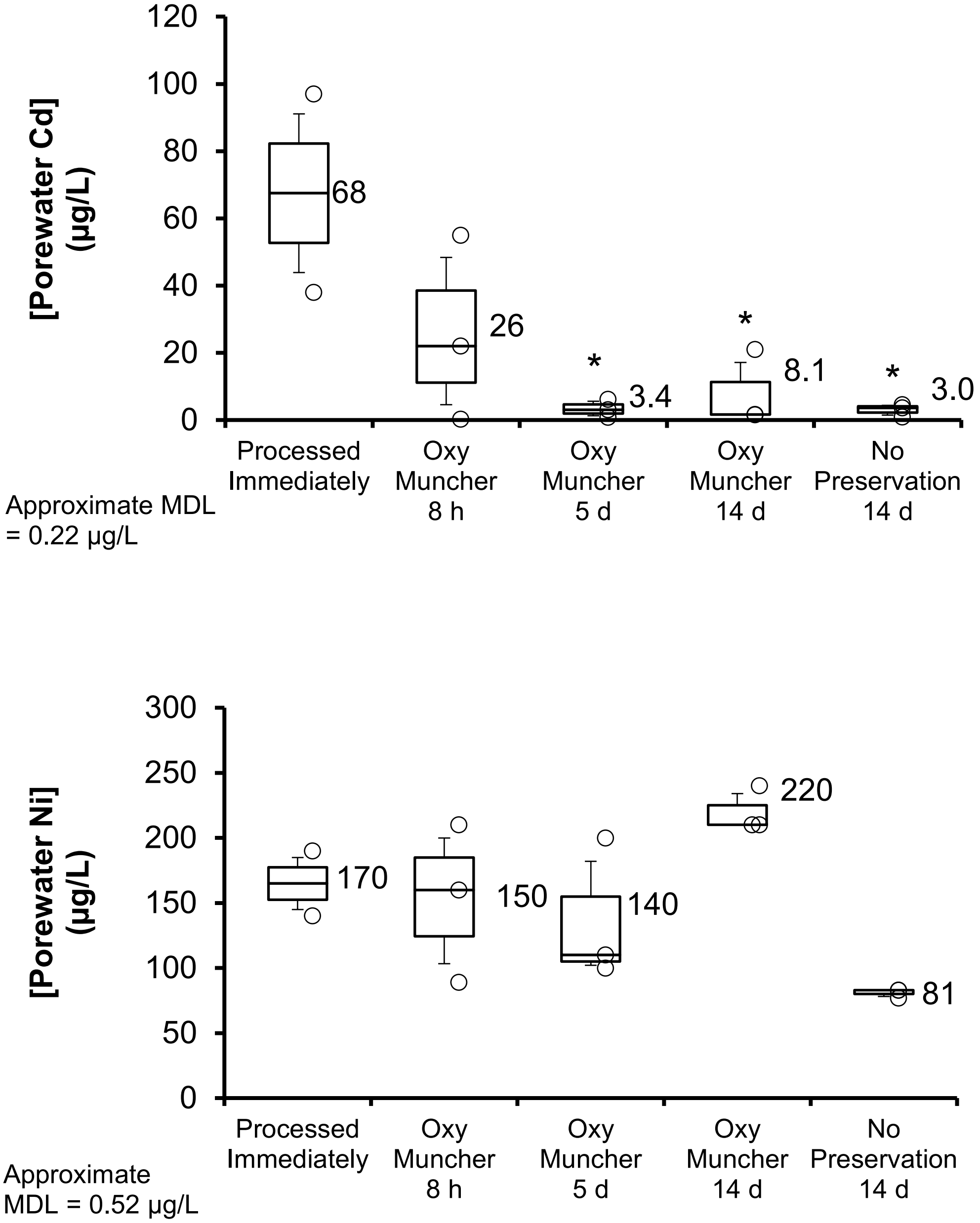

Figure 2-21: Concentrations of cadmium (top) and nickel (bottom) in spiked sediment-deployed peeper waters stored in various approaches with oxygen munchers and time periods prior to sample preservation. "*" symbols indicate results that differ significantly ($P < 0.05$) from results from peepers processed immediately. Results for cadmium indicate a potential effect of storage time on results, whereas results for nickel do not indicate an effect of storage time.

An example SOP for peeper processing is available in Appendix E. Perform the following to process peepers:

1. **Inspect peepers for any particles or damage to the membrane.** A damaged peeper with sediment particles inside (Figure 2-22) may result in higher metal concentrations that may overestimate Cfree if analyzed. Particles can intrude into peepers due to damage during handling, deployment, or retrieval of the peepers. Although it is generally a rare occurrence, it affected 10% of the peepers deployed in the field demonstration (Figure 2-16). As noted above, it is best to deploy additional peepers to ensure sufficient sample volumes are available in case of particle contamination or loss of peepers.
2. **Transfer peeper water to the sample storage container.** Typically, approximately 20 to 100 mL of peeper water is needed per sample for inorganic analysis. In the case of our project, the optimal volume (45 to 60 mL per sample) for the analysis of metals was obtained by compositing the peeper water from three to four of the 15-mL peepers deployed in a sediment mesocosm chamber (laboratory – Appendix B) or at a field station (field deployment – Appendix C). The use of four peepers per station for sediment and four peepers per station for surface water in the field deployment provided abundant sample volume for the surface sediment Cfree sample and surface water Cfree sample at each station. In cases where a peeper was damaged or affected by particles (Figures 2-19 or 2-22), the remaining 3 peepers were used to create the sample.

Figure 2-22: Contaminated peeper with particles (left) versus a peeper without any visible particle contamination (right).

Peeper water is generally transferred to a storage container that may contain a preservative. For metals analysis, usually a 100-mL or 125-mL HDPE container containing a small volume of concentrated acid (trace-metal grade nitric) was used as the sample storage container. Containers (with or without preservative) are best supplied by the commercial analytical laboratory in advance of the field work.

Transferring peeper water to the storage container is best done via pipette, which avoids potential contamination and provides optimal control of the peeper water (Figure 2-20). A laboratory experiment conducted in this project (Appendix B) indicated that processing does not need to be conducted in an inert atmosphere—it can be performed in air, as lab results indicate no difference for Cfree of metals from sediment-deployed peepers processed in air versus peepers processed in an inert (nitrogen) atmosphere (Figure 2-23).

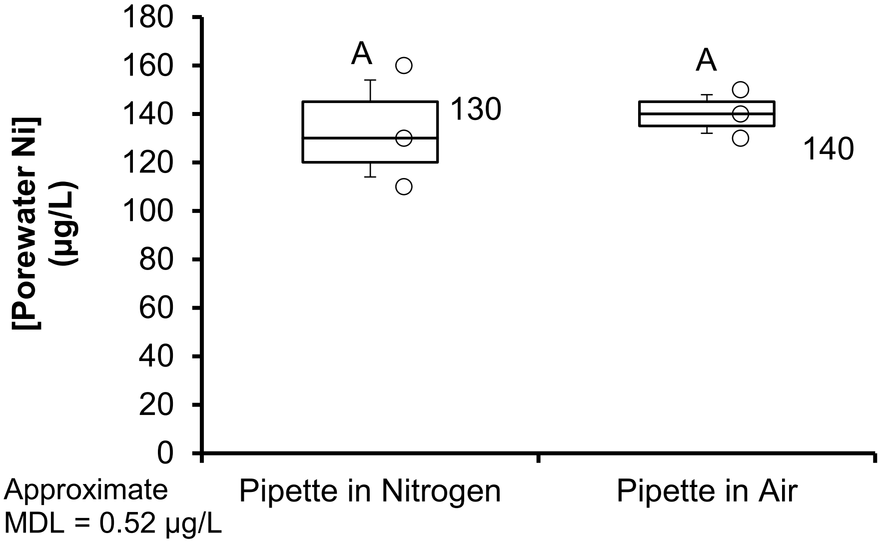

Figure 2-23: Concentrations of nickel in sediment-deployed peeper waters processed in an inert (nitrogen) atmosphere versus those processed in air.

3. **Package and ship the sample.** Once peeper water is present in the sample storage containers, samples should be packaged for shipping. As with typical water samples to be analyzed for most inorganics via USEPA SW-846 methods, samples are usually shipped to the analytical laboratory overnight in coolers containing ice so that samples are maintained at approximately 4°C while in transit.

Under most field conditions, peeper samples should be processed at the end of the field day within approximately 8 hours or less of peeper retrieval. Peeper processing is possible onboard the vessel immediately after the peepers are retrieved from the sediment or water, although this can be more complicated than onshore processing due to potential limited space and instability of vessels on the water. If peeper processing is conducted onshore, it is recommended to save at least 1 to 2 hours of time at the end of each field day for 2 technicians to process peepers. Between 10 to 20 peeper samples can be processed during a 1-to-2-hour period (including processing setup and breakdown, documentation, and sample packaging for shipment to a laboratory). Longer periods or more staff are required for more samples. Once processed, samples can be shipped to a commercial lab for analysis in a hard chest cooler on ice.

When and how do you process retrieved peepers?

- Peepers are processed by transferring peeper water into storage containers provided by the commercial analytical laboratory that will be analyzing the samples.
- Appendix C provides examples of peeper processing, including a how-to peeper processing video.
- An example SOP for peeper processing is available in Appendix E.
- Peepers should be processed within 8 hours of retrieval (longer holding times may be possible for some metals).
- Peeper processing can be conducted in air – processing does not need to be conducted in an inert atmosphere (e.g., nitrogen glove box).

2.14 How are the peeper samples analyzed and what detection limits can be attained?

Peeper samples can be analyzed via standard methods to quantify the concentration of analytes in a water sample. The analytes that were focused on for this project consisted of seven target metals typically evaluated at contaminated sediment sites, (e.g., manganese and iron, among others) and two tracers (bromide and lithium). These analytes can be measured by analytical laboratories using standard approaches. When investigations are under regulatory oversight (state or Federal), standard USEPA SW-846 methods for water samples be used. Table 2-1 provides an example table typical for a quality assurance (QA) plan or investigation work plan, depicting the SW-846 method to be used for each analyte, along with sample storage details, method detection limits, and potentially applicable criteria to which peeper data are to be compared (in this example, USEPA marine aquatic life criteria).

Table 2-1: Typical analytical specifications for inorganic analytes in peeper water.

Analyte	Analytical Method	Container	Preser-vative	Holding Time (days)	Average Method Detection Limit (µg/L)	USEPA Saltwater Criterion Continuous Concentration (µg/L)
Cadmium (Cd)	EPA Method 6020B	100-mL HDPE bottle	Nitric Acid	180	0.22	7.9
Chromium (Cr)	EPA Method 6020B	100-mL HDPE bottle	Nitric Acid	180	1.5	NA
Copper (Cu)	EPA Method 6020B	100-mL HDPE bottle	Nitric Acid	180	1.1	3.1
Iron (Fe)	EPA Method 6020B	100-mL HDPE bottle	Nitric Acid	180	28	NA
Lead (Pb)	EPA Method 6020B	100-mL HDPE bottle	Nitric Acid	180	0.17	8.1
Total Mercury (Hg)	EPA Method 7470A	100-mL HDPE bottle	Nitric Acid	180	0.13	0.94
Manganese (Mn)	EPA Method 6020B	100-mL HDPE bottle	Nitric Acid	180	1.3	NA
Nickel (Ni)	EPA Method 7470B	100-mL HDPE bottle	Nitric Acid	180	0.52	8.2
Zinc (Zn)	EPA Method 6020B	100-mL HDPE bottle	Nitric Acid	180	2.9	81
Lithium (Li)	EPA Method 6020B	100-mL HDPE bottle	Nitric Acid	180	0.83	NA
Bromide (Br)	EPA Method 9056A	100-mL HDPE bottle	None	180	2,700	NA

Peepers can be used to measure Cfree of various inorganic analytes, not just the target metals featured in this project. Considerations include the following:

1. **The peeper chamber and membrane material should not appreciably sorb the analyte.** Ideally, all materials involved in peeper and peeper support frames should be inert with regards to the analyte of interest. For example, many plastic materials would not be suitable for hydrophobic organic analytes, as the plastic of the peeper would compete with the peeper water as a sink for the compounds, interfering with the equilibration process between sediment porewater and the peeper water. Fortunately, most plastic materials and filter membranes like the types used in this project, and those highlighted in the literature review (Risacher et al., 2023a; Appendix A), are generally considered to be inert with regards to most inorganic analytes.
2. **The volume of water used in the peeper should be high enough to obtain the desired method detection limit.** For many of the analytes capable of being measured in water samples via standard USEPA SW-846 methods, a minimum sample volume is required by the analytical laboratory. Providing less than the minimum sample volume may cause an elevation in the detection limit that can be reached. For example, if the analytical laboratory requires 60 mL of water sample to obtain a detection limit of 1 microgram per liter (µg/L), providing peeper water from a 15-mL peeper (25% of the minimum required volume) could increase the detection limit by a factor of 4 (i.e., to 4 µg/L). If the objective of the investigation was to compare the Cfree data to a screening level of 2 µg/L, there would be uncertainty regarding the possibility of screening level exceedances for sample results that are reported as nondetect (e.g., < 4 µg/L).
3. **Diffusion speeds for analytes and tracers should be similar.** Using a tracer allows the percentage of equilibrium that is obtained during deployment to be measured, and, if the deployment period is insufficient to reach approximate equilibrium, tracers also allow the pre-equilibrium approach (Appendix B and Appendix F) to be applied. Diffusion speeds for the analytes should be similar to that of the tracer added to the peeper water (or faster than the tracer).

   Lithium was found to be an effective tracer according to this project's laboratory experiments (Appendix B) and field demonstration (Appendix C). The slowest diffusing inorganic in this project (chromium) was evaluated in the lab report; its equilibration was shown to be evaluated accurately using the lithium tracer for pre-equilibrium exposure deployments in water. Based on the table of diffusion values provided in Appendix F, only aluminum and vanadium are expected to diffuse slower than chromium. Diffusion values for these two analytes indicate diffusion would be 10% to 30% slower than that of chromium. Based on achieving a similar level of accuracy and precision for chromium, using the lithium tracer would likely be acceptable for pre-equilibrium uses with aluminum. However, it is recommended that if vanadium (the slowest diffusing inorganic noted in the table in Appendix F) is to be measured, the difference in equilibration speeds for vanadium and lithium are such that pre-equilibrium deployments may not be sufficiently accurate. Therefore, if vanadium is a target analyte, deployment times for the peeper used in this project should likely be extended to 21 days or more to ensure enough equilibration for vanadium (e.g., ≥ 80%).

The diffusion values shown in Appendix F are derived from diffusion calculations and measurements obtained from previously published scientific literature. These values are not without uncertainty; however, they were shown to be relatively accurate for the pre-equilibrium approach with the metals evaluated in this project. This approach could benefit from additional research with regards to diffusion speeds assumed from the literature-derived values, as well as from diffusion variability between metal categories. For example, vanadium diffusion into the peeper could be explicitly evaluated in a spiked-water experiments similar to that used in this project (Appendix B) to confirm its expected diffusion speed.

Research Opportunity

Evaluation of time series to confirm diffusion speeds of target analytes when used for peepers.

How are the peeper samples analyzed and what detection limits can be attained?

- Peeper water should be analyzed by a standard method, ideally a USEPA SW-846 standard method.
- Detection limits are contingent on achieving the required minimum volume of water specified by the method; consult the analytical laboratory as needed.
- Peepers can be analyzed for any analyte as long as the analyte does not sorb to the peeper, detection limits in water are low enough for the intended data uses, and the diffusion speeds of the analytes are similar to that of the tracer.

2.15 How can peeper data be validated?

Metal concentrations from peeper samples are measured using standard USEPA methods (e.g. SW-846), and QA/quality control (QC) data validation steps can be applied to peepers. Data validators typically review the measurements in water provided in the analytical report as they would do for measurements of any analyte in water that is measured via standard methods. The typical data validation focus during review of this information includes laboratory qualifiers, method blanks and lab control samples, and matrix spikes, if sufficient volume was available to generate matrix spikes.

For evaluating precision, a common data validation metric, field duplicate sample results for water samples are often compared. These are usually obtained by collecting two surface water or ground water samples at the same location simultaneously. Field duplicates for peepers can be produced in the field, although these are not “true” duplicates when samples from peepers in sediment are deployed. At most sites, it is not possible to deploy peepers in the exact same sediment that would yield the exact same Cfree result, as high heterogeneity can be present over the spatial scale of a few centimeters. An alternate approach is to use split samples. For example, it is possible to obtain the peeper water from two or more peeper samples and split them into two or more sample storage samples, which are analyzed separately.

Evaluating blanks is also a key part of many data validation programs. Trip blanks can also be produced using peepers that are not deployed in the field but are exposed to field conditions during deployment, retrieval, and processing. Field blanks allow contamination in the peeper water or from the field environment to be measured.

Additional data validation points for peeper samples should include review of chain-of-custody forms completed by the field and laboratory staff, as well as information provided by the laboratory during receipt of the samples, such as temperature and integrity of the shipment.

Data validation does not usually focus on additional data processing of the analyte concentrations provided by the analytical chemistry. This includes data processing used in the pre-equilibrium approach, where concentrations of a tracer in undeployed samplers, concentrations of a tracer in deployed samplers, and concentrations of analytes in deployed samplers are used to calculate the equilibrium concentration of analytes. This data processing approach is generally considered a modeling effort similar to fate modeling or risk assessment and should be communicated as such. Data validation results should be considered in data processing steps and communicated when final Cfree values are reported.

How can peeper data be validated?

- Standard data validation steps associated with USEPA methods and other quality control/quality assurance approaches are applicable to peepers.
- Data validation for peepers typically focuses on the review of the concentrations in the peeper water as reported by the analytical laboratory, ancillary information with regards to the shipment and receipt of the samples, and results from quality control/quality assurance samples (i.e., split samples and trip blanks).

2.16 How are peeper data used at a sediment site?

Peeper data can be used to enable sediment site-specific decision-making in a variety of ways. Peepers can provide measurements of metals and inorganics that can provide information on 1) nature and extent; 2) sources and fate; 3) the potential direct toxicity to aquatic life (e.g., invertebrates, fish); 4) the potential bioaccumulation of metals in aquatic life; and 5) the efficacy of sediment remediation.

Nature and Extent: Peepers can be very helpful in characterizing the presence of available metals and inorganics at a sediment site. Multiple peeper deployments in surface sediment can help delineate areas of increased metal availability in the same manner as traditional bulk sediment sampling. Peepers are especially helpful for sites with benthic substrates that may not be conducive to traditional bulk sediment sampling. For example, substrates that are comprised of coarse, relatively inert materials, such as gravel or shell hash, may be difficult to sample with sediment grab or coring techniques. Collecting and analyzing such material can be complicated, as much of the metals or inorganics present in the sample may be more associated with the porewater phase rather than the solid phase. Explicit measurement of Cfree in the porewater of coarse substrate samples can provide a more robust and precise measurement in these cases. Additionally, at sites where tidal pumping or groundwater flux may be influencing the nature and extent of inorganics, peepers can provide a distinct advantage to bulk sediment sampling or other point-in-time measurements, as peepers can provide an average measurement that integrates the variability in the hydrodynamic and chemical conditions over time.

Sources and Fate: A considerable advantage to using peepers is that the numerical product of a peeper measurement is Cfree, a concentration that is expressed in units of mass per volume (e.g., mg/L or µg/L). Cfree provides a common unit of measurement for evaluating the presence of inorganics across multiple aquatic media such as sediment, surface water, stormwater, and groundwater. For example, synchronous measurements of Cfree using peepers deployed in surface water and surface sediment can elucidate the potential flux of inorganics from sediment to surface water (or vice versa). Paired measurements of metals in Cfree in surface sediment and metals in bulk sediment can also allow site-specific sediment-porewater partition coefficients to be calculated. These values can be very useful in understanding and predicting fate, especially in situations where the potential dissolution of metals from surface sediment are critical to predict, such as when sediment is dredged or when dredged sediments are released into a water column during open ocean disposal.

Direct Toxicity to Aquatic Life: Peepers are frequently used to understand the potential direct toxicity to aquatic life, such as benthic invertebrates and fish. A Cfree measurement obtained from a passive sampler, such as a peeper deployed in sediment or surface water, can be compared to toxicological benchmarks for aquatic life to understand the potential toxicity to aquatic life and to set remediation goals (USEPA, 2017). Benchmarks are concentrations of chemicals that are associated with adverse effects (or a lack of adverse effects) to aquatic life and are usually obtained from peer-reviewed laboratory toxicity studies in which aquatic life are exposed to known concentrations in water. Formal regulatory benchmark values are available in the form of aquatic life criteria promulgated by environmental agencies such as the USEPA (https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table) and various states. These benchmark or screening values can be directly used with Cfree measurements and incorporated with more sophisticated approaches, such as the Biotic Ligand Model (Santore et al., 2022) to understand the potential for toxicity and need to conduct additional toxicological testing or ecological evaluations. Cfree measurements and benchmark values can also be applied in aquatic toxicity studies performed in the laboratory with samples of sediment or water, specifically using peepers to understand links between elevated inorganic Cfree measurements and toxicity.

Bioaccumulation of Inorganics by Aquatic Life: Peepers can also be used to understand site-specific relationships between Cfree and concentrations of inorganics in aquatic life. For example, measuring Cfree in surface sediment from which organisms are obtained and analyzed can enable the estimation of a site-specific uptake factor or predictive model relationship. This Cfree-to-organism uptake factor (or model) could then be applied for a variety of uses, including predicting the concentration of inorganics In aquatic life if measurements in organisms are unavailable, or estimating a Cfree value at a concentration in aquatic life that would be safe for consumption by fish, wildlife, or humans. Because several decades of research have found that the correlation between Cfree measurements and bioavailability is usually better than the correlation between measurements of chemicals in bulk sediment and bioavailability, Cfree-to-organism uptake factors (or models) are likely to be more accurate and precise than uptake factors based on bulk sediment (e.g., Biota Sediment Accumulation Factors).

Revaluating Sediment Remediation Efficacy: Passive sampling has been used widely to evaluate the efficacy of remediation treatments such as active amendments, thin layer placements, and capping to reduce the availability of chemicals at sediment sites. A particularly powerful data use is a simple comparison of baseline (pre-remedy) Cfree in sediment to Cfree in sediment after the sediment remedy has been applied. Peepers can be used in this context for inorganics, allowing the sediment remedy's success to be evaluated and monitored in laboratory benchtop remedy evaluations, pilot scale remedy evaluations, and full-scale remediation monitoring.

How are peeper data used at a sediment site?

- Peeper data can be used to enable sediment site-specific decision-making in a variety of ways, providing data that can be used to understand the nature, extent, sources and fate of inorganics, the potential for toxicity to aquatic life, the bioaccumulation or inorganics by aquatic life, and the efficacy of sediment remediation.

2.17 What is the cost of a peeper investigation?

For typical sediment investigations that rely primarily on analyzing inorganics in bulk sediment, peeper investigations do represent additional cost. However, Cfree data from peepers will benefit a project's budget in many ways, returning the investment several-fold by streamlining additional investigations, improving understanding of fate pathways, and reducing uncertainty and eliminating worst-case assumptions related to environmental risks. Throughout the course of a project, the high-value contributions of Cfree data can reduce costs associated with unnecessary investigations, unrealistic risk assessment assumptions, and overly stringent remediation approaches.

The cost of a peeper investigation depends on the scope of work and the project data needs. A peeper investigation usually includes the following efforts, each with its own costs:

- Planning, scoping, and work plan development
- General coordination and management among team members before, during, and after the investigation
- Preparation and shipment of peeper devices
- Field staff mobilization and/or travel
- Field deployment and retrieval efforts
- Vessel support
- Consumables, equipment, and associated shipping
- Peeper processing and shipment

- Chemical analysis of peeper water samples
- Data analysis and reporting

An example of a peeper field investigation, along with details on the logistical aspects of a typical peeper investigation, is provided in Appendix C. Included in this example field investigation are recommendations on typical number of field staff and approximate level of labor efforts associated with various phases of peeper deployment, processing, and retrieval. Labor costs generally comprise the largest cost component of a peeper field investigation; a general guideline is that approximately 50% of an investigation cost is represented by labor.

A summary of a typical scope of work and associated costs is presented in Table 2-2. This example cost ranges from approximately \$60,000 to \$150,000 (2023 dollars). The following key assumptions apply to this example cost estimate:

- 20 peepers are deployed at 20 stations in surface sediment (i.e., one peeper per station)
- The field site is accessible by boat via a relatively short (5- to 15-minute) transit time from boat launch to the site.
- Site stations are located within an approximate 5-minute vessel transit time from adjacent stations.
- Labor and vessel support are provided by local staff (i.e., no mobilization or travel costs are included).
- Peepers used are similar to those used in this project, deployed and retrieved from a vessel without the aid of SCUBA divers.
- A commercial analytical laboratory measures 5 to 10 target metal analytes and a lithium tracer in peeper water using EPA SW-846 methods.

Table 2-2 is an example; actual costs for a project will vary widely depending on site- and project-specific considerations. Costs in this table are based on 2023 costs, and the values presented in the table are subject to change. The cost ranges presented do not include contingency costs associated with unforeseen difficulties (site access challenges, weather delays, accidents, etc.).

Table 2-2: General ranges of costs for an example 20-station peeper investigation to measure metal availability in surface sediment.

Task	Notes	Approximate Cost Ranges [1]
Planning and scoping		\$2,000 - \$10,000
Work plan		\$5,000 - \$15,000
General coordination management during project		\$3,000 - \$8,000
Peeper costs, including analytical	Peepers, support frames, and chemical analysis (5-10 metals) for 20 stations (1 sample per station) Additional 5 samplers for QA/QC, and pre-equilibrium data calculations (if needed)	\$20,000 - \$40,000
Deployment labor	2–3 staff for 2–3 days Deployment from vessel (no SCUBA divers) Does not include travel, per diem, or mobilization	\$6,000 - \$14,000
Deployment consumables, equipment, shipping, etc.	2–3 days	\$500 - \$3,000
Deployment vessel support	Vessel for 2–3 days	\$5,000 - \$12,000
Retrieval and processing labor	2 staff for 2–3 days Retrieval from vessel (no SCUBA divers) Does not include travel, per diem, or mobilization	\$6,000 - \$14,000
Retrieval vessel support	Vessel for 2-3 days	\$5,000 - \$12,000
Retrieval consumables, equipment, shipping, etc.	2-3 days	\$500 - \$3,000
Data report		\$5,000 - \$20,000
Totals		\$60,000 - \$150,000

[1]: For illustration purposes only; costs will vary based on a variety of project-specific factors.

What is the cost of a peeper investigation?

- Peeper investigations represent an additional cost above and beyond analysis of bulk sediment, but the high value of the peeper Cfree data offers a high return on the investment by lowering uncertainty and conservatism in the decision-making process.
- Peeper investigation costs are highly dependent on the site and scope of the investigation; a hypothetical all-inclusive example 20-peeper investigation in surface sediment at a site is likely to range from approximately $60,000 to $150,000.

3. CONCLUSIONS

In response to the lack of standardization for using peepers to evaluate metal availability in sediment and water, a 3-year research effort, funded by ESTCP (project number: ER20-5261) was initiated by a team consisting of Geosyntec Consultants, SiREM, Texas Tech University, and the US Navy Naval Information Warfare Center. The overall objective was to enhance the standardization of, and confidence in, using of peepers for passive sampling of inorganic constituents, especially key target metals that are frequently the focus of sediment investigation and management at sediment sites.

To support this project's goals, the following resources were developed:

1. A **Literature Review** (Appendix A) to review the last 45 years of peeper best practices for peeper preparation, deployment, retrieval, and data analysis.
2. A series of **Laboratory Experiments** (Appendix B) to validate the best practices for use of peepers, specifically addressing methods for end-users to be able to prepare, ship, store, deploy, process, and preserve peeper samplers.
3. A **Field Demonstration** (Appendix C) in which peepers were deployed in surface sediment and surface water to demonstrate best practice methods and provide practical recommendations for planning and executing successful peeper investigations in the field.
4. A **Standard Operating Procedure for Peeper Preparation** (Appendix D) to provide step-by-step instructions for preparing peepers using the methods validated in this project.
5. A **Standard Operating Procedure for Peeper Deployment, Retrieval, and Processing** (Appendix E) to provide step-by-step instructions for deploying, retrieving, and processing peepers at field sites using the methods validated in this project.
6. An Excel file containing **Peeper Pre-equilibrium Calculation Spreadsheets** to facilitate calculations needed to process data for peepers deployed for a time period that is not sufficient to achieve approximate equilibration (i.e., pre-equilibrium sampling).

The above resources from this project were used to develop this guide, which aims to enable end-users to successfully prepare, deploy, and retrieve peepers, and interpret and use peeper data in a decision-making context at sediment sites under regulatory oversight. The best practices highlighted in this guide are presented as answers to FAQs for investigators wanting to measure the availability of inorganics in sediment and water using peepers. These FAQs, the section of this document in which they are detailed, and their basic answers are presented in Table 3-1.

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Table 3-1: Basic Answers to Frequently Asked Questions (FAQs) About Using Peepers to Measure the Availability of Inorganics in Sediment and Water.

FAQ	Section	Main Answers
Why measure metal availability in sediment?	2.1	• Allows an improved understanding of fate, risks, and remediation performance
What is a peeper, and how does it measure metal availability?	2.2	• Peepers are simple passive samplers that accumulate metals into a water sample via diffusion from the sediment or water in which the peeper is deployed
Are there other abiotic tools to measure metal availability?	2.3	• AVS/SEM analysis of bulk sediment and DGT passive samplers are also popular tools
Where can peepers be obtained?	2.4	• Commercial service providers and academic/government research laboratories
How are peepers prepared?	2.5	• Peepers are cleaned, filled with ultrapure water, and capped with a semipermeable membrane (see Appendix D for an example SOP)
Do peepers sample colloidal or other sorbed metals from sediment?	2.6	• Limited research suggests peepers do not sample these phases, and inorganic analytes that pass through peeper membranes are assumed to represent “dissolved” species
Do peepers and peeper water need to be deoxygenated prior to deployment in sediment?	2.7	• No – the presence of oxygen in peeper water at the time of deployment does not affect results
Does the peeper water salinity need to be the same as the salinity of the water or sediment in which it is to be deployed?	2.8	• No – peepers should be prepared with deionized water, even when deployed in marine or estuarine environments
How are peepers deployed in sediment or water?	2.9	• A variety of methods can be used (wading, from a vessel, using SCUBA divers, etc.) • See Appendix C for an example of peeper deployment, this how-to video, and Appendix E for an example deployment SOP
How long are peepers left to equilibrate in sediment and water?	2.10	• Typically a few days to a few weeks – it depends on the size of the peeper and its membrane, and whether the peeper is deployed in sediment or water • Pre-equilibrium approaches using tracers can be used to interpret peeper data when peepers are deployed for a period that is not sufficient to attain full equilibration
Does biofouling affect peepers?	2.11	• Usually not if deployment is only a few days or weeks

FAQ	Section	Main Answers
How are peepers retrieved from sediment or water?	2.12	• Using SCUBA divers, a grappling hook, or other methods • See Appendix C for an example of peeper retrieval, this how-to video, and Appendix E for an example retrieval SOP
When and how do you process retrieved peepers?	2.13	• Transfer of peeper water into storage containers provided by the commercial analytical laboratory should be completed within 8 hours of retrieval • Processing can be conducted in air – it does not need to be conducted in an inert atmosphere • See Appendix C for an example of peeper processing, this how-to video, and Appendix E for an example processing SOP
How are the peeper samples analyzed and what detection limits can be attained?	2.14	• Peeper water can be analyzed using any standard method • Detection limits depend on the minimum volume of water specified by the method
How can peeper data be validated?	2.15	• Standard data validation and QA/QC approaches for sediment and surface water sampling and analysis can be easily adapted to peepers
How are peeper data used at a sediment site?	2.16	• Peeper data can help quantify availability, nature and extent, and potential aquatic life toxicity of inorganics in sediment and water
What is the cost of a peeper investigation?	2.17	• Peepers represent an additional cost for most sediment investigations, but the high value of the data and its ability to reduce uncertainty provides a high return on the investment. • Hypothetical all-inclusive costs for an example 20-peeper investigation ranged from approximately $60K to $150K

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Appendix A: Literature Review

Towards Standardizing Peeper Samplers for Sediment Inorganics

A Review of Methods and Data Gaps

SERDP Project: ER20-5261

April 2021

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μg/L	micrograms per liter
μm	micrometer
AWQC	Ambient Water Quality Criterion
cm	centimeters
cm^2	square centimeters
DRP	dissolved reactive phosphorus
ESTCP	Environmental Security Technology Certification Program
FEP	fluorinated ethylene propylene
Geosyntec	Geosyntec Consultants, Inc.
HDPE	high density polyethylene
LDPE	low density polyethylene
mg/L	milligrams per liter
mL	milliliters
PE	polyethylene
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
PVDF	polyvinylidene difluoride
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey

ABSTRACT

Sediment porewater dialysis passive samplers, also known as "peepers," function by allowing sediment porewater to equilibrate across a micro-porous membrane with water contained in a small isolated compartment after insertion of the peeper into sediment. The resulting sample obtained after the deployment period can provide concentrations of freely-dissolved inorganics in sediment, which provides useful measurements that can be used for understanding fate and risk. Despite being developed more than 45 years ago, routine application of peepers for regulatory-driven decision making at sediment sites impacted by inorganic contaminants has been limited. To facilitate method standardization that would further encourage peeper use at these sites, over 85 documents on peepers were reviewed to identify key peeper methodological aspects that deserve additional empirical study. The review found that the use of peepers to monitor inorganics could be improved by optimizing 1) peeper chamber materials to prevent interactions; 2) volumes and geometries to facilitate analyses of peeper samples by commercial analytical laboratories using standardized analytical methods, minimizing analyte method detection limits, minimizing peeper deployment times, and minimizing peeper sampling efforts. Other areas that need further development include establishing the impact of deionized water in peeper cells when used in marine sediments and use of pre-equilibration sampling methods with reverse tracers (which allows shorter deployment periods). Both of these areas would benefit from a robust demonstration and validation with metals of concern typically evaluated at sediment sites. Finally, the effects of oxygen in initial equilibrium cell water on measured metals concentrations results should be evaluated to confirm the need for complicated approaches traditionally used to prevent oxygen contamination. Overall, it is expected that the evaluation of these technical aspects would address critical methodological challenges, encouraging the standardization of peeper methods and widespread adoption of peepers for regulatory-driven decision making at contaminated sediment sites.

1. INTRODUCTION

Contaminated sediments are a major environmental concern of the 21st century, with more than 70 Superfund sites in the United States requiring cleanup of more than 10,000 cubic yards each (approximately five acres) of impacted sediments (United States Environmental Protection Agency [USEPA], 2020). Aquatic sediments contaminated with inorganic constituents, primarily metals and metalloids, represent significant challenges at many of these sites. Currently, the default approach for evaluating the risk and fate of inorganics in sediment is via measurement of the total extractable concentrations of inorganics in bulk sediment. Because these measurements poorly reflect bioavailability, which is usually less than 100% in sediment, the use of these approaches overestimate fate and risk (Peijnenburg et al., 2014). This can result in overly protective and inaccurate site-specific sediment management approaches that waste financial and stakeholder resources.

It is well recognized that risk and fate of inorganics is best characterized by measurements that attempt to quantify the freely-dissolved fraction of contaminants in sediment and sediment porewater (Conder et al., 2015; Cleveland et al., 2017). Classical sediment porewater analysis for inorganics usually consists of collecting large volumes of bulk sediments which are then mechanically squeezed or centrifuged to produce a supernatant liquid (porewater) that is filtered to extract the water to be analyzed, or suction of porewater from intact sediment, followed by filtration and collection (Gruzalski et al., 2016). The measurement process presents challenges due to the heterogeneity of sediments, high reactivity of some complexes and interaction between the solid and dissolved phases, and the methods result in chemical and physical disturbance of the sediments that can cause the concentration of dissolved inorganics to deviate from the true porewater concentrations. For example, sampling disturbance can affect redox conditions (Teasdale et al., 1995; Schroeder et al., 2020), which can lead to under- or over-representation of inorganic chemical concentrations relative to the true dissolved phase concentration in the sediment porewater (Wise, 2009; Gruzalski et al., 2016).

To address the complications with mechanical porewater sampling for inorganics, passive sampling approaches for inorganics have been developed with the goal of providing a measurement of availability that has a low impact on the surrounding geochemistry of sediments and sediment porewater, enabling a more precise and accurate measurement (Cleveland et al., 2017). Sediment porewater dialysis passive samplers, also known as "peepers," were developed more than 45 years ago (Hesslein, 1976) as one potential approach to circumvent the problems associated with other methods of sampling inorganic chemicals in sediments. Since that time, peepers have been used for a variety of scientific applications (e.g., Vroblesky and Pravecek, 2001; United States Geological Survey [USGS] et al., 2007; Feyte et al., 2012; Gruzalski et al., 2016; Cleveland et al., 2017; Chen et al., 2017), and in regulatory investigations at Superfund and state-regulated sediment sites (e.g., Besser et al., 2009; Geosyntec Consultants, Inc. [Geosyntec] and AECOM, 2019).

Peepers (Figure 1) are inert containers with a small volume of purified water ("peeper water") capped with a semi-permeable membrane. The peeper water is sometimes deoxygenated prior to placement into the peeper, and in some cases, the peeper is maintained in a deoxygenated atmosphere until deployment. Deployment of a peeper consists of insertion into the sediment, where is it left for a period of a few days to a few weeks. During this time, passive sampling is achieved via the principle of diffusion, as the enclosed volume of peeper water equilibrates with the surrounding sediment porewater via transport of inorganics through the peeper semi-permeable membrane (Figure 2). It is assumed that the peeper and its insertion does not greatly alter geochemical conditions that affect freely-dissolved inorganics. Additionally, it is assumed that the peeper water equilibrates with freely-dissolved inorganics in sediment in such a way that the concentration of inorganics in the peeper water would be equal to that of the concentration of inorganics in the sediment porewater. After an equilibration period, the peeper is retrieved and brought to the surface.

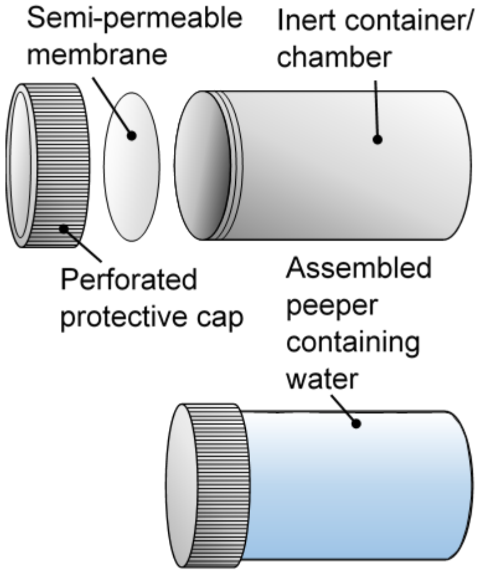

Figure 1. Example peeper construction showing (top, left to right) the peeper cap (optional), peeper membrane, and peeper chamber, and an assembled peeper containing peeper water (bottom).

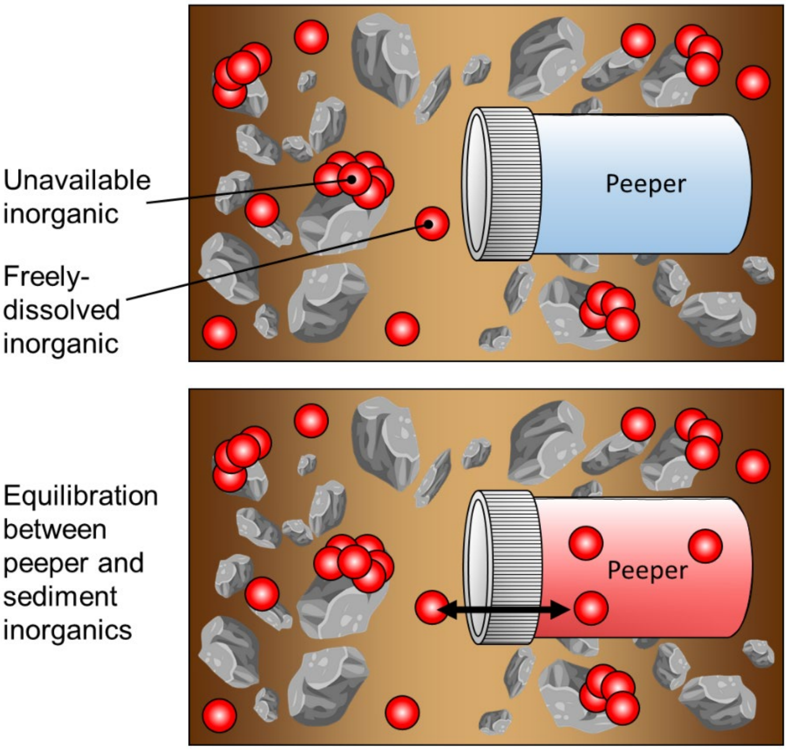

Figure 2. Conceptual illustration of peeper passive sampling in a sediment matrix, showing peeper immediately after deployment (top) and after equilibration between the porewater and peeper chamber water (bottom).

Usually, the peeper water is transferred as quickly as possible to a storage container, which usually contains a preservative (e.g. nitric acid for metals). The peeper itself can be retained, cleaned, and re-used, but in a typical commercial application, the efforts needed for shipping the peeper back to the laboratory and cleaning the peeper are so great that used peepers are discarded after a one-time use. Following shipment to an analytical laboratory, the liquid is analyzed for inorganics via standard (i.e., USEPA SW-846) methods for a water sample. The result predicted from the analysis is then reported as a concentration in water (i.e., milligram inorganic per liter of water [mg/L]) that can be compared to water criteria or used in fate modeling.

Due to their simplicity, peepers have been extensively used since their original development, and modifications to the platform have been made to answer some shortcomings or fit new environments. However, uncertainties remain regarding aspects of peeper field methodology, equilibration dynamics and device materials which hinder the use of peepers for regulatory work. Moreover, a broad variety of methods and formats for peepers exists and selecting a set of best-practices for sampling sediment porewater can be challenging due to the lack of standardized guidance. Thus, despite numerous research applications of peepers, routine application for decision making at sediment sites has been limited.

In this white paper, we detail a literature review of sediment passive sampling of inorganics[1] using peepers, specifically with the goal of identifying past and present best practices for peeper preparation, deployment, retrieval, and data analysis, and data gaps that, if addressed, would further improve peeper methods. This literature review was conducted in support of the "Standardizing Sediment Porewater Passive Samplers for Inorganic Constituents of Concern", project ER20-5261, funded by the Environmental Security Technology Certification Program (ESTCP). The review was conducted in November 2020 to April 2021, and focused on a survey of 85 key documents from 1976 to 2020 (annotated bibliography provided in Appendix A). The review does not include all potentially-available documents including peepers. The review is intended to present examples of the wide variety of peeper applications and methods that have been used, as well as key papers evaluating the methodological aspects of peepers. For some research groups that have used peepers, multiple documents may be available that utilize the same general approaches for peepers. In those cases, we generally highlight two to three example papers (additional papers from the research group may be available and may be of use to the reader).

The focus of the review included key technical aspects of peepers that were considered to be critical for standardizing peeper methods and improving the overall efficiency, speed, accuracy, and confidence in its applications for decision making at contaminated sediments sites. These aspects included: 1) peeper design; 2) pre-equilibrium sampling methods; and 3) oxygen contamination. Conclusions and recommendations are also presented to highlight the questions that need to be answered to enhance the standardized use of peepers for inorganic chemicals in sediment porewater.

The remainder of this white paper is organized into the following sections:

- Section 2: Peeper Design
- Section 3: Pre-equilibrium Sampling Methods
- Section 4: Oxygen Contamination
- Section 5: Conclusions and Recommendations

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[1] This review primarily focused on peeper techniques for the measurement of cadmium, chromium, copper, nickel, lead, zinc, and inorganic mercury, inorganics that often drive risk-based investigation and decision-making at contaminated sediment sites. In some cases, additional information is discussed regarding the application of peepers to measure methylmercury.

2. PEEPER DESIGN

2.1 Overview of Peeper Design

In the four decades since peepers were first reported in literature (Hesslein, 1976), many peeper designs have been developed to meet project-specific application needs. Most peeper designs are close adaptations of the original multi-chamber Hesslein (1976) design (Figure 3), which consists of an acrylic sampler body with multiple sample chambers machined into it. Peeper water inside the chambers is separated from the outside environment by a semi-permeable membrane, which is held in place by a top plate fixed to the sampler body using bolts or screws. Single-chamber peepers have also been constructed using a single sample vial with a membrane secured over the mouth of the vial, as shown in the conceptual example (Figure 1), and applied in Teasdale et al. (1995), Serbst et al. (2003), Thomas and Arthur (2010), and Passeport et al. (2016). The vial is filled with deionized water, and the membrane is held in place using the vial cap or an o-ring. Individual vials are either directly inserted into sediment or are incorporated into a support structure to allows multiple single-chamber peepers to be deployed at once over a given depth profile (Figure 4).

Figure 3. General Hesslein (1976) peeper design (42 peeper chambers), from USGS (https://www.usgs.gov/media/images/peeper-samplers).

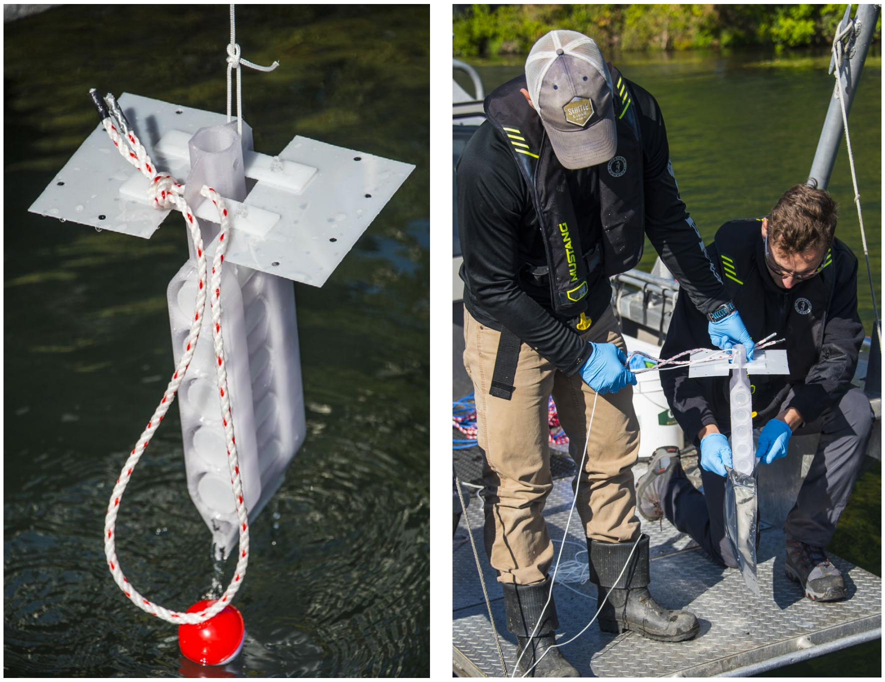

Figure 4. Peeper deployment structure to allow the measurement of metal availability in different sediment layers using five single-chamber peepers (Photo: Geosyntec Consultants).

In the remainder of this section, we will review the challenges associated with optimizing the following fundamental design components of peepers: sampler/vial material, membrane material and pore size, spatial resolution of sample chambers, chamber volume and design factor, and peeper water.

2.2 <u>Peeper Chamber Material</u>

Peepers chambers have been constructed from a variety of materials (Figure 5). It is common for multi-chambered Hesslein peepers to be constructed out of rigid plastics (e.g. acrylic, polycarbonate, polypropylene) because such materials are relatively inexpensive, strong, and easy to machine. Vial peeper designs typically employ glass vials or polyethylene (low density polyethylene [LDPE], high density polyethylene [HDPE]). These styles are advantageous because such vials are readily available commercially, are simpler to work with, and are commonly used by analytical laboratories to store aqueous samples for inorganics analysis. However, they do have some drawbacks such as longer equilibration time (due to large volumes) and lower resolution compared to smaller multi-chambered designs (e.g., Figure 3).

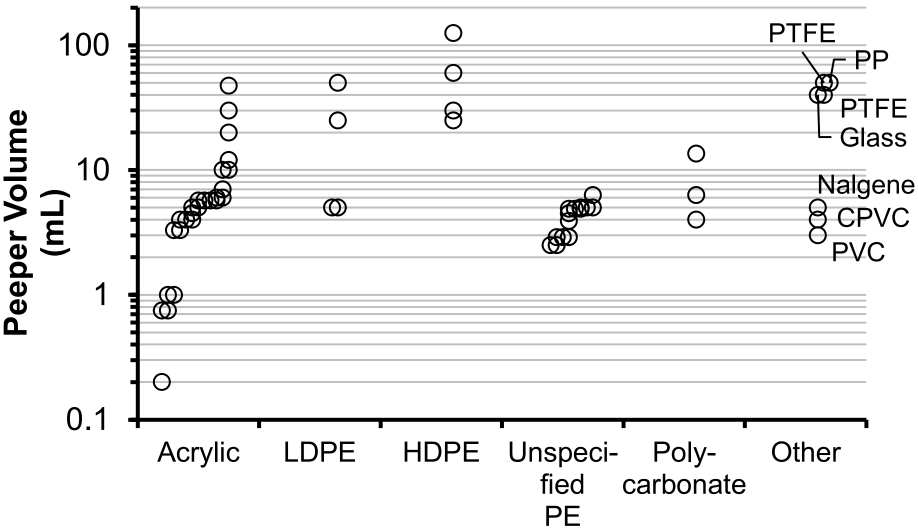

Figure 5. Peeper chamber volume by peeper material type. Labels next to each symbol represent the peeper water volume (milliliters [mL]) and material type (for the peepers in the "Other" category). The figure is on a logarithmic scale.

Peeper chamber material should be relatively inert with regards to the potential sorption of freely-dissolved inorganics in water. A material should not act as a significant diffusive sink for freely-dissolved inorganics such that it could compete with the peeper water during peeper deployment in such a way that it depletes the mass of available inorganics surrounding the sampler. Additionally, the material should not act as a sink that will significantly sorb inorganics from peeper water, which is important for the time period in which the peeper water remains inside the peeper during deployment and after retrieval from the sediment. In general, for common contaminated sediment chemicals of concern such as cadmium, chromium, copper, nickel, lead, zinc, and inorganic mercury, the materials that have been used for most peeper designs (e.g., PE, acrylic) are considered to be relatively inert with regards to significant sorption. Research results for evaluating the sorption of dissolved metals to materials used for sample containers has yielded inconsistent results, such that significant sorption to materials can occur within minutes (Sekaly et al., 1999) or that dissolved metals are not significantly affected for storage times of 24 hours to 40 days (Jensen et al., 2020). Typical polymer materials such as fluoropolymers, conventional or linear polyethylene, polycarbonate, or polypropylene are approved for contact with water samples for trace metal analysis (USEPA, 1996), as these are assumed to not affect results. Polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP) are considered to be among the better materials regarding low sorption of metals (Sekaly et al., 1999; USEPA, 1996; USEPA, 1998), but these materials can be much more expensive compared to other materials (adding approximately \$50-\$100 or more in costs per sampler).

Other chemicals of concern, such as methylmercury, may present a challenge, as methylmercury may have an affinity to adsorb to polyethylene (both LDPE and HDPE) and other typical peeper materials such as polyvinyl chloride (PVC), polypropylene, and glass (Leermakers et al., 1990; Lansens et al., 1990; Yu and Yan, 2003; Stoichev et al., 2006). In general, studies show that adsorptive losses of mercury in PTFE or FEP containers are observed to be lower than those in glass containers (Bately, 1989). Lansens et al. (1990) concluded that methylmercury solutions (10 micrograms per liter [µg/L] in distilled, deionized water) stored in PTFE containers at room temperature remain stable for up to six months. Parker and Bloom (2005) primarily used PTFE containers for their study on storage techniques for low-level mercury speciation, which they attribute to the durability and relative inertness of the material. However, the authors note that "excellent" mercury speciation results were also obtained from samples stored in glass bottles that were acid-cleaned or treated overnight with bromium chloride and indicate a preference for glass bottles ("certified clean for trace metals sampling" I-CHEM® level 300) over PTFE due to high cross-contamination risk of PTFE at sites with a wide range of mercury concentrations (e.g. 0.5-2000 nanograms per liter total mercury; Parker and Bloom, 2005). USEPA Methods 1669 and 1630 recommend collecting methylmercury samples in borosilicate glass or FEP containers (USEPA, 1996; USEPA, 1998). Rigaud et al. (2013) was the only peeper study in this review that sampled for methylmercury and despite finding no artifacts with their methods, others have pointed out the potential for sorption of methylmercury on plastics and peeper membranes, and artifacts related to processing (Taylor et al., 2019; Liu et al., 2011). The level of effort required to fully evaluate proper methods for use of peepers for sampling methylmercury is much more complicated than for other metals typically of concern at contaminated sediment sites and is likely best addressed after key basic questions are answered.

It is possible that material type may be an inconsequential issue for sorption of inorganics, however even if the peeper material has an ability to sorb metals from the surrounding porewater matrix, it is possible that metal sorbed from the porewater would be replaced by desorption and geochemical equilibrium processes over the many days or weeks of peeper deployment. Thus, all phases (sediment porewater, peeper material, and peeper water) could be in relative equilibrium at the end of peeper deployment such that there would be no differences in results for a peeper composed of slightly sorptive material versus a peeper composed of completely inert material. Additionally, if equilibration of the peeper material and peeper water is assumed, additional sorption of the dissolved metal to the interior of the peeper chamber after the deployment period ends would not be significant, especially if the time period between the end of deployment and transfer of the peeper water from the peeper chamber is minimized (e.g., less than 24 hours).

►Chamber Material Conclusions: The selection of appropriate materials for contact with and/or storage of water samples for trace metal analysis is fairly well characterized by surface and ground water sampling and analysis methods, and suggests materials typically used for most peeper designs do not present artifacts to the sampling process. However, the longer contact times between peeper and surrounding sediment and between peeper and peeper water may complicate this assumption. The best candidate materials from this review suggests a polymer ideal for trace metal analysis of water samples (i.e., polyethylene, polycarbonate, polypropylene, or FEP/PTFE) as a standard peeper material. FEP/PFTE is considered to be the most inert. Additionally, FEP/PFTE can represent considerable additional costs, and empirical comparison of sample results with a less expensive material (i.e., HPDE) would be helpful.

2.3 Peeper Membrane Material

A variety of materials with pore size diameters of approximately 0.2- to 1-micrometer (µm) have been used as peeper membranes (Figure 6). Carignan (1984) compared the performance of raw cellulose, cellulose acetate, PVC, and polysulfone membranes in measuring porewater concentrations of inorganics in lake sediments and concluded the following: 1) raw cellulose rapidly degrades and creates a local nutrient demand that skews concentrations of dissolved reactive phosphorous and ammonia, 2) deformation of cellulose acetate membrane was observed after 25 days of deployment, and 3) polysulfone and PVC membranes performed equally well and had no perceived drawbacks. Polysulfone and polyethersulfone are similar in performance and are the most commonly-used membrane types (Figure 6), and have been used for most recent studies because of the chemical inertness and resistance to biofouling (e.g., Teasdale et al., 1995; Doig and Liber, 2000; Teasdale et al., 2003; MacDonald et al., 2013; Passeport et al., 2016).

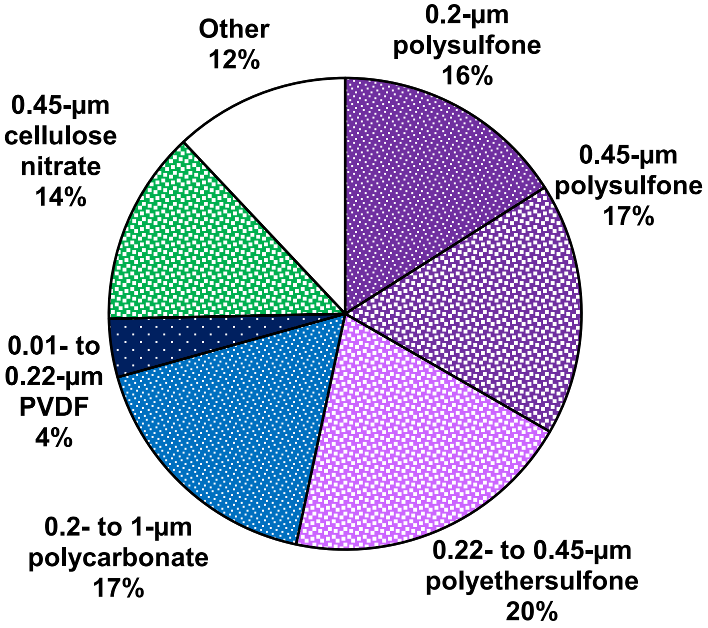

Figure 6. Peeper membrane type for the 75 studies reporting membrane details. Values reflect the percentage of studies using peepers with the specified membrane type.

Jacobs (2002) compared the mechanical stability, diffusion rate, and resistance to biofouling of polycarbonate, PTFE, polyvinylidenfluoride (PVDF), and cellulose acetate membranes after six weeks of sediment contact and concluded that the PTFE membrane performed the best across the three categories. Polysulfone was not evaluated in the study. A 0.45-µm PTFE membrane was selected for their rechargeable peeper design, which tested long-term membrane stability with deployment times ranging from four weeks to eight months.

Membrane pore sizes of 0.2 µm (Doig and Liber, 2000; MacDonald et al., 2013) to 0.45 µm (Teasdale et al., 1995; Grigg et al., 1999; Jacobs, 2002; Teasdale et al., 2003) are typical in peeper designs. The largest membrane pore size identified in the literature review was a 1.0-µm polycarbonate membrane. Serbst et al. (2003) used 1.0-µm polycarbonate membranes to compare equilibration times and cadmium concentrations in a vial peeper covered with a single membrane versus a vial peeper covered with a double membrane. No differences were observed in equilibration time or cadmium concentrations between the two vials. However, less variability was observed in data obtained from the double-membrane vials. Hypothetically, the smaller pore sizes (i.e., 0.2-µm) would better prevent inorganics sorbed to fine particulates material, which are not truly dissolved, from entering the peeper. However, Carignan et al. (1985) noted that peeper results with seven metals for peepers with a 0.45-µm membrane were identical to those obtained with a much finer pore size of 0.03-µm. Thus, a pore size of 0.45-µm is reasonable for limiting the entry of sorbed inorganics. Additionally. the 0.45-µm pore size is the most commonly used pore size for peeper membranes (Figure 6), and almost 60% of the 29 studies reporting membrane materials used a membrane with a pore size of 0.45 µm or greater. Furthermore, the fraction of metals in water passing through a 0.45-µm filter has been traditionally considered to be dissolved by regulatory organizations (USEPA, 1996), allowing the comparison of peeper results to risk-based criteria typically using measurements of dissolved analytes in water.

►Membrane Material Conclusions: Overall, given the widespread use of the polysulfone/polyethersulfone and degree to which the material has performed adequately, polysulfone/ polyethersulfone makes for a good membrane choice. Given the widespread use of the 0.45-µm pore size in typical environmental sampling applications that evaluate “dissolved” chemicals in aqueous samples and common methods that rely on 0.45-µm filters to obtain an aqueous sample that represents “dissolved” metals, the use of 0.45-µm pore diameter polysulfone membranes is a reasonable material to use. Although not observed in the research reviewed, smaller pore sizes may decrease the proportion of inorganics bound to solid material or colloids that may permeate larger pore diameter membranes, potentially providing a more accurate estimate the of the freely-dissolved phases. However, this may decease equilibration speed, necessitating longer peeper deployment times. Additional experiments could be conducted to examine these effects but they are likely lower in priority than research needs associated with other technical aspects of peeper design.

2.4 Peeper Chamber Volume and Design Factor

A complex aspect of peeper design is the balance between the peeper chamber volume and the shape of the peeper in terms of the area of the peeper membrane relative to the peeper chamber volume, referred to as the design factor (F, where F = volume [mL] ÷ diffusion area [square centimeters (cm^2)]) or specific surface area. Larger chamber volumes allow for broader analyte scopes and/or lower detection limits. Higher specific surface areas (smaller F) allow for faster equilibration with porewater and therefore shorter deployment times. These aspects of peeper design also affect the spatial resolution of sampling. For example, if the peeper membrane diffusional area is 5 centimeters (cm) in diameter or height, the peeper integrates the porewater sampling over a 5-cm depth interval when inserted into sediment (a spatial resolution of 5 cm). Therefore, the optimal peeper design maximizes volume to allow low method detection limits, minimizes F to decrease peeper deployment periods, and targets the correct dimensions of the peeper membrane so that the measurement can be made over a relevant spatial scale. The remainder of this section describes these aspects of optimization as they apply to peeper chamber design.

Method detection limits for peeper water samples are inversely related to peeper chamber volumes – larger volumes enable the lowest detection limits. For commercial analytical laboratories that rely on standard USEPA SW-846 methods, 100 mL is often the preferred minimum volume for a water sample (USEPA, 1992; USEPA, 1996; USEPA, 1998). In some cases, this can be reduced to smaller volumes (e.g., approximately 50 mL), although reductions in sample volumes affect the number of metals than can be analyzed in a single sample and affect the method detection limit. For example, the relationship between typical method detection limit in water for copper versus sample volume size (peeper chamber volume) is show in Figure 7. The lowest detection limit (0.3 µg/L) is for a large peeper volume of 100 mL. The detection limit for a 50-mL sample would be approximately twice this value (i.e., 0.6 µg/L). If one were evaluating the likelihood of copper toxicity in a marine system, one might compare measured concentrations of porewater to the USEPA chronic Ambient Water Quality Criterion for copper (3.1 µg/L) as a potential screening threshold for the potential for toxicity to aquatic life. As shown in Figure 7, the detection limits for peepers with chamber volumes of 10 mL and greater are below the Ambient Water Quality Criterion (AWQC), suggesting that peepers larger than 10 mL would be sufficient to detect copper at concentrations above the AWQC. However, allowing for larger volumes because of variability in the detection limit, potential pre-equilibrium sampling conditions (which can result in an increase in an equilibrium-corrected detection limit), and extra capacity for added precision, attaining lower detection limits would be ideal. For example, in the example shown in Figure 7, only peeper volumes 50 mL and greater could attain typical commercial analytical laboratory detection limits that were five times lower than the copper AWQC (i.e., approximately 6 µg/L).

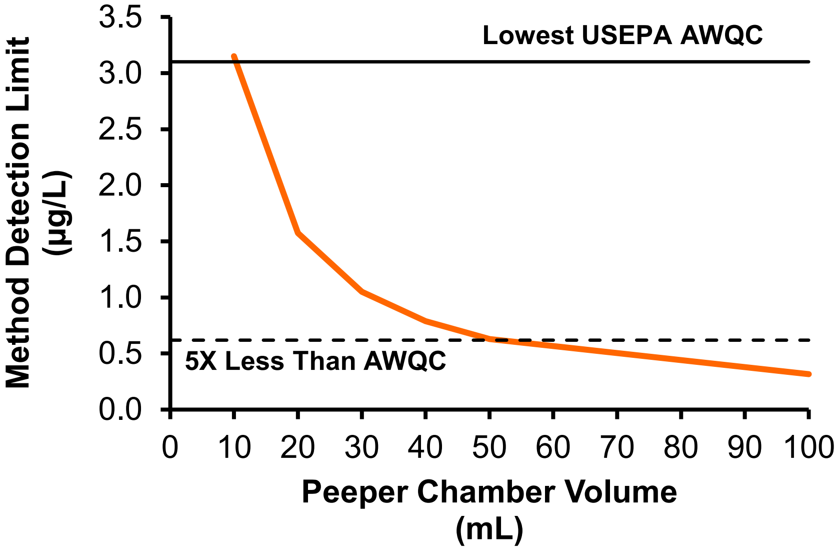

Figure 7. Typical commercial analytical laboratory method detection limits for various peeper chamber volumes for copper versus method detection limit. The USEPA AWQC for copper (3.1 µg/L) is shown as the solid line. The dotted line represents a threshold five times less than the AWQC.

For widespread and routine application at contaminated sites under regulatory oversight, it would be most ideal to enable peeper analysis by state and federally-accredited commercial analytical laboratories following standard analytical protocols for the analysis of inorganics in water samples. As noted above, this goal translates to peeper water volume sample requirements of approximately 50 mL or higher in many cases. Peeper volumes have varied based on project-specific objectives, but have ranged from less than 1 mL to over 100 mL (Figure 8). Attaining peeper volumes necessary to match commercial analytical laboratory volume requirements is feasible, as peeper volumes approximately 50 mL and larger (Mason et al., 1998; Jacobs, 2002; Brumbaugh et al., 2007; MacDonald et al., 2013; Greenstein et al., 2014; Geosyntec and AECOM, 2019; Frost et al., 2019) have been successfully implemented with deployment periods of approximately 14 to 28 days. However, as shown in Figure 8, many peeper chamber volumes fall within the range of 5 to 8 mL (e.g., Teasdale et al., 1995; Serbst et al., 2003; Thomas and Arthur, 2010; Burbridge et al., 2012), and commercially-available multi-chamber peeper samplers (e.g., Figure 3) typically feature volumes of approximately 10-15 mL per chamber. Volumes less than 1 mL (Doig and Liber, 2000; Xu et al., 2012; Chen et al., 2015; Chen et al., 2017) have also been used. Although these smaller peeper volumes have enabled comparative short deployment times (e.g., 1 to 7 days in some cases), these projects did not rely on the standardized commercial methods typically required for contaminated sites under state or federal regulatory oversight.

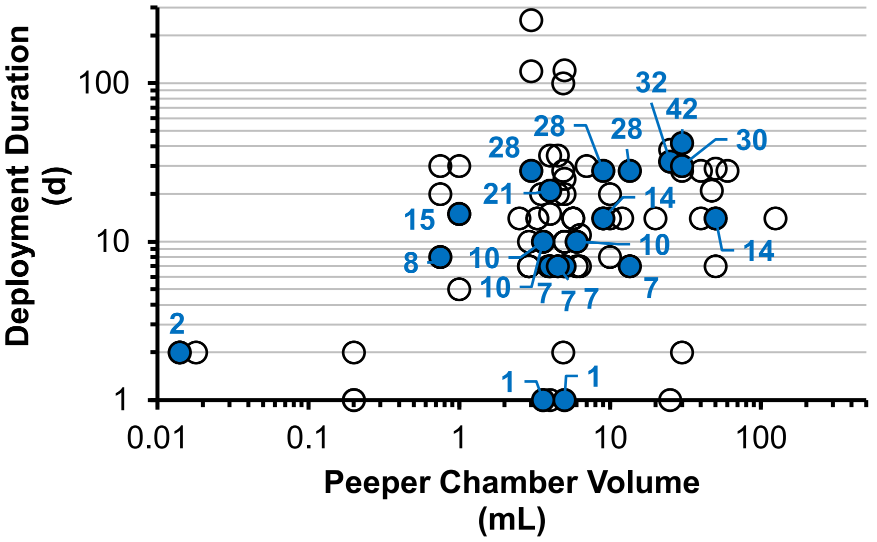

Figure 8. Deployment duration versus peeper chamber volume. The figure is on a logarithmic scale. Blue-filled symbols indicate peepers that were confirmed to be at equilibrium at the deployment time indicated by the blue label (note that equilibration may have been reached prior to the deployment time). Hollow symbols represent peepers that were not at equilibration or instances in which equilibration status was not confirmed.

Although larger peeper volumes would be desired from an analytical perspective, larger volumes present logistical challenges. One potential drawback to maximizing chamber volume is the effect on peeper equilibration – larger peeper volumes typically require longer equilibration times that result in longer deployment periods (Figure 8). Although the time needed for a peeper to equilibrate with sediment porewater is affected by the diffusivity of the analyte (i.e., analytes diffuse at different rates in water) and site-specific characteristics (e.g., sorption to sediment, sediment porosity, temperature, salinity, and other environmental factors), the physical characteristics of the peeper (e.g., volume, sample chamber geometry [F] and orientation) are under the control of the investigator (Carignan, 1984; Teasdale et al., 1995; Webster et al., 1998).

Few experiments have confirmed equilibrium status of peepers (via successive measurements over a time series, use of conservative species, or use of reverse tracers). Data from 60-mL peepers (F of approximately 8 mL/cm^2, unpublished data courtesy of SiREM) deployed in a variety of field sites reached approximately 50 to 80% of equilibrium (as determined with a bromide reverse tracer) in an approximate 30-day deployment period (Figure 9). Based on this tracer data, approximate equilibrium (90% of equilibrium) would be reached within approximately 40 to 100 days, which is longer than typical passive sampling field deployments (i.e., 14 to 28 days). In general, cadmium, copper, nickel, lead, zinc, and mercury kinetics are such that equilibrium requires twice the amount of time as for bromide. However, full equilibration is not required, as pre-equilibration results can be corrected to equilibrium using modeling (Section 3). Nonetheless, even when using pre-equilibrium sampling, achieving as much equilibration within the peeper deployment period is generally preferred.

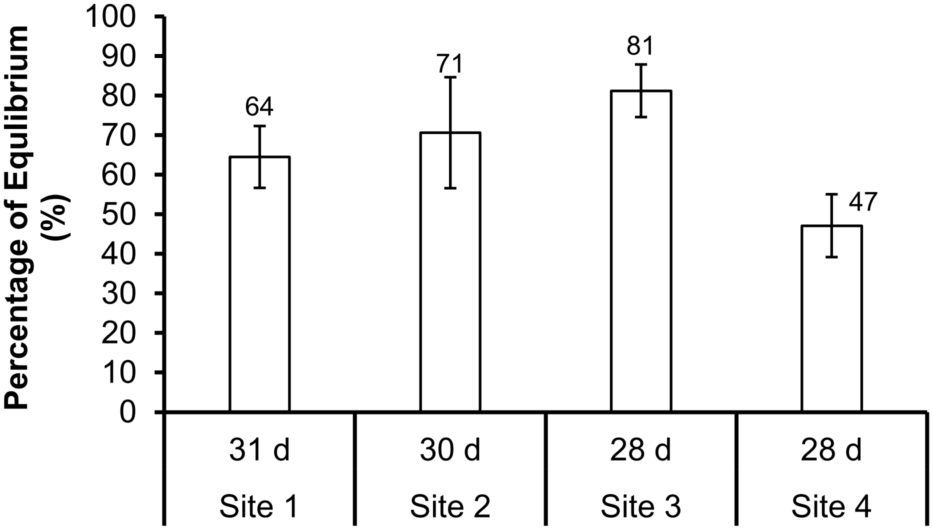

Figure 9. Percentage of equilibration (mean ± standard deviation) measured with a bromide tracer in four different site sediments (60-mL peeper with F = 8 mL/cm^2, unpublished data courtesy of SiREM).

As noted above, decreasing the design factor (F) will reduce the time required to reach equilibrium. As shown in Figure 10, data from Webster et al. (1998) indicate that the approximate equilibrium (90% of equilibrium) time for strontium and potassium scales linearly with F for three different peeper designs deployed in sediment. Thus, decreasing F by 50% will reduce deployment times by approximately 50%. Typically, F values are approximately 1 mL/cm^2 or higher. Values for commercially-available multi-chamber peeper samplers (e.g., Figure 3) are approximately 1.5 to 2 mL/cm^2, whereas F for typical vial-based designs (using mass-produced sample bottles as peeper chambers) range from approximately 2 to 15 mL/cm^2.

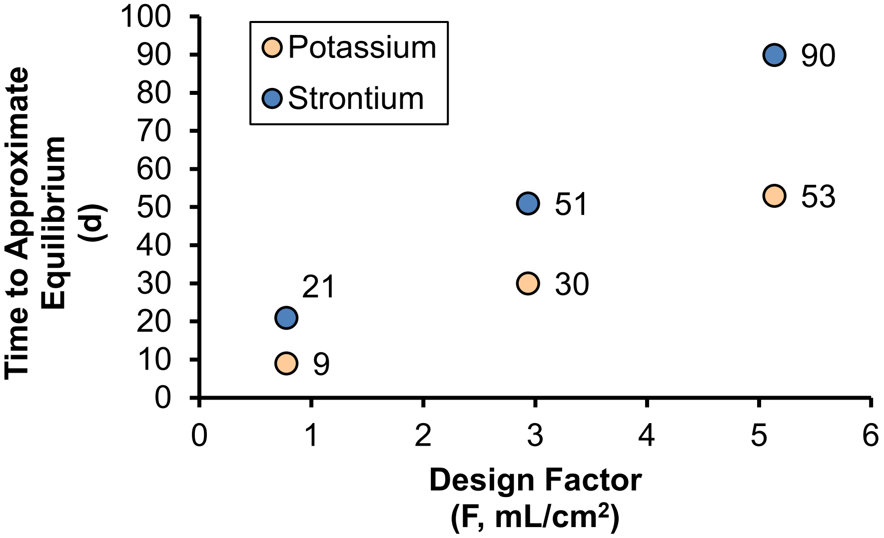

Figure 10. Time required to reach approximate equilibrium (90% of equilibrium) for strontium and potassium in sediment using three peepers with different design factors (figure created from data in Webster et al. [1998]).

In general, given the same approximate membrane area, lower F values can be obtained simply by reducing the volume of peeper chamber. Given this assumption, it is possible to decrease sampling time via combining (compositing) the peeper waters from multiple smaller peepers (with lower F) into a single sample rather than relying on a single larger peeper. For example, if 50 mL of peeper water is needed to attain the desired detection limit (as in the copper example for Figure 7), one could deploy five 10-mL peepers and combine them into a single 50-mL sample for analysis. Compositing volumes less than 10-mL (to attain a 50-mL volume) is not likely to be efficient from a labor effort perspective and risks contamination or mishaps due to the multiple times the peepers and sample storage container must be opened and handled. Given that the 10-mL peepers would exhibit a lower F, the 10-mL samplers would also approach equilibrium more quickly than a 50-mL sampler, potentially reducing deployment times by weeks. However, reducing the deployment period would need to be balanced against the potential negative logistical and financial impacts of constructing, deploying, and processing five times the number of peepers. This evaluation of design and logistics has not been conducted, but would potentially be useful in standardizing a peeper design.

Another aspect of peeper design is the spatial resolution for sampling. Based on typical mass-produced sample bottle shapes, a 100-mL peeper has a diffusional area (mouth of the bottle, over which a membrane would be placed) of approximately 5 cm in diameter, preventing the evaluation of freely-dissolved measurements at very fine scales (i.e., 1-cm layer resolution). A straightforward approach to increase volume without sacrificing spatial resolution is to increase the depth of the peeper cell. This approach has two potential disadvantages: 1) potential increase in thickness of the peeper body, which can lead to more difficult deployment and greater sediment disturbance, and 2) increase in F (which increases deployment time). In general, however, 1-cm resolution is often difficult to attain with high confidence. Also, 1-cm resolution is not often needed for typical sediment investigations under regulatory oversight, as risk-based evaluations of metal availability generally focus on surface sediment, which is often defined by regulatory authorities in terms of the uppermost 5, 10, or 15 cm of sediment.

►Chamber Volume and Design Factor Conclusions: Peeper chamber shape and design influences analyte method detection limits, peeper deployment periods, and spatial resolution of samples. Typical volume requirements for trace metal analysis of peeper waters by commercial laboratories attempting to reach low detection limits with standard methods tend to be approximately 50-100 mL. Samplers in this range have been used successfully at sites, although they may not fully reach equilibrium, even for deployment times of approximately 30 days. Samplers with a smaller volume and design factor (F) increase equilibration speed, reducing deployment times and allowing finer spatial resolution in the sediment. However, smaller peepers require compositing multiple chamber volumes to attain the 50-100 mL necessary for commercial labs. Additional experimentation to evaluate the potential advantages of multiple small peepers versus one of approximately 50-100 mL and/or large peepers with small design factors would be helpful in identifying the most optimal and efficient design.

2.5 Peeper Water Salinity

Peepers chambers are typically filled with deionized water that is devoid of detectable concentrations of analytes, even when deployed in marine sediments (Rigaud et al., 2013; Teasdale et al., 2003; Serbst et al., 2003; Schroeder et al., 2020). In contrast, Simon et al. (1985), Dattagupta et al. (2007), and Grigg et al. (1999) used peeper with artificial saline water in the peeper chambers to prevent diffusion artifacts from the peeper due to density differences between peeper water and external water for marine deployments. These are the only two studies identified in the literature review that used artificial saline water during the deployment of passive samplers in marine sediments. Webster et al. (1999) specifically tested equilibration dynamics of peepers containing deionized water in marine sediments and noted that the initial difference in salinities created a convection that may affect the concentrations of magnesium in the sediment porewater adjacent to the peeper, especially in short time periods (1-5 days).

The effect of initial peeper water salinity on peeper results for metals over longer time periods and reverse tracer equilibration has not been well studied. It may be useful to evaluate with experimentation comparing the results of peepers made with deionized versus synthetic saltwater. Deionized water presents the advantage of being virtually trace metal free – the addition of salts to increase salinity risks introducing trace levels of target analytes that could interfere with target analyte measurements. Additionally, in estuarine and marine sediments porewater salinity is likely to vary, so the initial salinity configured for the peeper water is unlikely to be accurate. Additional experiments would be necessary to understand the impact of using saltwater versus deionized water in peeper chambers.

►Peeper Water Salinity Conclusions: Peepers traditionally use deionized water, even for deployments in marine sediments. The effects of the different salinity on sampling has not been evaluated. Additional experimentation to evaluate the feasibility of and need for constructing peepers containing saline porewater for deployments in marine and estuarine sediments would be helpful.

3. PRE-EQUILIBRIUM SAMPLING METHODS

As noted in Section 2, the approximate time periods needed for equilibration of peepers can be as long as several weeks depending on deployment conditions, analyte of interest, and peeper design. In many cases, it is advantageous to use pre-equilibrium methods that can rely on measurements in peepers deployed for shorter periods and predict concentrations at equilibrium. Pre-equilibration methods are standardly used for passive samplers applied to measure freely-dissolved organic chemicals in sediment (USEPA, 2017).

Although one can evaluate the equilibrium concentration of an analyte in a sediment by evaluation of analyte results for peepers deployed for multiple time periods (i.e., a time series), this is impractical for typical field investigations, as it would require several mobilizations to the site to retrieve samplers at multiple events. Alternately, one can use a reverse tracer (referred to as a performance reference compound when used with organic compound passive sampling) to evaluate the percentage of equilibrium reached by a passive sampler. For example, a reverse tracer can be added to the peeper water at a concentration of 100 mg/L. After deployment in sediment, if the concentration of the reverse tracer is determined to be 50 mg/L, one can infer that the peeper has reached 50% of equilibration. Assuming that the diffusion of a target analyte (which has diffused into the peeper during deployment) has related properties to that of the reverse tracer, a measured concentration of a target analyte can be corrected to the predicted concentration at complete equilibrium.

Thomas and Arthur (2010) studied the use of a potassium bromide reverse tracer to estimate percent equilibrium in lab experiments and a field application. They concluded that bromide (Br) can be used to estimate concentrations of anions and metals in porewater using measurements obtained before equilibrium is reached. The study included a mathematical model for estimating concentrations in porewater (C_0) at time (t) based on measured concentrations of reverse tracer in the peeper chamber ($C_{p,t}$), assuming tracer concentration in the porewater is negligible.

$$C_0 = \frac{C_{p,t}}{1 - e^{-Kt}}$$

Where K is the elimination rate of the target analyte, calculated using the ratio of free-water diffusivity (D) of the tracer and the target analyte (Thomas and Arthur, 2010).

$$K = K_{tracer}\left(\frac{D}{D_{tracer}}\right)$$

The elimination rate of the tracer (K_{Tracer}) is calculated based on measured concentrations in the peeper chamber prior to deployment ($C_{p,i}$) and at the time of retrieval ($C_{p,t}$).

$$K_{tracer} = -\frac{1}{t}\ln\left(\frac{C_{p,t}}{C_{p,i}}\right)$$

The exponential decay equations detailed above were evaluated alongside comparatively complex analytical approximations based on an infinite plane source and an infinite point source. The study concluded that the point source correction resulted in significant inaccuracy at low values of K_{Tracer}, while both the plane source and exponential decay corrections improved estimations of porewater concentrations. The authors recommended using the exponential decay correction in the interest of simplicity (Thomas and Arthur, 2010).

Despite the use of this approach, the accuracy of a bromide reverse tracer to calculate the percentage of equilibrium obtained by metals typically evaluated at contaminated sediment sites (i.e., cadmium, copper, nickel, lead, zinc, and mercury) has not been evaluated in sediment. Such an evaluation would be useful for validating the approach and building confidence that the bromide tracer is reliable for pre-equilibrium sampling methods with peepers. Documenting the performance of the bromide tracer in different salinities (i.e., a freshwater sediment and a marine sediment) would also be useful, as salinity may affect equilibration dynamics. Although temperature also affects diffusivity of the bromide tracer and inorganic analytes of interest, it is assumed that the ratio of bromide and the target analyte remains constant in a manner such that the bromide tracer will accurately reflect the percentage of equilibration for the target analyte. Colder temperatures will slow equilibration; however, this is likely negligible for typical ranges of temperatures in sediments. For example, Carignan (1984) used peepers to measure porewater concentrations of manganese and iron and concluded that the time period required to reach equilibration in sediments at 4-6°C was 25% longer than required for sediments at 20-25°C. This magnitude of differences in sample equilibration time would not greatly influence experimental designs for peeper investigations in cold (4-6°C) sediments.

4. OXYGEN CONTAMINATION

4.1 Oxygen Contamination Overview

Natural and contaminated sediments often exhibit anoxia and low redox potential in surface sediment layers that are typically evaluated for the presence and potential risks of inorganics. These anoxic zones in sediments have the potential to attenuate or enhance diffusion of nutrients and contaminants to the overlying waters. Peepers present the advantage of measuring the truly dissolved phase of inorganic chemicals, providing a better understanding of the fraction of the constituents that are available to benthic organisms and has the potential to diffuse out of the sediments into the water cap. This makes the use of peepers in anoxic sediments an attractive option for sediment characterization, remedial action efficacy measurement and ecotoxicological studies.

One of the main challenges with the sampling involving inorganics in anoxic sediment is that some inorganics can react with oxygen contamination arising from the peeper sampling process. For example, reduced species of iron, sulfur, phosphorus, and manganese react within seconds after exposure to oxygen (Xu et al., 2012; Carignan, 1984). The oxidation of these reduced species can lead to various effects on their water solubilities and may lead to the precipitation of insoluble metal oxides or the enhance the dissolution of oxidized metal sulfide complexes (Wise, 2009). These reactions can also affect the solubility of other inorganics that are less reactive to oxygen. Therefore, exposure of peepers to oxygen during sampling can lead to inaccurate concentrations of dissolved inorganics. In this section, we will review the most common issues encountered with oxygen and peepers and look at the methods that can be used to minimize oxidation of the peeper content as well as discuss their impact on sampling. Two major issues have been identified: 1) oxygen contamination introduced from the peeper during deployment; and 2) oxygen contamination of the peeper water during peeper retrieval and processing.

4.2 Oxygen Contamination During Deployment

Oxygen contamination from the peeper during deployment was highlighted by Carignan (1984), who observed a solid precipitate in the peeper water within peepers made from polycarbonate. Peepers made from acrylic did not exhibit this precipitate. Additionally, polycarbonate peepers exhibited lower concentrations of dissolved reactive phosphorus (DRP), iron, and manganese compared to acrylic peepers. This issue was attributed to oxygen diffusing out of the polycarbonate into the chamber and causing precipitation of redox sensitive species. Dissolved oxygen present in the peeper at the point in which the peeper is inserted into the sediment could also present a source of oxygen contamination. The introduction of oxygen from the peeper and/or peeper water could result in changes to redox conditions adjacent to the peeper that could result in changes in concentrations of freely-available metal (Figure 11). Additional investigation by Carignan (1984), showed that deoxygenation of the peeper and peeper water had the highest impact on concentrations of DRP, iron, and manganese. Carignan (1984) recommended the use peeper materials with lower oxygen adsorption capacity, deoxygenation of the peepers, and storage of peepers in an oxygen free environment prior to deployment.

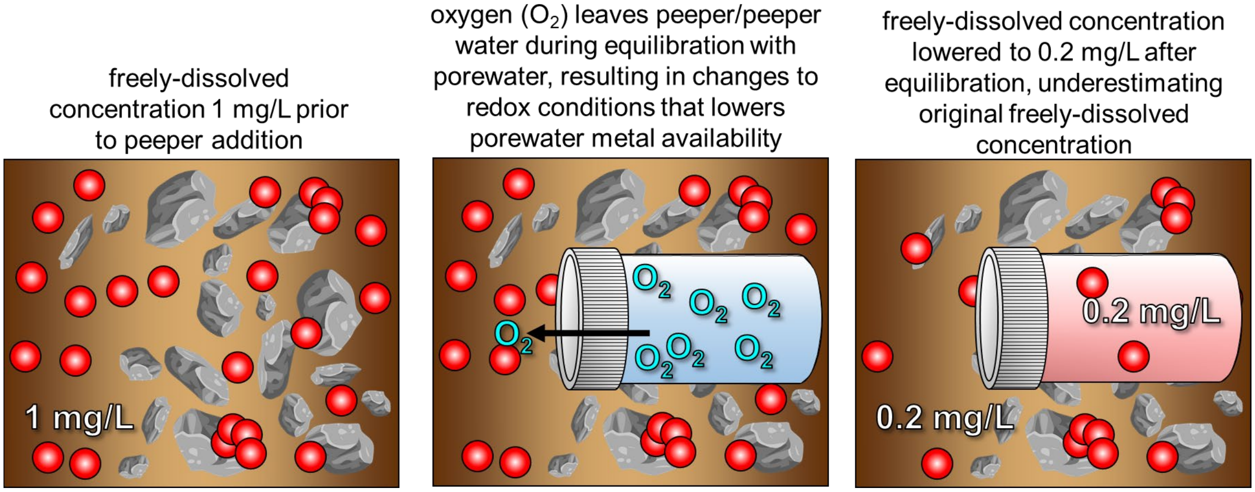

Figure 11. Example of an oxygen contamination from a deployed peeper changing redox conditions and concentrations of freely-dissolved metals in a sediment.

Other plastic peeper chamber materials were also noted as a source of oxygen contamination that may lead to misrepresentation of metals concentrations by others (Teasdale et al., 1995; Serbst et al. 2003; Teasdale et al., 2003). Teasdale et al. (1995) evaluated oxygen solubility and elimination kinetics in various peeper sampler types and noted that PFTE and polycarbonate exhibited the highest oxygen solubilities (2.8% and 3.7% on a volume basis, respectively), whereas HDPE and PVDF exhibited the lowest oxygen solubilities (0.6% and 0.8%, respectively). The solubility of oxygen in acrylic, a commonly-used material for peepers (Figure 5), was intermediate (1.8%). Mason et al. (1998) noted that results for methylmercury may have been affected by a PTFE peeper that was not completely deoxygenated prior to the seven-day deployment. Thus, selection of peeper material may influence the degree to which oxygen contamination may represent a risk.

In contrast, experiments conducted by Wise (2009) did not observe an artifact of oxygen contamination introduced from the peeper. To understand the importance of oxygen contamination during preparation of peepers, Wise (2009) tested if peeper deployment times of at least seven days would allow oxygen to diffuse out of peepers and redox chemistry within the peeper chamber to equilibrate back to the unaffected (reduced) state. Wise (2009) found that, although some variability in the iron concentrations of the deoxygenated vs non-deoxygenated peepers was present, no significant differences were observed for any of the metals tested once equilibration was achieved (as soon as 7 to 14 days). It was also noted that the use of some plastics like polycarbonate that were reported to exhibit high oxygen retention had no impact on the concentrations of redox sensitive species in peepers. Wise (2009) concluded that deoxygenating peepers was not a necessary step and that oxygen introduced in the sediments by the peeper does not affect sampling results.

Despite the lack of consensus in the literature regarding the importance of deoxygenating peepers prior to deployment, commonly applied procedures for peeper preparation (Xu et al., 2012; Geosyntec and AECOM, 2019) tend to err on the side of caution and follow the recommendations of Carignan (1984). Deoxygenating peepers and isolating peepers from oxygen prior to deployment is challenging since our atmosphere is composed of 21% oxygen, and most waters overlying sediments are relatively well oxygenated. Procedures to deoxygenate peepers increases the time and cost required to prepare peeper in the lab due to the lengthy deoxygenation of the peeper water and plastic as well as heavy use of inert gases (nitrogen, argon, helium, etc.). These methods require detailed protocols, trained personnel, and the use of more materials and consumables. In some cases, the need for inert gases to maintain peepers can include the use of compressed gas cylinders in the field on sampling vessels, which is cumbersome, complicated, and can present added health and safety issues. Moreover, removing oxygen from each part of the sampler is not always feasible and oxygen can be introduced via other structural parts of the peeper deployment hardware, such as support or deployment structures for peepers (Urban et al., 1997).

Additionally, keeping the sampler oxygen free for periods of time when they are required to travel from the lab to the field is challenging. For example, the use of inert-gas filled bags have been used during peeper transport (Geosyntec and AECOM, 2019) and during deployment and retrieval (Bufflap and Allen, 1995; Burbridge et al., 2012) to ensure minimal oxygen contamination. There is little evidence to show how successful these techniques are in terms of preserving the anoxic integrity of the sampler. Thus, the deoxygenation “shelf life” of peeper samplers remains unquantified, and the need for a standard protocol for preservation of deoxygenated peepers would be helpful if oxygen contamination is a significant concern.

►Oxygen Contamination During Deployment Conclusions: During deployment, oxygen present in the peeper and peeper water may have the potential to modify conditions affecting the concentrations of freely-dissolved metals. The impact of this possible phenomenon on sample results remains unknown. To counter this, peepers are usually deoxygenated prior to deployment. Additional experimentation to evaluate the importance of deoxygenation would be helpful. If it is truly necessary, standardization of an approach is needed (e.g., best peeper materials, deoxygenation methods, and shelf life for deoxygenated peepers).

4.3 Oxygen Contamination After Deployment

The second major issue related to oxygen is oxygen contamination after retrieval from the sediment (Figure 12). Given the rapid kinetics of oxygen-sensitive species and potential effects on geochemical conditions within the peeper, oxygen contamination has the ability to affect results. For example, upon removal from a sediment, peeper water may be contaminated with oxygen if the peeper is exposed to oxygenated water or air. When exposed to air, oxygen was found to diffuse into peepers at a rate of 0.13 mg/L per minute (Carignan, 1984). Thus, this could suggest that peeper waters could reach relatively oxygenated levels (i.e., 5 to 7 mg/L) within approximately 30 to 60 minutes during exposure of the peeper to air. Removal of the membrane or covering of the peeper water (i.e., to facilitate removal of the peeper water) could further speed this process. Hypothetically, oxygen entering the peeper could trigger precipitation reactions that could remove dissolved inorganics from solution, forming a precipitate. In some cases, this precipitate would be transferred to the storage vial where it is preserved and would be ultimately be quantified in the analysis once the sample is acidified.[2] However, it is also possible that the precipitate could adhere to the interior of the peeper vial (Figure 12) and would not be transferred to the storage vial, resulting in an underestimation of the original dissolved concentration within the peeper at the time of retrieval from the sediment.

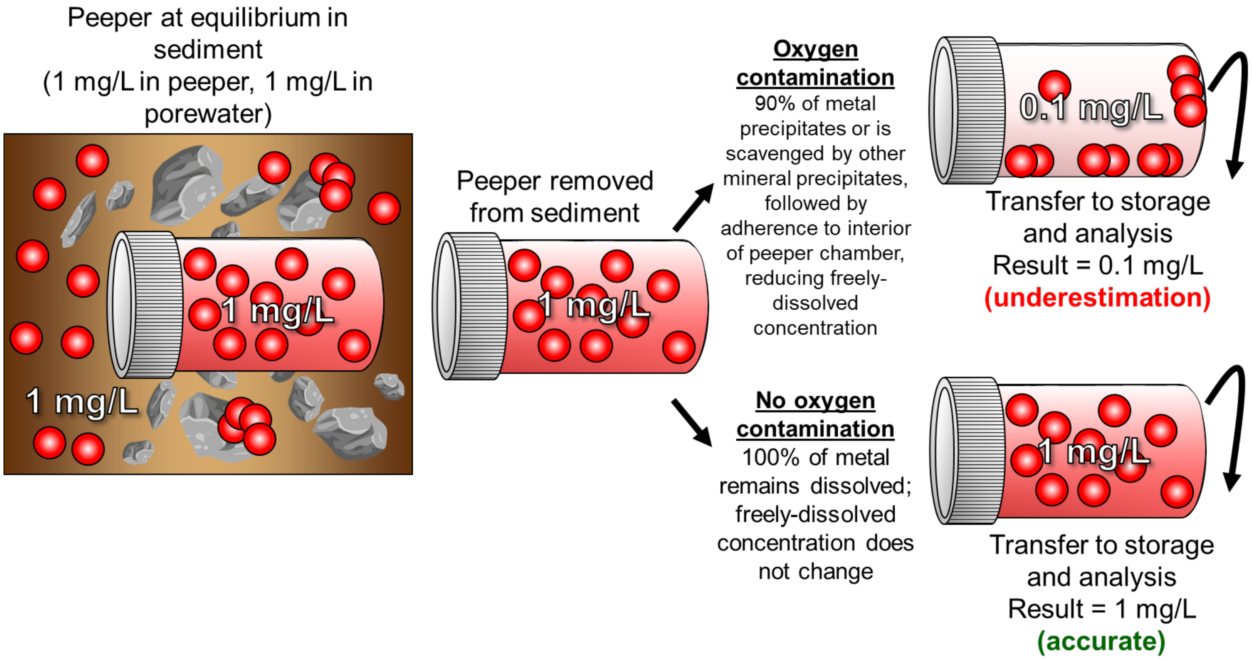

Figure 12. Example of an oxygen contamination changing redox conditions of the peeper after removal from sediment, and effects on the resulting measured concentration of freely-dissolved metals in the peeper water.

Despite these hypotheses, the effects on peeper water oxygen contamination after removal from sediment has not been rigorously evaluated, leading researchers to take considerable precautions to avoid oxygen contamination. Rapid processing of the peeper water and stabilization of redox sensitive species have been used to minimize the reactions of anoxic peeper water after it is removed from the sediments (Burbridge et al., 2012). Conditions for processing peepers in the field are often not as ideal as in an analytical chemistry laboratory and can result in higher

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[2] Simpson et al. (1998) noted that even after acidification, some metals such as copper may partition to the walls of the storage vessel. The researchers proposed addition of a strong oxidant in the storage vessel prior to acidification, which resulted in better sample preservation. This step would be suggested for other sulfide-reactive metals such as cadmium, nickel, lead, and zinc. Oxidation would not be recommended for the analysis of methylmercury, as oxidation could affect speciation.

probabilities of inadvertent sample contamination or other sample handling errors. If peeper water cannot be transferred to storage containers within minutes after retrieval, peepers are often stored in oxygen free containers, such as bags or containers purged with inert gases. This requires the use of compressed inert gases, which complicate field sampling, especially on vessels or in remote locations. Maintaining inert atmospheres in typical sample storage containers can be difficult and can complicate shipping, so often peepers are transferred to storage containers in the field or temporary shelters.

As noted above, concern regarding the potential for oxygen to enter the peeper after exposing it directly to the air before transfer to the storage container has necessitated complicated transfer procedures. Common procedures employ a needle to pierce the peeper membrane and retrieve the sample with a syringe after cleaning the sediments from the peeper membrane (Tan et al., 2005; Doussan et al.,1998; Geosyntec and AECOM, 2019). A second syringe can be filled with nitrogen gas and inserted into the peeper during removal of the liquid such that oxygen is not introduced into the peeper during transfer. Alternately, transfer of the peeper water to the storage container can be completed in an anaerobic chamber such as a glove box purged with inert gas. These methods are complicated. The use of syringes can represent a health and safety hazard, especially on vessels or in the field, and a potential contamination source of metals if metal syringe needles are used. The reliance on inert gases also presents complications as described previously. An alternative to preservation with inert gas is to freeze the peepers after retrieval, which can help minimize the oxidation of the water before processing, as described in Xu et al. (2012). However, freezing porewater samples within minutes or hours of removal from sediment at most field sites would be extremely difficult, and steps required to thaw and process the sample for analysis are complicated. It is possible that these methods may not be needed. For example, Wise (2009) showed that working in an anaerobic chamber was not necessary as it did not provide a significant difference to concentrations of redox sensitive constituent, this can likely be attributed to the short contact time with the atmosphere if processing of the peeper water is rapid.

►Oxygen Contamination After Deployment Conclusions: Oxygen has the potential to contaminate the peeper water after the peeper is removed from sediment, potentially altering results. The impact of this possible phenomenon on sample results remains unknown. Additional experimentation to standardize the best approaches transferring peeper water to storage containers are needed, including quantification of holding times for peeper water after removal from sediment.

5. CONCLUSIONS AND RECOMMENDATIONS

This white paper provides a comprehensive literature review of over 85 peer-reviewed and grey literature documents over the last 45 years on the applications of peepers to measure freely-dissolved inorganics in sediment porewater. The review has identified several key technical aspects where additional work would be beneficial to promote the routine application of peepers to aid in regulatory-driven decision making at contaminated sediment sites (Table 1).

Several aspects of peeper design deserve additional evaluation:

- The sorption of metal analytes to peeper materials has the potential to represent an artifact to sample results. This issue has not been well studied and should be evaluated with a standard material(s) and compared to a material that is considered to be most inert, such as FEP or PTFE.
- It is possible that peeper chamber volumes and design factors could be better optimized with regards to the logistical tradeoffs between enabling analyses of peepers by commercial analytical laboratories using standardized analytical methods, minimizing method detection limits, minimizing peeper deployment times, and minimizing sampling efforts.
- It is unknown if the peeper equilibration process in marine sediments is affected by the use of deionized water.

Additionally, the use of pre-equilibration sampling methods with peepers containing reverse tracers is very helpful in reducing peeper deployment times. A robust demonstration and validation of the approach with metals of concern typically evaluated at sediment sites would establish additional confidence in the methods.

Oxygen contamination from deployed peepers and oxygen contamination of peeper water after removal from sediment has been assumed to potentially affect the ability to affect results. As approaches traditionally used to prevent oxygen contamination are complicated, the effects of oxygen contamination on peeper results should be evaluated to confirm these protective approaches are truly necessary.

Overall, it expected that evaluation of the technical aspects identified in this paper would address critical methodological challenges, furthering the standardization of peeper methods and widespread adoption of peepers for regulatory-driven decision making at contaminated sediment sites.

Table 1. Key technical aspects identified from the literature review, and potential additional studies to address data gaps.

Technical Aspect	Literature Review Summary	Potential Additional Studies
Sorption of metals to peeper	Acrylic, LDPE, and HDPE materials have been used most often for peepers and are considered to be relatively inert with regards to the sorption of metals during and after deployment FEP/PTFE may represent the most inert materials	Compare results for standard peeper material versus FEP or PTFE; Evaluate effects of storage time
Peeper membrane material	Polysulfone/ polyethersulfone have been widely used and tested in modern peeper designs 0.45-µm pore sizes are reasonable for limiting unavailable metals from entry into the peeper chamber	None needed, as 0.45-µm polysulfone/polyethersulfone are robust choices for peeper membranes
Peeper chamber volume and design factor	A variety of peeper designs ranging from approximately 0.01 to 100 mL have been used successfully 50-100 mL volumes are optimal for commercial analysis, but require longer deployment times (several weeks) Use of multiple smaller peepers (with compositing) is an option, but increases sampling effort	Compare equilibrium speed and sampling logistics between large (50-100 mL) and multiple smaller peepers (e.g., 10-15 mL), and/or large peepers with small design factors
Peeper water salinity	Peepers are usually constructed with deionized water; it is unknown if the initial difference in peeper water and marine sediment porewater salinity affects the equilibration process	Compare reverse tracer approach in marine sediment using deionized peeper water and artificial marine peeper water
Pre-equilibration sampling	The use of reverse tracers can reduce peeper deployment periods Validation and demonstration with metals of concern often evaluated at sediment sites would improve confidence in methods	Demonstrate ability of reverse tracers to predict concentrations of at equilibrium, including at different sediment salinities
Oxygen contamination during deployment	Oxygen contamination from peeper materials and peeper water that have not been deoxygenated may change conditions in sediment in which peepers are deployed	Evaluate effects of deoxygenation on peeper results, best approaches, peeper materials, and storage time for deoxygenated peepers
Oxygen contamination after deployment	The importance of oxygen contamination of peeper water after removal from sediment is not clear	Evaluate best procedures for transferring peeper water to storage container and hold time for peepers removed from sediment

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APPENDIX A

Annotated Bibliography Table of Reviewed Papers

Appendix A

Reference	Deployment Environment	Deployment Duration (d)	Constituent of Concerns	Equilibrium Confirmed with Measurement?	Peeper Design				Comments	Full Reference
					Type	Membrane (thickness (µm) and material)	Chamber Material	Chamber Volume (mL)		
Abi-Ghanem et al. (2011)	Marine sediments	14	Hg, MeHg	No	Multichambered	0.45 Polycarbonate	Acrylic	Unspecified	-	Abi-Ghanem, C., Nakhlé, K., Khalaf, G., & Cossa, D. (2011). Mercury distribution and methylmercury mobility in the sediments of three sites on the Lebanese coast, eastern Mediterranean. Archives of Environmental Contamination and Toxicology, 60(3), 394–405. https://doi.org/10.1007/s00244-010-9555-9
Azcue et al. (1994)	Freshwater lake	15	As	No	Multichambered	0.45 Cellulose	Unspecified	Unspecified	-	Azcue, J. M., Nriagu, J. O., & Schiff, S. (1994). Role of sediment porewater in the cycling of arsenic in a mine-polluted lake. Environment International, 20(4), 517–527. https://doi.org/10.1016/0160-4120(94)90200-3
Azcue et al. (1996a)	Lake Erie	2-30	Be, Cd, Pb, Mg, V	Yes, using multiple peeper deployment times: 21 days at 4°C, 14 days at 20°C	Multichambered	0.45 Cellulose	HDPE	30	Methods paper describing large volume peeper using bottles	Azcue, J. M., Rosa, F., & Lawson, G. (1996). An improved dialysis sampler for the in situ collection of larger volumes of sediment pore waters. Environmental Technology (United Kingdom), 17(1), 95–100. https://doi.org/10.1080/09593331708616365
Azcue et al. (1996b)	Lake Erie	28	As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn, Sr, Al, Ca, Fe, K, Mg, Na, Si, T	No	Multichambered	0.45 Cellulose	Unspecified	Unspecified	-	Azcue, J. M., Rosa, F., & Mudroch, A. (1996). Distribution of major and trace elements in sediments and pore water of Lake Erie. In Journal of Great Lakes Research (Vol. 22, pp. 389–402). International Association of Great Lakes Research. https://doi.org/10.1016/S0380-1330(96)70964-4
Azcue et al. (1998)	Lake Ontario	Unspecified	Hg, Cr, Ni, Cu, Zn, Cd, Sn, Pb, As	No	Multichambered	0.45 Cellulose	Unspecified	Unspecified	-	Azcue, J. M., Zeman, A. J., Mudroch, A., Rosa, F., & Patterson, T. (1998). Assessment of sediment and porewater after one year of subaqueous capping of contaminated sediments in Hamilton Harbour, Canada. In Water Science and Technology (Vol. 37, pp. 323–329). https://doi.org/10.1016/S0273-1223(98)00214-5
Berry et al. (1996)	Estuarine sediments in lab	10	Cd, Cu, Ni, Pb, Zn	No	Single vials	1.0 Polycarbonate	PE	5	Toxicity test on estuary sediments	Berry, W. J., Hansen, D. J., Mahony, J. D., Robson, D. L., Di Toro, D. M., Shipley, B. P., … Boothman, W. S. (1996). Predicting the toxicity of metal-spiked laboratory sediments using acid- volatile sulfide and interstitial water normalizations. Environmental Toxicology and Chemistry, 15(12), 2067–2079. https://doi.org/10.1002/etc.5620151203
Besser et al. (2009)	Freshwater river	7	Pb, Zn, Cd, Cu, Ni	No	Single vials	0.45 Polyethersulfone	PE	2.9	Assessment of sediment quality of lead mining-impacted river	Besser, J. M., Brumbaugh, W. G., Hardesty, D. K., Hughes, J. P., & Ingersoll, C. G. (2009). Assessment of metal-contaminated sediments from the Southeast Missouri (SEMO) mining district using sediment toxicity tests with amphipods and freshwater mussels. USGS, 1–59.
Besser et al. (2015)	Freshwater sediments in lab	7	Pb, Zn, Cd, Cu, Ni	No	Single vials	0.45 Polyethersulfone	PE	2.9	Based on Besser et al. (2009)	Besser, J. M., Ingersoll, C. G., Brumbaugh, W. G., Kemble, N. E., May, T. W., Wang, N., … Roberts, A. D. (2015). Toxicity of sediments from lead-zinc mining areas to juvenile freshwater mussels (*Lampsilis siliquoidea*) compared to standard test organisms. Environmental Toxicology and Chemistry, 34(3), 626–639. https://doi.org/10.1002/etc.2849
Besser et al. (2018)	Upper Columbia river sediments	7	As, Cd, Cr, Cu, Pb, Ni, Zn	No	Single vials	0.45 Polyethersulfone	PE	3.9	Based on Besser et al. (2009)	Besser, J. M., Steevens, J., Kunz, J. L., Brumbaugh, W. G., Ingersoll, C. G., Cox, S., … MacDonald, D. (2018). Characterizing toxicity of metal-contaminated sediments from the Upper Columbia River, Washington, USA, to benthic invertebrates. Environmental Toxicology and Chemistry, 37(12), 3102–3114. https://doi.org/10.1002/etc.4276
Boothman et al. (2001)	Marine sediment in lab	119	Cd, Cu, Ni, Pb, Zn	No	Single vials	1.0 Polycarbonate	PE	2-3	Based on Pesch et al. (1995)	Boothman, W. S., Hansen, D. J., Berry, W. J., Robson, D. L., Helmstetter, A., Corbin, J. M., & Pratt, S. D. (2001). Biological response to variation of acid-volatile sulfides and metals in field-exposed spiked sediments. Environmental Toxicology and Chemistry, 20(2), 264–272. https://doi.org/10.1002/etc.5620200206
Brumbaugh et al. (1994)	Freshwater river	11	As, Cd, Cu, Zn	No	Single vials	1.0 Polycarbonate	PE	6.3	Investigation of mining and smelting impacted river sediments	Brumbaugh, W. G., Ingersoll, C. G., Kemble, N. E., May, T. W., & Zajicek, J. L. (1994, December). Chemical characterization of sediments and pore water from the upper Clark Fork river and Milltown reservoir, Montana. Environmental Toxicology and Chemistry. https://doi.org/10.1002/etc.5620131211
Brumbaugh et al. (2007)	Freshwater river	14	Co, Ni, Zn, Cd, Pb	Yes, using analytes: 5 days	Single vials	0.45 Polyethersulfone	Polypropylene	50	Investigation of lead mining impacted sediments	Brumbaugh, W. G., May, T., Besser, J. M., Allert, A., & Schmitt, C. (2007). Assessment of elemental concentrations in streams of the new lead belt in southeastern Missouri 2002-05. U.S. Geologi
Brumbaugh et al. (2013)	Freshwater sediments	7	Ni, Fe, Mn	No	Single vials	0.45 Polyethersulfone	PE	2.9	Based on Besser et al. (2009)	Brumbaugh, W. G., Besser, J. M., Ingersoll, C. G., May, T. W., Ivey, C. D., Schlekat, C. E., & Garman, E. R. (2013). Preparation and characterization of nickel-spiked freshwater sediments for toxicity tests: Toward more environmentally realistic nickel partitioning. Environmental Toxicology and Chemistry, 32(11), 2482–2494. https://doi.org/10.1002/etc.2272
Bufflap and Allen (1995)	-	-	-	-	-	-	-	-	Review of sampling methods for trace metals in sediment porewater	Bufflap, S. E., & Allen, H. E. (1995, January 1). Sediment pore water collection methods for trace metal analysis: A review. *Water Research* . Pergamon. https://doi.org/10.1016/0043-1354(94)E0105-F
Burbridge et al. (2012)	Harbor in lake Ontario	20	Cr(VI)	No	Multichambered	1.0 Polycarbonate	LDPE	5	Chromium speciation in sediment	Burbridge, D. J., Koch, I., Zhang, J., & Reimer, K. J. (2012). Chromium speciation in river sediment pore water contaminated by tannery effluent. *Chemosphere* , *89* (7), 838–843. https://doi.org/10.1016/j.chemosphere.2012.05.005
Call et al. (1999)	Freshwater lakes	7	Ag	No	Multichambered	0.2 Polyethersulfone	Acrylic	6	-	Call, D. J., Polkinghorne, C. N., Markee, T. P., Brooke, L. T., Geiger, D. L., Gorsuch, J. W., & Robillard, K. A. (1999). Silver toxicity to *Chironomus tentans* in two freshwater sediments. Environmental Toxicology and Chemistry, 18(1), 30–39. https://doi.org/10.1002/etc.5620180105
Carignan (1984)	Lake sediments	3-20	Methane, inorganic carbon phosphorus, ammonium, Fe	Yes, using equilibration curves: 15 - 20 days	Multichambered	Cellulose, PVC, or polysulfone	Acrylic or polycarbonate	Unspecified	Test of different membranes and plastics for peepers and deoxygenation	Carignan, R. (1984). Interstitial water sampling by dialysis: Methodological notes. Limnology and Oceanography. John Wiley & Sons, Ltd. https://doi.org/10.4319/lo.1984.29.3.0667
Carignan and Nriagu (1985)	Freshwater lake	15-30	Pb, Zn, Ni, Co, Cu, Cd, Cr	No	Multichambered	Unspecified	Acrylic	1	Trace metal analysis in peeper	Carignan, R., & Nriagu, 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. https://doi.org/10.1016/0016-7037(85)90146-2

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					Type	Membrane (thickness (µm) and material)	Chamber Material	Chamber Volume (mL)		
Carignan et al. (1985)	River sediments in lab	7-28	Zn, Cu, Ni, Cr, Co, Cd	Yes, using multiple deployment times: 7 days	Multichambered	0.45 Polysulfone, 0.03 polycarbonate, Amicon 0.002 and Amicon 0.001	Acrylic	Unspecified	Comparison of peeper and centrifugation for porewater sampling	Carignan, R., Rapin, F., & Tessier, A. (1985). Sediment porewater sampling for metal analysis: A comparison of techniques. *Geochimica et Cosmochimica Acta* , *49* (11), 2493–2497. https://doi.org/10.1016/0016-7037(85)90248-0
Chapman et al. (2002)	-	-	-	-	-	-	-	-	Letter on the advantages and disadvantages of porewater testing	Chapman, P. M., Wang, F., Germano, J. D., & Batley, G. (2002). Pore water testing and analysis: The good, the bad, and the ugly. *Marine Pollution Bulletin* , *44* (5), 359–366. https://doi.org/10.1016/S0025-326X(01)00243-0
Chen et al. (2015)	Freshwater lake sediment in lab	2	Fe, phosphorus	No	Multichambered	0.45 Cellulose nitrate	Unspecified	0.018	Use of DGT and peeper	Chen, M., Ding, S., Liu, L., Xu, D., Han, C., & Zhang, C. (2015). Iron-coupled inactivation of phosphorus in sediments by macrozoobenthos (chironomid larvae) bioturbation: Evidences from high-resolution dynamic measurements. *Environmental Pollution* , *204* , 241–247. https://doi.org/10.1016/j.envpol.2015.04.031
Chen et al. (2017)	Freshwater lake sediment in lab	2	Pb, Cd, Zn, Co, Ni	No	Multichambered	0.45 Cellulose nitrate	Acrylic	0.2	Use of DGT and peeper	Chen, M., Ding, S., Zhang, L., Li, Y., Sun, Q., & Zhang, C. (2017). An investigation of the effects of elevated phosphorus in water on the release of heavy metals in sediments at a high resolution. *Science of the Total Environment* , *575* , 330–337. https://doi.org/10.1016/j.scitotenv.2016.10.063
Chen et al. (2019)	Freshwater lake in Lab	1	Co, Zn, Ni	No	Multichambered	0.45 Cellulose	Unspecified	0.2	Similar to Xu et al. (2012)	Chen, M., Ding, S., Gao, S., Xu, S., Yang, C., Wu, Y., … Wang, Y. (2019). Long-term effects of sediment dredging on controlling cobalt, zinc, and nickel contamination determined by chemical fractionation and passive sampling. Chemosphere, 220, 476–485. https://doi.org/10.1016/j.chemosphere.2018.12.138
Chowdhury and Al Bakri (2006)	Freshwater reservoir	14	Nutrients	No	Multichambered	Polysulfone	Unspecified	Unspecified	-	Chowdhury, M., & Al Bakri, D. (2006). Diffusive nutrient flux at the sediment-water interface in Suma Park Reservoir, Australia. *Hydrological Sciences Journal* , *51* (1), 144–156. https://doi.org/10.1623/hysj.51.1.144
Cleveland et al. (2017)	Contaminated mine sediments	10	Ni, Cu, Zn, As, Cd, Pb, Na, Mg, K, Ca, Fe, Mn, Sr, TOC	No	Single vials	0.45 Polyethersulfone	Unspecified	2.9	Comparison of peepers vs other sampling methods for metals and TOC in sediment porewater; Based on Besser et al. (2009) design	Cleveland, D., Brumbaugh, W. G., & MacDonald, D. D. (2017). A comparison of four porewater sampling methods for metal mixtures and dissolved organic carbon and the implications for sediment toxicity evaluations. *Environmental Toxicology and Chemistry* , *36* (11), 2906–2915. https://doi.org/10.1002/etc.3884
Costello et al. (2015)	River sediment in lab	7	Cu, Fe, Mn, DOC	No	Single vials	0.45 Polyethersulfone	PE	4.9	Based on Besser et al. (2009)	Costello, D. M., Hammerschmidt, C. R., & Burton, G. A. (2015). Copper sediment toxicity and partitioning during oxidation in a flow-through flume. Environmental Science and Technology, 49(11), 6926–6933. https://doi.org/10.1021/acs.est.5b00147
Costello et al. (2016)	River sediment in lab	2-100	DOC, Ni	No	Single vials	0.45 Polyethersulfone	PE	4.9	Based on Besser et al. (2009)	Costello, D. M., Hammerschmidt, C. R., & Burton, G. A. (2016). Nickel Partitioning and Toxicity in Sediment during Aging: Variation in Toxicity Related to Stability of Metal Partitioning. Environmental Science and Technology, 50(20), 11337–11345. https://doi.org/10.1021/acs.est.6b04033
Costello et al. (2019)	River sediment in lab	28	DOC, Cu and Ni	No	Single vials	0.45 Polyethersulfone	PE	4.9	Based on Besser et al. (2009)	Costello, D. M., Harrison, A. M., Hammerschmidt, C. R., Mendonca, R. M., & Burton, G. A. (2019). Hitting Reset on Sediment Toxicity: Sediment Homogenization Alters the Toxicity of Metal-Amended Sediments. Environmental Toxicology and Chemistry, 38(9), 1995–2007. https://doi.org/10.1002/etc.4512
Dattagupta et al. (2007)	Deep sea sediment	35	pH, salinity, sulfate, sulfide, dissolved methane, sulfur stable isotope ratios	No, but empirical calculation of diffusion coefficients	Multichambered	0.005-0.010 PVDF [1]	CPVC	4	unmanned deployment using submarine	Dattagupta, S., Telesnicki, G., Luley, K., Predmore, B., McGinley, M., & Fisher, C. R. (2007). Submersible operated peepers for collecting porewater from deep-sea sediments. *Limnology and Oceanography: Methods* , *5* (SEP), 263–268. https://doi.org/10.4319/lom.2007.5.263
Dewitt et al. (1996)	Marine sediments in lab	7-35	Cd	Yes: 7 days	Single vials	1.0 Polycarbonate	PE	4.5	Saltwater used in marine deployment of peepers	Dewitt, T. H., Swartz, R. C., Hansen, D. J., Mcgovern, D., & Berry, W. J. (1996). Bioavailability and chronic toxicity of cadmium in sediment to the estuarine amphipod *Leptocheirus plumulosus* . Environmental Toxicology and Chemistry, 15(12), 2095–2101. https://doi.org/10.1002/etc.5620151205
Di Toro et al. (1990)	Estuarine Sediments in Lab	1-10	Cd	Yes: 1 day	Multichambered	1.0 Polycarbonate	Acrylic	5	Sediment toxicity experiments	Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Hicks, M. B., Mayr, S. M., & Redmond, M. S. (1990). Toxicity of cadmium in sediments: The role of acid volatile sulfide. Environmental Toxicology and Chemistry, 9(12), 1487–1502. https://doi.org/10.1002/etc.5620091208
Ding et al. (2018)	Freshwater lake	2-3	Phosphorus, Fe	No	Multichambered	0.45 Cellulose	Unspecified	0.2	Similar to Xu et al. (2012)	Ding, S., Chen, M., Gong, M., Fan, X., Qin, B., Xu, H., … Zhang, C. (2018). Internal phosphorus loading from sediments causes seasonal nitrogen limitation for harmful algal blooms. Science of the Total Environment, 625, 872–884. https://doi.org/10.1016/j.scitotenv.2017.12.348
Doig and Liber (2000)	Lake sediments in lab	0.04-8	Ni, Zn	Yes, Spiked sediments. 2 - 4 days	Multichambered	0.2 Polysulfone	Acrylic	0.75	Lab test of mini peepers	Doig, L., & Liber, K. (2000). Dialysis minipeeper for measuring pore-water metal concentrations in laboratory sediment toxicity and bioavailability tests. Environmental Toxicology and Chemistry: An International Journal, 19(12), 2882-2889.
Doussan et al. (1998)	River sediment	15	Ammonia	No	Multichambered	0.2 Nylon	Unspecified plastic	Unspecified	Peeper based on Hesslein (1976)	Doussan, C., Ledoux, E., & Detay, M. (1998). River-Groundwater Exchanges, Bank Filtration, and Groundwater Quality: Ammonium Behavior. Journal of Environmental Quality, 27(6), 1418–1427. https://doi.org/10.2134/jeq1998.00472425002700060019x
Fan et al. (2019)	Freshwater lake in Lab	1	Cr(VI), Cr(V), S, DOC, Ca, Mg, Fe, Mn	No	Multichambered	0.45 Cellulose	Unspecified	0.2	Similar to Xu et al. (2012)	Fan, X., Ding, S., Chen, M., Gao, S., Fu, Z., Gong, M., … Zhang, C. (2019). Peak Chromium Pollution in Summer and Winter Caused by High Mobility of Chromium in Sediment of a Eutrophic Lake: In Situ Evidence from High Spatiotemporal Sampling. Environmental Science and Technology, 53(9), 4755–4764. https://doi.org/10.1021/acs.est.8b07060
Fawcett et al. (2015)	Freshwater lake	14	As, Mn, Sb, Sulfate	No	Multichambered	0.45 Polysulfone	Acrylic	5.7	Based on Martin et al. (2001)	Fawcett, S. E., Jamieson, H. E., Nordstrom, D. K., & McCleskey, R. B. (2015). Arsenic and antimony geochemistry of mine wastes, associated waters and sediments at the Giant Mine, Yellowknife, Northwest Territories, Canada. Applied Geochemistry, 62, 3–17. https://doi.org/10.1016/j.apgeochem.2014.12.012

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Fortin et al. (2004)	Tailing pond	1	Cu, Pb, Zn, Ni, Cd, As, Tl	No	Multichambered	0.2 Polysulfone	Acrylic	4	Detailed description of deployment and recovery	Fortin, C., Rancourt, L., & Campbell, P. G. C. (2004). *METAL FLUXES AT THE WATER-SEDIMENT INTERFACE OF SHALLOW MINE TAILINGS PONDS, HEATH STEELE MINE, NEW BRUNSWICK* .
Frost et al. (2019)	Stormwater Sediment pond	14	Phosphorus	No	Single vials	0.2 Polycarbonate	HDPE	125		Frost, P. C., Prater, C., Scott, A. B., Song, K., & Xenopoulos, M. A. (2019). Mobility and Bioavailability of Sediment Phosphorus in Urban Stormwater Ponds. *Water Resources Research* , *55* (5), 3680–3688. https://doi.org/10.1029/2018WR023419
Gaillard et al. (1989)	Marine bay sediment	20	Ca, Sulfide, Sulfate, Br, Mg, Mn, Phosphate, Cl	No	Multichambered	0.2 Acrylic	Unspecified	3.5-10	Investigation of carbonate system in marine sediments porewater	Gaillard, J. F., Pauwels, H., & Michard, G. (1989). Chemical diagenesis in coastal marine sediments. Oceanologica Acta, 12(3), 175–187. Retrieved from https://www.scholars.northwestern.edu/en/publications/chemical-diagenesis-in-coastal-marine-sediments
Geosyntec and AECOM (2019)	River sediment	28	As, Mn	Using Br tracer: 100 days (90% of equilibrium)	Single vials	0.45 Polysulfone	HDPE	60		Geosyntec, & AECOM. (2019). PDI Evaluation Report Portland Harbor Pre-Remedial Design Investigation and Baseline Sampling Portland Harbor Superfund Site Portland, Oregon. US Environmental Protection Agency.
Greenstein et al. (2014)	Urban estuary	29	Ag, As, Cd, Cd, Cr, Cu, Ni, Pb, Sn, Zn	No	Single vials	0.45 Polyethersulfone	LDPE	50	-	Greenstein, D. J., Bay, S. M., Young, D. L., Asato, S., Maruya, K. A., & Lao, W. (2014). The use of sediment toxicity identification evaluation methods to evaluate clean up targets in an urban estuary. Integrated Environmental Assessment and Management, 10(2), 260–268. https://doi.org/10.1002/ieam.1512
Grigg et al. (1999)	Marine sediments in lab	1-10	Mn	Yes, using NaCl concentrations: 8 days	Multichambered	0.45 Polysulfone	Unspecified	3.6	Numerical model and laboratory experiment on porewater convection after peeper insertion	Grigg, N. J., Webster, I. T., & Ford, P. W. (1999). Pore-water convection induced by peeper emplacement in saline sediment. *Limnology and Oceanography* , *44* (2), 425–430. https://doi.org/10.4319/lo.1999.44.2.0425
Hansen et al. (1996)	Fresh and saltwater sediments in lab	10	Cd, Cu, Ni, Pb, Zn	No	Single vials	1.0 Polycarbonate	PE	5	Toxicity test on five saltwater and four freshwater sediments from USA, Canada and China	Hansen, D. J., Berry, W. J., Mahony, J. D., Boothman, W. S., Di Toro, D. M., Robson, D. L., … Pesch, C. E. (1996). Predicting the toxicity of metal-contaminated field sediments using interstitial concentration of metals and acid-volatile sulfide normalizations. Environmental Toxicology and Chemistry, 15(12), 2080–2094. https://doi.org/10.1002/etc.5620151204
Harper et al. (1997)	-	-	-	-	-	-	-	-	Modeling equilibration dynamics for peepers and DET samplers, effect of solute resupply on equilibration time	Harper, M. P., Davison, W., & Tych, W. (1997). Temporal, spatial, and resolution constraints for in situ sampling devices using diffusional equilibration: dialysis and DET. Environmental science & technology, 31(11), 3110-3119.
Hesslein (1976)	River sediment	7	Methane and phosphate	Yes, using Cl ions: 7 days	Multichambered	Unspecified	Acrylic	4	Earliest example of peeper application to measure sediment porewater	Hesslein, R. H. (1976). An in situ sampler for close interval pore water studies. Limnology and Oceanography. John Wiley & Sons, Ltd. https://doi.org/10.4319/lo.1976.21.6.0912
Holmes and Lean (2006)	Marsh	15	MeHg	No	Multichambered	0.2 Polysulfone	Polycarbonate	4	-	Holmes, J., & Lean, D. (2006). Factors that influence methylmercury flux rates from wetland sediments. Science of the Total Environment, 368(1), 306–319. https://doi.org/10.1016/j.scitotenv.2005.11.027
Hu et al. (2013)	Synthetic sediments	21	Cu, Zn, Ni, Co, Mn , DOC, chloride	Yes, using Cl ions: 1 days	Multichambered	0.22 PVDF	Acrylic	4	Testing the effect of humic acid on metal diffusion in peepers	Hu, C., Zhang, Y., & Luo, W. (2013). Retention effects of soil Humic substances on the diffusive transportation of metal ions during sediment porewater membrane dialysis sampling. Water, Air, and Soil Pollution, 224(6), 1–9. https://doi.org/10.1007/s11270-013-1577-2
Huerta-Diaz et al. (2007)	San Francisco Bay estuary	7	Ag, Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn	No	Multichambered	0.45 Polycarbonate or 0.001 PTFE	Polycarbonate	6.3	-	Huerta-Diaz, M. A., Rivera-Duarte, 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, 22(11), 2509–2525. https://doi.org/10.1016/j.apgeochem.2007.07.001
Jackson et al. (2005)	Rhizosphere	14	VOC, chloroacetic acids, organic acids, chloride	No	Multichambered	0.2 polysulfone and 8.0 nylon	Acrylic	20	Peeper use to monitor phytoremediation	Jackson, W. A., Martino, L., Hirsh, S., Wrobel, J., & Pardue, J. H. (2005). Application of a dialysis sampler to monitor phytoremediation processes. *Environmental Monitoring and Assessment* , *107* (1–3), 155–171. https://doi.org/10.1007/s10661-005-5436-5
Jacobs (2002)	Lake sediment	21	Na, Fe, Ni	No	Multichambered	0.45 Polytetrafluorethylene	Acrylic	47.3	in situ rechargeable peeper, lab and field tested	Jacobs, P. H. (2002). A new rechargeable dialysis pore water sampler for monitoring sub-aqueous in-situ sediment caps. *Water Research* , *36* (12), 3121–3129. https://doi.org/10.1016/S0043-1354(01)00542-5
Johnston et al., (2009)	Acid sulfate soils	32-38	Fe, bicarbonate, chloride, potassium	Yes, Cl ions: 32-38 days	Multichambered with vials	0.45 Polysulfone	HDPE	25	Originally used a 14-16 days equilibration but found it insufficient	Johnston, S. G., Burton, E. D., Keene, A. F., Bush, R. T., Sullivan, L. A., & Isaacson, L. (2009). Pore Water Sampling in Acid Sulfate Soils: A New Peeper Method. Journal of Environmental Quality, 38(6), 2474–2477. https://doi.org/10.2134/jeq2009.0135
Koretsky et al. (2006)	Freshwater lake sediment	21-28	Fe, Anions, nutrients, organic and inorganic carbon	No	Unspecified	Unspecified	Unspecified	Unspecified		Koretsky, C. M., Haas, J. R., Miller, D., & Ndenga, N. T. (2006). Seasonal variations in pore water and sediment geochemistry of littoral lake sediments (Asylum Lake, MI, USA). *Geochemical Transactions* , *7* (1), 1–26. https://doi.org/10.1186/1467-4866-7-11
Langer et al. (2001)	Salt marsh	14	MeHg	No	Multichambered	0.0003 Polysulfone [3]	PTFE	40	-	Langer, C. S., Fitzgerald, W. F., Visscher, P. T., & Vandal, G. M. (2001). Biogeochemical cycling of methylmercury at Barn Island Salt Marsh, Stonington, CT, USA. Wetlands Ecology and Management, 9(4), 295–310. https://doi.org/10.1023/A:1011816819369
Larson et al. (2012)	Freshwater sediments	18-22	As, U	No	Multichambered	0.45 Nylon	Acrylic	4.5	-	Larson, L. N., Kipp, G. G., Mott, H. V., & Stone, J. J. (2012). Sediment pore-water interactions associated with arsenic and uranium transport from the North Cave Hills mining region, South Dakota, USA. Applied Geochemistry, 27(4), 879–891. https://doi.org/10.1016/j.apgeochem.2012.01.008

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Lewis et al. (2016)	Freshwater pond	25-121	Hg, MeHg	No	Multichambered	0.45 Polysulfone	Acrylic	5	-	Lewis, A. S., Huntington, T. G., Marvin-Dipasquale, M. C., & Amirbahman, A. (2016). Mercury remediation in wetland sediment using zero-valent iron and granular activated carbon. Environmental Pollution, 212, 366–373. https://doi.org/10.1016/j.envpol.2015.11.047
Liber et al. (1996)	Freshwater pond	10	Zn	Yes, using Zn: 7 days	Multichambered	0.2 Polysulfone	Acrylic	6	Study of sulfide effect on bioavailability of Zn	Liber, K., Call, D. J., Markee, T. P., Schmude, K. L., Balcer, M. D., Whiteman, F. W., & Ankley, G. T. (1996). Effects of acid-volatile sulfide on zinc bioavailability and toxicity to benthic macroinvertebrates: A spiked-sediment field experiment. Environmental Toxicology and Chemistry, 15(12), 2113–2125. https://doi.org/10.1002/etc.5620151207
Liber et al. (2011)	Lake sediment in lab	20-30	Al, As, B, Ba, Cd, Co, Cr, Cs, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Sr, Th, U, Zn	No	Multichambered	0.2 Polyethersulfone	Acrylic	0.75	Based on Doig and Liber (2000)	Liber, K., Doig, L. E., & White-Sobey, S. L. (2011). Toxicity of uranium, molybdenum, nickel, and arsenic to *Hyalella azteca* and *Chironomus dilutus* in water-only and spiked-sediment toxicity tests. Ecotoxicology and Environmental Safety, 74(5), 1171–1179. https://doi.org/10.1016/j.ecoenv.2011.02.014
Liu et al. (2011)	Rice paddy sediment and reservoir sediment	30	MeHg	No	Multichambered	0.22 Acrylic	Acrylic	7	Included comparison of peepers to other porewater techniques	Liu, J., Feng, X., Qiu, G., Yao, H., Shang, L., & Yan, H. (2011). Intercomparison and applicability of some dynamic and equilibrium approaches to determine methylated mercury species in pore water. Environmental Toxicology and Chemistry, 30(8), 1739–1744. https://doi.org/10.1002/etc.565
MacDonald et al. (2013)	Wetland	28-250	Cl, Sulfide, DOC, Cr, Fe	Yes, using Cl ions: 10 days	Multichambered	0.22 Polyethersulfone	PVC	3	Example of semi-permanent peeper. Sample tubes running up to surface for sampling-recharging	MacDonald, L. H., Paull, J. S., & Jaffé, P. R. (2013). Enhanced semipermanent dialysis samplers for long-term environmental monitoring in saturated sediments. Environmental Monitoring and Assessment, 185(5), 3613–3624. https://doi.org/10.1007/s10661-012-2813-8
Martin and Pedersen (2002)	Freshwater tailings pond	14	Mn, Fe, As	No	Multichambered	0.45 Polysulfone	Acrylic	5.7	Based on Martin et al. (2001)	Martin, A. J., & Pedersen, T. F. (2002). Seasonal and interannual mobility of arsenic in a lake impacted by metal mining. Environmental Science and Technology, 36(7), 1516–1523. https://doi.org/10.1021/es0108537
Martin et al. (2001)	Freshwater lake	14	Cu, Fe, Mn, Ni, Pb, Sulfate, Sulfide, Zn	No	Multichambered	0.45 Polysulfone	Acrylic	5.7	Investigation of mining-impacted sediments	Martin, A. J., McNee, J. J., & Pedersen, T. F. (2001). The reactivity of sediments impacted metal-mining in Lago Junin, Peru. Journal of Geochemical Exploration, 74(1–3), 175–187. https://doi.org/10.1016/S0375-6742(01)00183-2
Mason et al. (1998)	Marine bay sediment	7	Hg, MeHg	Using Cl and Sulfate: 9-90 days depending on design	Multichambered	0.0001 Polysulfone [2]	PTFE	50	Hypothesized results for MeHg may have been affected by a poorly-deoxygenated peeper	Mason, R., Bloom, N., Cappellino, S., Gill, G., & Benoit, J. (1998). Investigation of porewater sampling methods for mercury and methylmercury. Environmental Science and Technology, 32(24), 4031–4040. https://doi.org/10.1021/es980377t
Muresan et al. (2007)	Lagoon	8	Fe, Hg, MeHg, Sulfide	No	Multichambered	0.22 PVDF	Acrylic	10	-	Muresan, B., Cossa, D., Jézéquel, D., Prévot, F., & Kerbellec, S. (2007). The biogeochemistry of mercury at the sediment-water interface in the Thau lagoon. 1. Partition and speciation. Estuarine, Coastal and Shelf Science, 72(3), 472–484. https://doi.org/10.1016/j.ecss.2006.11.015
Murphy et al. (2001)	Lake sediment	14	Phosphorus	No	Multichambered	0.45 Polysulfone	Acrylic	12		Murphy, T., Lawson, A., Kumagai, M., & Nalewajko, C. (2001). Release of phosphorus from sediments in Lake Biwa. *Limnology* , *2* (2), 119–128. https://doi.org/10.1007/s102010170007
Passeport et al. (2016)	Freshwater canal	28	VOCs	No	Multichambered	0.45 Polysulfone	Glass	40	Deployed from boat, detailed description of methods	Passeport, E., Landis, R., Lacrampe-Couloume, G., Lutz, E. J., Erin Mack, E., West, K., … Lollar, B. S. (2016). Sediment monitored natural recovery evidenced by compound specific isotope analysis and high-resolution pore water sampling. *Environmental Science and Technology* , *50* (22), 12197–12204. https://doi.org/10.1021/acs.est.6b02961
Peijnenburg et al. (2014)	-	-	-	-	-	-	-	-	Review paper	Peijnenburg, W. J. G. M., Teasdale, P. R., Reible, D., Mondon, J., Bennett, W. W., & Campbell, P. G. C. (2014). Passive sampling methods for contaminated sediments: State of the science for metals. *Integrated Environmental Assessment and Management* , *10* (2), 179–196. https://doi.org/10.1002/ieam.1502
Pesch et al. (1995)	Marine sediments in lab	10	Cd, Ni	No	Single vials	1.0 Polycarbonate	PE	5	Saltwater used in marine deployment of peepers	Pesch, C. E., Hansen, D. J., Boothman, W. S., Berry, W. J., & Mahony, J. D. (1995). The role of acid-volatile sulfide and interstitial water metal concentrations in determining bioavailability of cadmium and nickel from contaminated sediments to the marine polychaete *Neanthes arenaceodentata* . Environmental Toxicology and Chemistry, 14(1), 129–141. https://doi.org/10.1002/etc.5620140115
Rigaud et al. (2013)	Lagoon	21	Fe, Mn, As, Co, Cr, Ni, Hg, MeHg	No	Multichambered	0.45 Polycarbonate	Acrylic	Unspecified	Diver deployment	Rigaud, S., Radakovitch, O., Couture, R. M., Deflandre, B., Cossa, D., Garnier, C., & Garnier, J. M. (2013). Mobility and fluxes of trace elements and nutrients at the sediment-water interface of a lagoon under contrasting water column oxygenation conditions. *Applied Geochemistry* , *31* , 35–51. https://doi.org/10.1016/j.apgeochem.2012.12.003
Schroeder et al. (2020)	Estuary	14	Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, V, Zn, nutrients	No	Multichambered	0.45 Polyethersulfone	Acrylic	10	Diver deployment	Schroeder, H., Duester, L., Fabricius, A. L., Ecker, D., Breitung, V., & Ternes, T. A. (2020). Sediment water (interface) mobility of metal(loid)s and nutrients under undisturbed conditions and during resuspension. *Journal of Hazardous Materials* , *394* , 122543. https://doi.org/10.1016/j.jhazmat.2020.122543
Schuh et al. (2018)	Freshwater lake	14	As, Fe, Mn, S, Sb,	No	Multichambered	0.45 Polyethersulfone	Acrylic	5.7	Based on Martin et al. (2001)	Schuh, C. E., Jamieson, H. E., Palmer, M. J., & Martin, A. J. (2018). Solid-phase speciation and post-depositional mobility of arsenic in lake sediments impacted by ore roasting at legacy gold mines in the Yellowknife area, Northwest Territories, Canada. Applied Geochemistry, 91, 208–220. https://doi.org/10.1016/j.apgeochem.2017.10.025
Serbst et al. (2003)	Marine sediment in lab	10	Cd	No	Single vials	1.0 Polycarbonate (single or double membrane)	LDPE	5	Lab experiment to look at peeper precision	Serbst, J. R., Burgess, R. M., Kuhn, A., Edwards, P. A., Cantwell, M. G., Pelletier, M. C., & Berry, W. J. (2003). Precision of dialysis (peeper) sampling of cadmium in marine sediment interstitial water. *Archives of Environmental Contamination and Toxicology* , *45* (3), 297–305. https://doi.org/10.1007/s00244-003-0114-5

Reference	Deployment Environment	Deployment Duration (d)	Constituent of Concerns	Equilibrium Confirmed with Measurement?	Peeper Design				Comments	Full Reference
					Type	Membrane (thickness (µm) and material)	Chamber Material	Chamber Volume (mL)		
Simon et al. (1985)	Estuarine river	5-15	Cl, Sulfate, Phosphate, bromide, nitrate, ammonia	Yes, using multiple peeper deployment times: 5-10 days at 5°C, 7 days at 21°C	Multichambered	0.2 Polycarbonate	Acrylic	1	Experiment noted slower equilibration at lower temperatures	Simon, N. S., Kennedy, M. M., & Massoni, C. S. (1985). Evaluation and use of a diffusion-controlled sampler for determining chemical and dissolved oxygen gradients at the sediment-water interface. Hydrobiologia, 126(2), 135–141. https://doi.org/10.1007/BF00008680
Steinmann and Shotyk (1997)	Sphagnum peat bog	28-42	Anions, Fe, Al, Mg	Yes, using Cl ions: 28-46 days	Multichambered	0.2 Polysulfone	Acrylic	30	Deployed in bog	Steinmann, P., & Shotyk, W. (1997). Chemical composition, pH, and redox state of sulfur and iron in complete vertical porewater profiles from two Sphagnum peat bogs, Jura Mountains, Switzerland. Geochimica et Cosmochimica Acta, 61(6), 1143–1163. https://doi.org/10.1016/S0016-7037(96)00401-2
Steward and Malley (1999)	Freshwater lakes	14	Cd, Cu, Ni, Pb, Zn	No	Multichambered	0.2 Polysulfone	PE	2.5	-	Stewart, A. R., & Malley, D. F. (1999). Effect of metal mixture (Cu, Zn, Pb, and Ni) on cadmium partitioning in littoral sediments and its accumulation by the freshwater macrophyte *Eriocaùlon septangulàre* . Environmental Toxicology and Chemistry, 18(3), 436–447. https://doi.org/10.1002/etc.5620180311
Tan et al., (2005)	Groundwater fed streams	14-28	Perchlorate, anions	Yes, using Cl ions: 14 days	Multichambered	0.2 Polysulfone	Unspecified	9	Use of needle to pierce membrane and extract water	Tan, K., Anderson, T. A., & Jackson, W. A. (2005). Temporal and spatial variation of perchlorate in streambed sediments: Results from in-situ dialysis samplers. Environmental Pollution, 136(2), 283–291. https://doi.org/10.1016/j.envpol.2004.12.037
Teasdale et al. (1995)	-	-	-	-	-	-	-	-	Review paper	Teasdale, P. R., Batley, G. E., Apte, S. C., & Webster, I. T. (1995). Pore water sampling with sediment peepers. *Trends in Analytical Chemistry* , *14* (6), 250–256. https://doi.org/10.1016/0165-9936(95)91617-2
Teasdale et al. (2003)	Estuarine sediments	5-6	Cu	No	Multichambered (double sided)	0.45 Polysulfone	Acrylic	Unspecified	Diver deployment	Teasdale, P. R., Apte, S. C., Ford, P. W., Batley, G. E., & Koehnken, L. (2003). Geochemical cycling and speciation of copper in waters and sediments of Macquarie Harbour, Western Tasmania. *Estuarine, Coastal and Shelf Science* , *57* (3), 475–487. https://doi.org/10.1016/S0272-7714(02)00381-5
Tessier et al. (1989)	Lake sediments	14	Zn	No	Multichambered	0.2 Polysulfone	Acrylic	3.3	Zn study from multiple Ontario and Quebec lakes	Tessier, A., Carignan, R., Dubreuil, B., & F, R. (1989). Partitioning of zinc between the water column and the oxic sediments in lakes. Geochimica et Cosmochimica Acta, 53(7), 1511–1522. https://doi.org/10.1016/0016-7037(89)90234-2
Tessier et al. (1993)	Lake sediments	14	Cd	No	Multichambered	0.2 Polysulfone	Acrylic	3.3	Based on Tessier et al. (1989)	Tessier, A., Couillard, Y., Campbell, P. G. C., & Auclair, J. C. (1993). Modeling Cd partitioning in oxic lake sediments and Cd concentrations in the freshwater bivalve Anodonta grandis. Limnology and Oceanography, 38(1), 1–17. https://doi.org/10.4319/lo.1993.38.1.0001
Thomas and Arthur (2010)	Bog	7	Anions, ORP, bromide, acetate	Yes, using Br tracer: 7 days	Multichambered	0.2 Polypropylene	Unspecified Nalgene	5	Demonstration of reverse tracer, detailed methodology and math on equilibration times	Thomas, B., & Arthur, M. A. (2010). Correcting porewater concentration measurements from peepers: Application of a reverse tracer. *Limnology and Oceanography: Methods* , *8* (AUG), 403–413. https://doi.org/10.4319/lom.2010.8.403
Urban et al. (1997)	Eutrophic Lake	14	Major cations, anions, methane	No	Multichambered	0.2 Polysulfone	Acrylic	Unspecified	Deployed with a tripod and inspected with a camera	Urban, N. R., Dinkel, C., & Wehrli, B. (1997). Solute transfer across the sediment surface of a eutrophic lake: I. Porewater profiles from dialysis samplers. *Aquatic Sciences* , *59* (1), 1–25. https://doi.org/10.1007/BF02522546
Webster et al. (1998)	Water or Sediment	1-75	K, Na, Ca, Sr	Yes, using K and Sr: 9-90 days depending on design	Single vials	0.45 Polysulfone	LDPE	25	Modeling and experimentation on equilibration dynamics, use of bromide tracer	Webster, I. T., Teasdale, P. R., & Grigg, N. J. (1998). Theoretical and experimental analysis of peeper equilibration dynamics. *Environmental Science and Technology* , *32* (11), 1727–1733. https://doi.org/10.1021/es970815g
Webster et al. (1999)	Marine sediment in lab	1-10	Mg	Yes, using multiple peeper deployment times: 1 day	Multichambered	0.45 Polysulfone	Unspecified	3.6	Experiment to evaluate use of deionized water in peepers deployed in marine sediment	Webster, I. T., Ford, P. W., & Grigg, N. J. (1999). Pore-water convection induced by peeper emplacement in saline sediment. Limnology and Oceanography, 44(2), 425–430. https://doi.org/10.4319/lo.1999.44.2.0425
Wise (2009)	Freshwater sediment, lab and field	7-35	Fe, Cd, Cr	Yes, using multiple peeper deployment times: 7 days (field), 28 days (lab)	Multichambered	0.2 Polysulfone	Polycarbonate	13.5	Review of peepers and experiments with sampling techniques	Wise, D. E. (2009). *Sampling techniques for sediment pore water in evaluation of reactive capping efficacy* . *ProQuest Dissertations and Theses* . Retrieved from https://scholars.unh.edu/thesis/502
Xu and al. (2012)	Lake sediment	2	Phosphate, Fe	Yes, using multiple peeper deployment times: 2 days	Multichambered	0.45 Cellulose	Unspecified	0.014	Peeper frozen after retrieval	Xu, D., Wu, W., Ding, S., Sun, Q., & Zhang, C. (2012). A high-resolution dialysis technique for rapid determination of dissolved reactive phosphate and ferrous iron in pore water of sediments. Science of the Total Environment, 421–422, 245–252. https://doi.org/10.1016/j.scitotenv.2012.01.062

Notes and Non-elemental Acronyms

[1]: Membrane pore size was reported as 500 kiloDaltons, which was assumed to correspond to an approximate 0.005-0.010 µm pore size.
[2]: Membrane pore size was reported as 10 kiloDaltons, which was assumed to correspond to an approximate 0.0001 µm pore size.
[3]: Membrane pore size was reported as 30 kiloDaltons, which was assumed to correspond to an approximate 0.0003 µm pore size.

CPVC	chlorinated polyvinyl chloride
HDPE	high density polyethylene
LDPE	low density polyethylene
ORP	oxidation-reduction potential
PE	polyethylene
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene difluoride
VOCs	volatile organic compounds

Appendix B: Laboratory Experiments Report

Laboratory Testing Report

Standardizing Sediment Porewater Passive Samplers for Inorganic Constituents of Concern
ESTCP ER20-5261

October 2023

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Figure 3-9: Concentrations of metals and lithium tracer in sediment-deployed peeper waters extracted using two different methods. Peepers were deployed for 14 days in unaerated (anoxic) sediment for 14 days prior to sample extraction. Red-filled symbols are raw data that are plotted (and included in calculation of average) that are below the MDL, with the value being used representing 1/2 of the MDL. Data are not shown for mercury due to the high number of ND results.

Figure 3-10: Concentrations of copper, zinc, manganese, an iron in sediment-deployed peeper waters pipetted in air (a) or nitrogen (b). Peepers were deployed in either aerated (hypoxic) standard sediment or unaerated (anoxic) spiked sediment for 14 days prior to sample extraction. Data shown only for copper, zinc, manganese, and iron because other target metals were added to the sediment after the aerated (hypoxic) sediment test, but before the unaerated (anoxic) sediment test.

Figure 3-11: Oxygen concentrations in peepers stored using various methods, graphed over time (note Log10-scale x-axis).

Figure 3-12: Concentration of oxygen in peepers left exposed to the ambient atmosphere.

Figure 3-13: Concentrations of metals in spiked sediment-deployed peeper waters stored in various approaches with oxygen munchers and time periods prior to sample preservation. Data are not shown for mercury due to the high number of ND results. "*" symbols indicate results that differ significantly ($P < 0.05$) from peepers processed immediately. Outliers are not shown in the cadmium, copper, and nickel figures because they would distort the figure scale.

Figure 3-14: One-compartment first-order uptake models applied to concentrations of target metals for peepers deployed in metal-spiked water for various time periods.

Figure 3-15: One-compartment first-order elimination models applied to concentrations of lithium and bromide tracers for peepers deployed in metal-spiked water for various time periods.

Figure 3-16: Percent to equilibrium for the lithium tracer over the 28-day exposure in water.

Figure 3-17: Model-predicted equilibrium concentrations for each peeper sample (deployed in metal-spiked water for various time periods) divided by the average measured concentration in the water in which peepers were deployed. The dotted green line indicates perfect agreement (i.e., a value of 1) between the model-predicted equilibrium concentration in the peeper and the average measured concentration of the water.

Figure 3-18: Concentrations of target metals, iron, and manganese for peepers deployed in standard metal-spiked sediment (aerated) for various time periods up to 28 days. One-compartment first-order uptake models are shown for iron and manganese, and an elimination model is shown for zinc. Data is not shown for mercury due to the high number of ND results.

Figure 3-19: Percent to equilibrium for the lithium tracer over the 28-day exposure in the standard spiked sediment.

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Acronyms and Abbreviations

Σ SEM-AVS/OC	the sum of the organic-carbon normalized AVS-SEM value for the five metals
°C	degrees Celsius
µg/L	micrograms per liter
µmol/g	micromoles per gram
AVS	acid volatile sulfide
CI	confidence interval
cm	centimeters
DI	deionized
DO	dissolved oxygen
dw	dry weight
HDPE	High Density Polyethylene
ID	identification number
MDL	Method Detection Limit
mg/L	milligrams per liter
mL	milliliters
mm	millimeter
ND	non detect (no detection above the MDL)
PTFE	Polytetrafluoroethylene
RO	reverse osmosis
SD	standard deviation
SEM	simultaneously extracted metals
SOP	Standard Operating Procedure
USEPA	Environmental Protection Agency
ww	wet weight

1. INTRODUCTION

The purpose of this laboratory report is to provide the results of experiments that were conducted to validate the best practices for the field deployment of sediment porewater passive samplers ("peepers") for inorganic contaminants. This report is a continuation of the work conducted as part of ER20-5261 and provides additional peeper method development based on the identified data gaps from this project literature review (Risacher et al., 2023a). The laboratory work presented here focused on peeper sampler preparation and processing best practices, specifically for end-users to be able to prepare, ship to the field, process and preserve peeper samplers. For information on field deployment best practices, a field demonstration report (Risacher et al., 2023b) was also produced under ER20-5261.[1]

The remainder of this report is organized as follows:

- Section 2. Methods and Materials: Provides a general overview of the methods and materials used in the laboratory experiments, including an overview of peeper technology.
- Section 3. Experiment-by-Experiment Details: Provides the objectives, methods and materials (where different from those described in Section 2), results, and conclusions of the 7 laboratory experiments.
- Section 4. Conclusions: Provides a concise summary of the conclusions from each of the 7 laboratory experiments.
- Section 5. References: A list of references cited in the report.
- Appendix A, Peeper Preparation Standard Operating Procedure: Provides a standard operating procedure for preparation of the peepers used in these laboratory experiments.
- Appendix B, Analytical Laboratory Reports: Provides the commercial analytical reports for measurements completed in the laboratory experiments.

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[1] Project details can be found at https://serdp-estcp.org/projects/details/db871313-fbc0-4432-b536-40c64af3627f.

2. METHODS AND MATERIALS

2.1 Overview of Peeper Technology

Dialysis samplers, also called peepers (Figure 2-1), are a type of passive sampler which function by allowing a small water compartment to chemically equilibrate with sediment porewater via passive diffusion through a semi-permeable membrane (Vroblesky and Pravecek, 2001; United States Geological Survey et al., 2007; Feyte et al., 2012; Gruzalski et al., 2016; Cleveland et al., 2017; Chen et al., 2017).

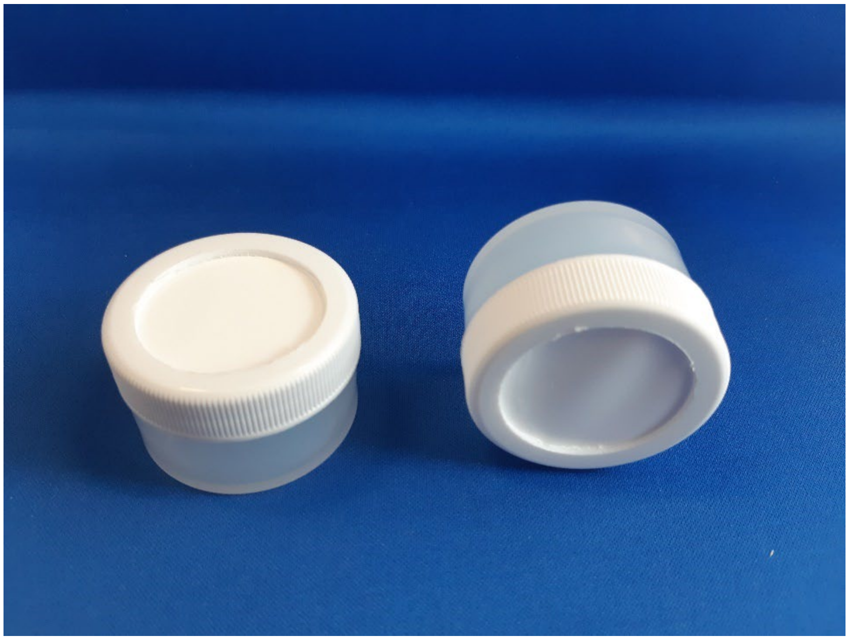

Figure 2-1: Photographs of the peeper design selected for the laboratory experiment and field demonstration (SiREM Laboratories), showing the peeper vial and membrane surface. The peeper vial contains 15 milliliters (mL) of peeper water.

The water inside the peeper is deionized, thus creating a concentration gradient that facilitates diffusion of inorganic chemicals through the membrane into the solution within the peeper. Peepers are usually deployed via insertion into surface sediment by divers, waders, or from a vessel. After an equilibration period (e.g., several days to several weeks), the concentration inside the peeper will approach the concentration in the sediment porewater. To ensure that equilibrium has been reached, a reverse tracer consisting of a known concentration of an inert inorganic chemical in the peeper that is not present in the porewater (or present at a much lower concentration) can be used (Thomas and Arthur, 2010). Once the peeper is retrieved, and the liquid is analyzed via standard (i.e., United States Environmental Protection Agency [USEPA] SW-846) methods and reported as a concentration in water that can be easily compared to water criteria or used in fate modeling. The concentration of the reverse tracer can be used to determine the diffusion properties of the constituents of concern, providing an estimate of the proportion of equilibrium attained during a short-term (pre-equilibrium) exposure. This data can be used to estimate the concentration of analytes at equilibrium for pre-equilibrium exposures. For example, if only 50% of the tracer is found to be remaining in a deployed sampler, one can assume that analytes present in a peeper (if they diffuse into the peeper at the same rate of the tracer elimination) are present at 50% of the concentrations expected at equilibrium. To estimate the concentration of analytes at equilibrium in this case, one would multiply the concentration observed during the short-term deployment by 2.

A detailed literature review (Risacher et al., 2023a) conducted prior to the development of Laboratory experiments highlighted a few potential critical issues of peepers for measurement of inorganics in sediment porewater that were investigated in the laboratory experiments:

1. Sorption of metals to peeper during deployment and retrieval
2. Peeper chamber volume and design factor for optimum deployment time and analytical volume
3. Effect of oxygen contamination on redox sensitive compounds during all stages of peeper preparation and use
4. Pre-equilibration sampling and use of reverse tracer to calculate true porewater concentrations
5. Peeper salinity and the impact of density gradient differences between peeper water and sediment porewater

These factors do not necessarily imply general limitations or critical flaws of the peeper technology; however, they should be fully evaluated to encourage regulatory confidence in the methods and adoption/commercialization by the end-user community. The laboratory experiments that were conducted were aiming to address these limitations. Some of the findings of this laboratory study were applied for a field demonstration for this project (Risacher et al., 2023b), which is available in a separate report for the overall ER20-5261 project.

2.2 General Experimental Design and Methods

This section described the general conditions and methods used for the laboratory experiments conducted. In cases in which methods varied due to the goals of the experiment, deviations from the general approaches are provided in the experiment-by-experiment details (Section 3). All laboratory experiments were conducted at SiREM Laboratory in Guelph, Ontario, Canada, at a room temperature of approximately 23 degrees Celsius (°C), unless otherwise specified.

2.2.1 Peeper Preparation

A detailed Standard Operating Procedure (SOP) reflecting the final recommendations and best practices for peeper construction and storage is provided in Appendix A. Most of the experiments used a peeper constructed from a commercially available 15-mL plastic container with a screw cap lid (see the section on Experiment 1 for other designs). The caps were drilled with a 1.25-inch diameter hole in the center to serve as an opening for the membrane. Once the caps were drilled, all peeper materials were cleaned with laboratory-grade detergent and reverse osmosis (RO) water, followed with an RO water rinse, and a final ultrapure deionized (DI) water rinse. All peeper materials and material used for construction were then acid washed for 24 hours in a 5% trace metal grade nitric acid bath. Following the acid bath, all materials were then rinsed 5 times with DI water. The acid bath and rinse steps were repeated a second time and the materials were then submerged for 24 hours in a DI bath to remove any residual contamination.

Once trace metal clean, the peeper materials were added to a bath of ultrapure water and reverse tracer (100 milligrams per liter [mg/L] potassium bromide for Experiment 1, 1000 mg/L lithium bromide for all additional experiments in sediment[2]). For Experiments 1 and 2, the preparation bath was under constant deoxygenation using argon gas bubbling via a diffuser stone until dissolved oxygen (DO) levels were less than 0.1 mg/L. Deoxygenation was not used in other experiments because it was found to not affect results (see results for Experiment 2). The vials were filled with the bath solution and a 47-millimeter (mm) diameter, 0.45-micrometer (µm) polyethersulfone membrane was held at the mouth of the container and secured by screwing on the cap while the peepers were submerged (Figure 2-2). The last few experiments (Experiments 5 and 7) used peepers in which the water was added to the container by pipette, followed by careful addition of the membrane, ensuring no bubble.

Although the source water used did not exhibit detectable metals (based on prior testing), some of the blank (unexposed) peepers indicated occasional concentrations of detectable copper and relatively consistent concentrations of detectable zinc. The source of copper and zinc could not be resolved in this study, but, as discussed below, the presence of copper and zinc did not affect experimental results. Detections of copper and zinc in blank peepers were usually near Method Detection Limits (MDLs), and generally much lower than concentrations observed in peepers exposed to test sediment and water. Concentrations in all but five results were also below conservative screening criteria (e.g., Criterion Continuous Concentration) that are often applied to measurements in porewater. Importantly, with the exception of the time series experiment (Experiment 6), all peepers were left in contact with sediment and water a sufficient time for the concentration in the peeper to reach a sufficient degree (approximately 60-70% or more) of equilibration. Thus, metal present in the blank, although less than ideal, will not affect sample results assuming the peeper has achieved a relative degree of equilibration during the deployment. In Experiment 6, kinetics indicated that zinc detected in the blank had fully equilibrated by approximately day 14 (copper was not detected in the blank of Experiment 6). Thus, for the laboratory experiments, the same results would have been reached regardless of the presence of trace copper and zinc in the peeper at the beginning of the exposure.

Once assembled, peepers for Experiments 1 and a portion of the peepers for Experiment 2 were kept in Mylar bags filled with deoxygenated water to ensure anoxic peeper water. In other experiments (as Experiment 2 indicated anoxic peeper water is not required), approximately 5 mL of the peeper water was added to the Mylar bag to keep the peepers moist before deployment if the peepers were not deployed immediately. Peepers were usually stored at room temperature prior to deployment in test sediment or water.

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[2] 1000 mg/L lithium bromide results in a concentration of 80 mg/L lithium and 920 mg/L bromide.

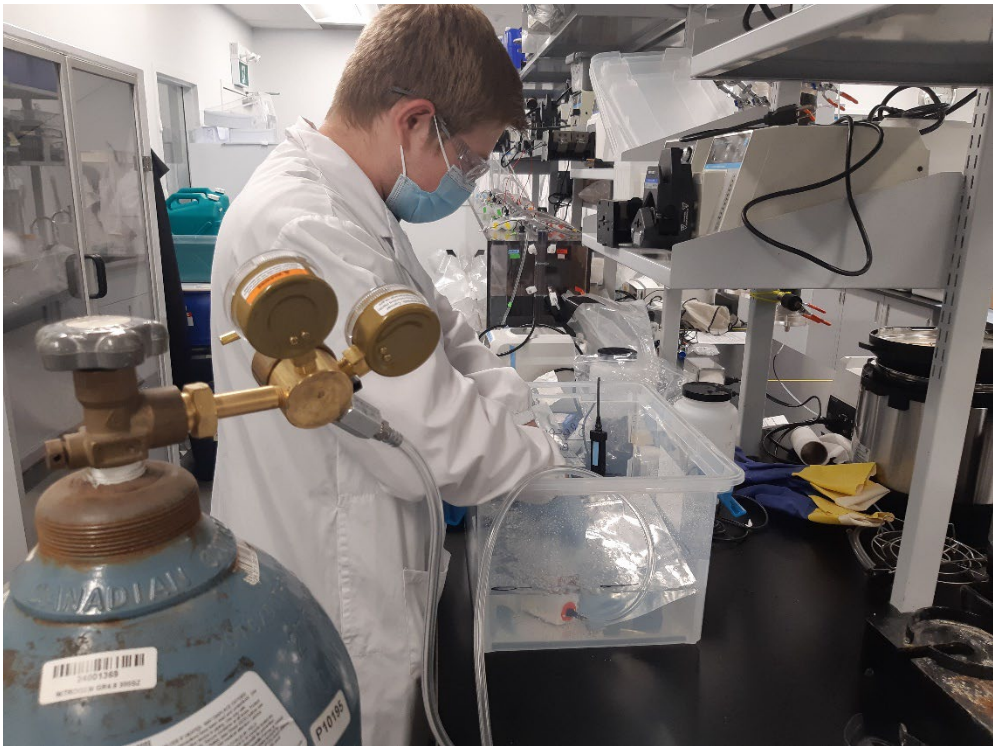

Figure 2-2: Peeper preparation, showing the peeper water bath being purged with argon gas during filling of the peepers within the bath.

2.2.2 Sediment Used for the Peeper Deployments

In most experiments (except for Experiment 4 and part of Experiment 6), peepers were deployed in a standard homogenized test sediment. The sediment was a fine-grained, debris-free marine sediment (Figure 2-3). Prior to and during the experiments, when not in use, sediment was preserved in cold storage (4°C).

Figure 2-3: Test sediment used in the laboratory experiments.

The test sediment was collected from the uppermost 10 centimeters (cm) of the sediment bed at a marine sediment site with a history of elevated concentrations of metals in sediment due to multiple sources (e.g., sandblasting, marine paints). The concentration of copper in the bulk sediments was measured and determined to be approximately 500 to 600 milligrams per kilogram, dry weight (dw), which exceeds many screening levels for copper in surface sediment (Figure 2-4). Organic carbon content of the sediment was measured (USEPA Method 9060A) and was found to be 1.49% (i.e., 0.0149 grams of organic carbon per gram of sediment, dw).

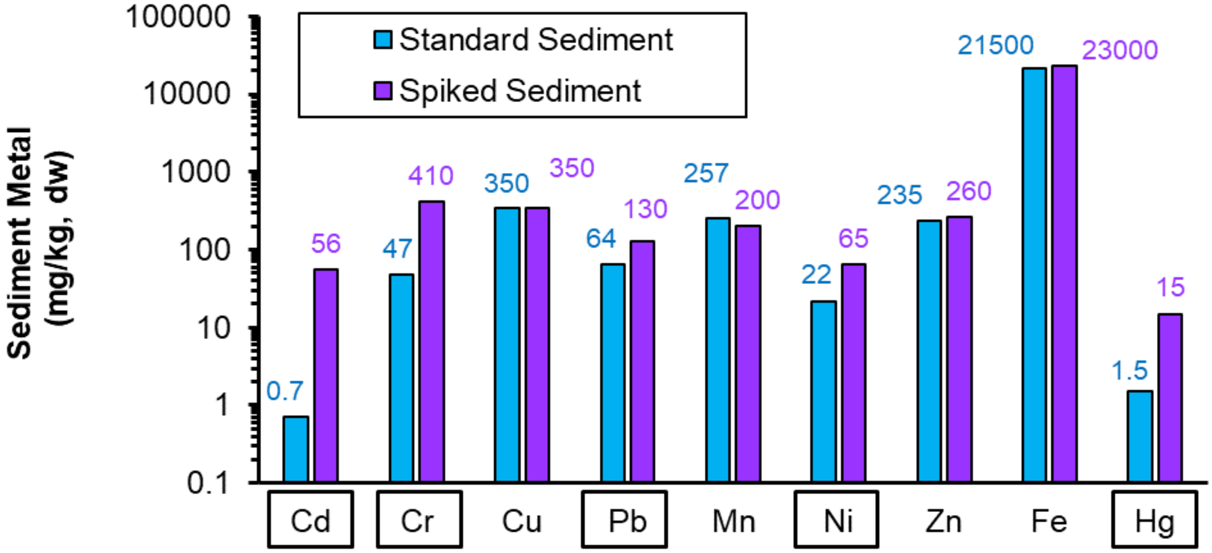

Figure 2-4: Bulk sediment metal concentration for standard and spiked sediments. Metals with a box around them were spiked, and the resulting spiked sediment was used in a part of Experiment 3 and the entirety of Experiments 5, 6, and 7 (see Table 2-1 and associated text).

An analysis of acid volatile sulfide and simultaneously extracted metals (AVS/SEM) on the sediment was also conducted. AVS/SEM has been used to evaluate metal availability for nearly 20 years in sediments (USEPA, 2005). This measurement evaluates the availability of divalent metals (cadmium, copper, lead, nickel, and zinc) corrected for concentrations of a chelating agent (sulfide). SEM measurements in the standard sediment (Figure 2-5) indicated the highest values for copper and zinc. Considering the organic carbon content (1.49%), the sum of the organic-carbon normalized AVS-SEM value for the five metals (Σ SEM-AVS/OC) was 71 micromoles per gram (µmol/g) dw organic carbon. Per USEPA (2005), chronic effects on benthic invertebrates are uncertain in the range of 130 to 3,000 µmol/g, organic carbon for the sum of the SEM for divalent metals. The sample result for the standard sediment (71 µmol/g dw organic carbon) would be expected to be nontoxic, as it is below this 130 to 3,000 µmol/g, organic carbon range.

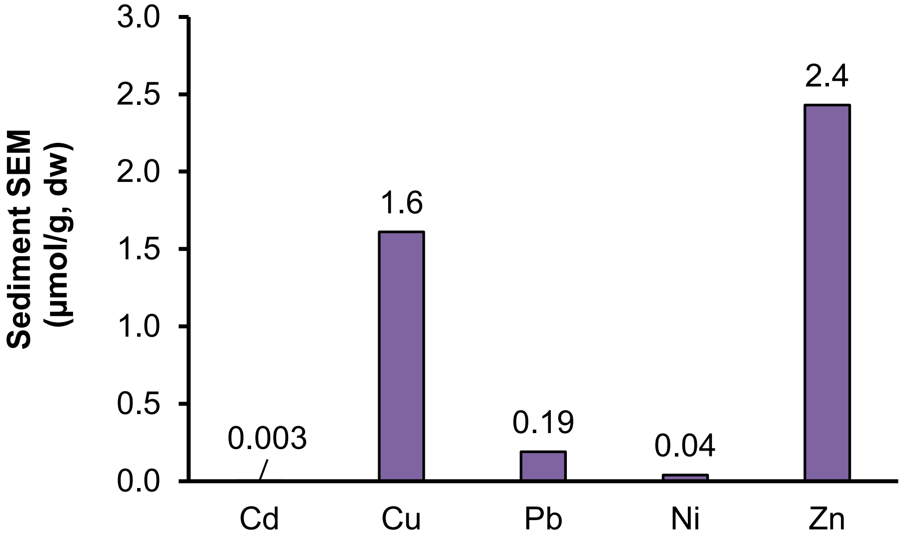

Figure 2-5: SEM results for the five divalent metals, as measured in the standard sediment.

Sediments were reused for multiple experiments. After each experiment, sediments were returned to a large storage bin and re-mixed prior to the next experimental setup. A portion of Experiment 3, and all of Experiments 5, 6, and 7 were conducted with reused sediments that were spiked with metals salts (

Table 2-1) to prevent depletion of contaminants in the porewater and to increase the detectability of several metals (e.g., cadmium and mercury) in porewater. The concentration of metals in the spiked sediment is presented in Figure 2-4.

Table 2-1: Mass of metal salt added to spiked sediment.

Metal	Salt form	Mass of sediment (kilograms, wet weight)	Metal salt added (grams)
Cadmium	$CdCl_2$	18	2.0
Chromium	$CrCl_2$	18	21
Lead	$PbCl_2$	18	2.4
Nickel	$NiCl_2$- $6H_2O$	18	3.6
Mercury	$HgCl_2$	18	0.48

In addition, in Experiment 6, additional field-collected surface sediment “Indian Head Sediment” from a freshwater sediment collected near Indian Head, Maryland, was also used to evaluate uptake kinetics of peepers in sediment. An analysis of metals in surface sediment was not conducted with this sediment, although it did indicate detectable concentrations of metals in sediment porewater, as measured by the peepers.

2.2.3 Peeper Sediment Deployments

In most experiments, peepers were deployed in sediment contained in test mesocosms in the laboratory. The mesocosms were prepared from acid-cleaned, 2-liter high-density polyethylene (HDPE) screw-top jars containing approximately 1.2 kilograms of wet weight (ww) of the test sediment. This amount of sediment represents a sediment volume of approximately 700 mL, which was sufficient to enable enough peepers to comprise a single replicate peeper sample (i.e., four 15-mL peepers that were composited to a 60-mL sample) to be buried within the sediment of the mesocosm. Following addition of sediment to each mesocosm, 5 cm of overlying water was added. The overlying water was composed of a standard sea salt mix (i.e., "Instant Ocean") dissolved in laboratory DI water at the standard sea salt product recommended dosing (36 grams of Instant Ocean per liter of water) such that the overlying water was similar to seawater. This was to avoid a density driven diffusion and the migration of sediment porewater ions to the overlying water. In most of the experiments, the overlying water of each mesocosm was gently aerated with air to prevent complete anoxia within the water and uppermost layers of the mesocosms. Once the mesocosms were prepared, they were allowed to equilibrate for 7 days prior to peeper deployment. For most experiments (except Experiment 1 which used other peeper designs), four of the 15-mL peepers were used and deployed in a "cross" formation (Figure 2-6). This allowed sufficient volume for the metal and bromide analysis to be conducted. In some experiments, bromide analysis was not conducted, so only three peepers were deployed, in a similar configuration as shown in Figure 2-6. A photo of the setup for a typical experiment is shown in Figure 2-7.

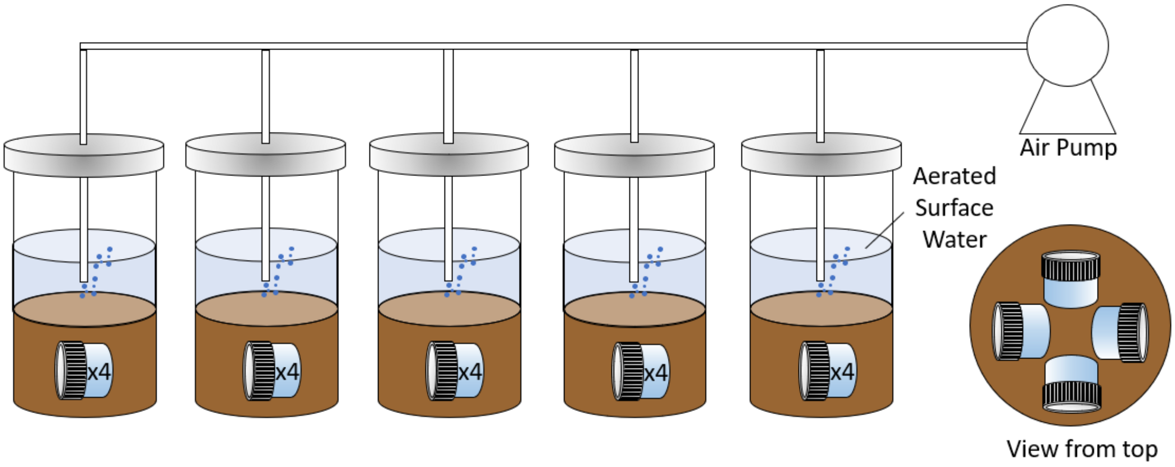

Figure 2-6: Schematic of the experimental mesocosm design. The top view shows the peeper on top of the sediment for clarity, as they were always completely buried in the sediments.

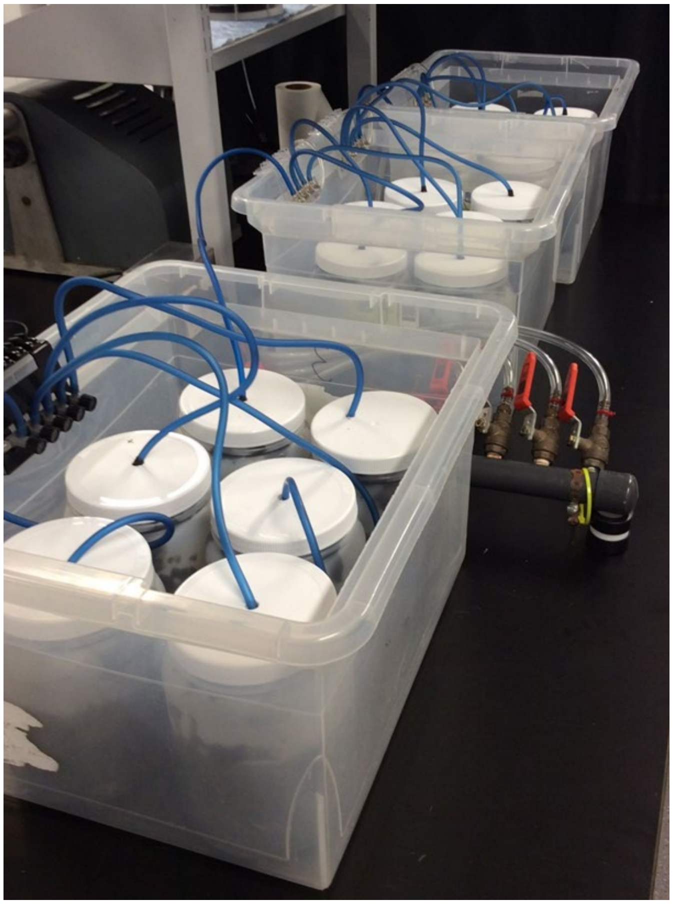

Figure 2-7: Test mesocosms containing peepers.

Peepers were deployed into each mesocosm (as shown in Figure 2-6) by removing the peepers from their storage bag and inserting by them carefully by hand. The peepers were placed in the surficial sediment layer such that the membrane was covered by sediment and perpendicular to sediment-water interface. After insertion, the mesocosms were checked every 1 to 2 days, and artificial seawater was added to each mesocosm to ensure an overlying water layer of approximately 5 cm.

2.2.4 Peeper Deployment, Retrieval, and Processing

After the deployment period, the peepers were retrieved by hand from the mesocosms. Peepers were rinsed with DI water to remove visible sediment particles, especially from the membrane and cap. To process and sample the peeper water, a 25-mL serological pipette was inserted into the bottom of the peeper by puncturing the membrane, and the water inside the peeper was drawn up (Figure 2-8). Five mL of peeper water from each of the four peepers (approximately 20 mL total) was dispensed into a sample container for bromide analysis (100-mL polypropylene bottle, supplied by the commercial analytical laboratory). The remaining of the peeper water (approximately 40 mL total) was dispensed into the sample container for metal analysis (125-mL HDPE bottle containing 1 mL 1:1 concentrated trace-metal grade nitric acid:water, as supplied by the commercial analytical laboratory. A side experiment was conducted in which 1 gram (0.95 to 1.05 grams) of trace-metal grade sodium metabisulfite was added to the peeper water prior to the acidification step (following recommendations by Simpson et al. [1998]); however, this was shown to not affect concentrations of the target metals for peepers (compared to no addition of sodium metabisulfite) deployed in the unaerated (anaerobic) test sediment.

Detailed step-by-step procedures and tips for the processing of peeper waters are available in the ER20-5261 Field Deployment Report (Risacher et al., 2023b).

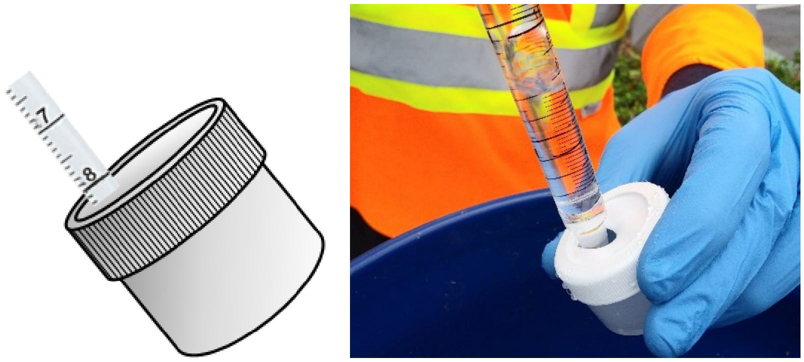

Figure 2-8: Peeper water extraction using a serological pipette.

Blank samples were prepared in this manner using four unexposed peepers that were held in storage during deployment of peepers. All sample bottles were capped and labeled with their sample identification numbers (IDs), placed in cold storage (4°C), and shipped to a commercial analytical laboratory such that the analysis could be completed within the 180-day holding times specified by the USEPA methods.

2.2.5 Peeper Water Sample Analysis

Analysis of inorganics in peeper water were conducted by Eurofins Environment Testing America, a National Environmental Laboratory Accreditation Program (NELAP) accredited commercial laboratory that routinely performs inorganics analysis of environmental samples (e.g., water, sediment, tissue) for the United States Department of Defense in support of contaminated site investigations under the direction of state and federal environmental regulatory agencies.

Analysis of the target metals[3] and the lithium tracer in peeper water was conducted via USEPA Method 6020A (USEPA, 1998), for chromium (Cr), copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd) and Lithium (Li) and USEPA Method 7470A (USEPA, 1994) for total mercury. The bromide (Br) tracer was measured via USEPA Method 300 (USEPA, 1993). In addition, for some experiments (as noted below), redox-sensitive analytes iron (Fe), and manganese (Mn) were also measured via Method 6020A (USEPA, 1998). Approximate method detection limits (MDL for each analyte (based on a 50- to 60-mL sample volume) are presented in Table 2-2 below.

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[3] The inorganics targeted ("Target Metals") are cadmium, chromium, copper, nickel, lead, zinc, and total mercury since they are common chemicals of concern in contaminated sediment.

Table 2-2: Analytical specifications for inorganic analytes in peeper water.

Analyte	Analytical Method	Container	Preservative	Holding Time (days)	Approximate Method Detection Limit (µg/L)
Target Metals					
Cadmium	USEPA Method 6020A	125-mL HDPE bottle	Nitric Acid	180	0.2
Chromium	USEPA Method 6020A	125-mL HDPE bottle	Nitric Acid	180	2
Copper	USEPA Method 6020A	125-mL HDPE bottle	Nitric Acid	180	1
Lead	USEPA Method 6020A	125-mL HDPE bottle	Nitric Acid	180	0.2
Total Mercury	USEPA Method 7470A	125-mL HDPE bottle	Nitric Acid	180	0.1
Nickel	USEPA Method 6020A	125-mL HDPE bottle	Nitric Acid	180	0.3
Zinc	USEPA Method 6020A	125-mL HDPE bottle	Nitric Acid	180	3
Tracers					
Bromide	USEPA Method 300.0	30-mL HDPE bottle	None	180	3,000
Lithium	USEPA Method 6020A	125-mL HDPE bottle	Nitric Acid	180	0.8
Other Analytes					
Manganese	USEPA Method 6020A	125-mL HDPE bottle	Nitric Acid	180	1
Iron	USEPA Method 6020A	125-mL HDPE bottle	Nitric Acid	180	20

Note: µg/L - micrograms per liter

In some experiments, DO was measured in peepers via insertion of a probe directly into the water within a peeper (e.g., via insertion of the probe through a punctured membrane of a peeper, or in a separate container after the water was transferred from the peeper via pipette). DO was analyzed using HACH HQ30D meter with LDO101 probe and was calibrated every day before use following the manufacturer's protocol.

2.3 Data Analysis and Presentation

Raw data produced in the experiments is provided in the experiment-by-experiment details (Section 3) in tables. Commercial analytical laboratory reports presenting the analysis of metals in peeper water is provided for each experiment in Appendix B.

The MDL for analytes was generally consistent for each metal among the experiments and among the samples. In the raw data tables and figures for each experiment, the "approximate MDL" is provided. This value corresponds to the most common MDL (i.e., the mode) for the samples analyzed in that particular experiment. In some cases, concentrations of analytes were below the MDL (i.e., non detect [ND]). ND data were generally assigned a value of one-half the MDL, and this value was used in subsequent calculation of summary statistics and statistical comparisons. In cases in which treatment groups exhibited a high proportion of ND results, statistical analysis was not conducted. In cases in which most of the results for a metal were ND (as noted in the results), figures were not produced. In cases in which ND data are shown in figures, ND results are plotted with a solid red circle at a value of one-half the MDL.

Most experiments compared concentrations of metals or oxygen in peepers statistically among different treatments. Prior to testing, data were evaluated for outliers using a combination of visual inspection and Grubb's test. In cases in which raw data are graphed and inclusion of the outlier on the graph does not result in having to expand the y-axis scale orders of magnitude, outliers are shown on plots as red "X" symbols. In some cases (as noted in the experiment-by-experiment details) outliers were removed prior to statistical comparisons and calculations of summary statistics. Statistical comparisons relied on parametric (e.g., ANOVA) and nonparametric (e.g., Wilcoxon) evaluations on non-transformed data, Log_{10}-transformed data, and ranks while testing for heterogeneity of variance using Levene's test. The results of parametric approaches were generally relied upon unless alternate methods indicated superior discriminatory power (e.g., lower P values, homogeneity of variance, etc.). Statistical testing assumed an alpha of 0.05 for rejecting null hypotheses of no differences among treatment groups. For tests in which P less than 0.05, *ad hoc* multiple comparisons were employed. In most cases, Tukey's Honestly Significant Difference was used to compare all groups, but in some experiments where one treatment group represented a "control," "treated" groups were compared to the "control" group using Dunnett's test. All statistical comparisons were evaluated via JMP.[4]

For tracer data, the percentage of equilibration for bromide and lithium was calculated by Equation 1:

$$\%\ equilbration = 100\% \times \left(1 - \frac{\mathrm{Tr}_{p,t}}{\mathrm{Tr}_{p,0}}\right) \qquad \text{(Equation 1)}$$

Where:

- $\mathrm{Tr}_{p,0}$ is the measured concentrations of the tracer in the peeper prior to deployment (mg/L or µg/L)
- $\mathrm{Tr}_{p,t}$ is the measured concentrations of the tracer in the peeper at time of retrieval (mg/L or µg/L)

For all peepers deployed in the sediments and in the surface water in Experiment 6, the bromide and lithium tracer data were used to estimate the equilibrium freely dissolved concentration of the target metals using the modeling techniques of Thomas and Arthur (2010). Thomas and Arthur (2010) studied the use of the bromide reverse tracer to estimate percent equilibrium in laboratory experiments and a field application. They concluded that bromide can be used to estimate concentrations in porewater using measurements obtained before equilibrium is reached. The study included a mathematical model for estimating concentrations of ions in external media ($C_{e,i}$) based on measured concentrations in the peeper chamber ($C_{p,i}$), the elimination rate of the target analyte (K_i) and the deployment time (t), as shown in Equation 2:

$$C_{e,i} = \frac{C_{p,i}}{1-e^{-K_i t}} \qquad \text{(Equation 2)}$$

Where K_i is the elimination rate of the target analyte ($days^{-1}$), calculated with Equation 3 using the ratio of the free-water diffusion coefficient of the tracer (D_t) and the target analyte (D_i) (Thomas and Arthur, 2010):

$$K_i = K_t \left(\frac{D_i}{D_t}\right) \qquad \text{(Equation 3)}$$

D values for the 7 target analytes and 2 tracers are provided in Table 2-3.

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[4] https://www.jmp.com/

Table 2-3: Free-water diffusion coefficient (D) for inorganics.

Analyte	D (x10^{-5} square centimeters per second)	Reference
Cadmium	0.63	Calculated from Buffle et al. (2007), assuming 20°C[5]
Chromium	0.52	
Copper	0.62	
Iron	0.63	
Lead	0.83	
Manganese	0.62	
Mercury	0.74	
Nickel	0.62	
Zinc	0.61	
Bromide	1.82	
Lithium	0.90	

The elimination rate of the tracer (K_t) is calculated using Equation 4:

$$K_t = \frac{-ln\,(1 - \frac{Tr_{p,t} - Tr_{p,0}}{Tr_{e,t} - Tr_{p,0}})}{t} \quad \text{(Equation 4)}$$

Where:

- K_t is the elimination rate of the tracer (days^{-1})
- $Tr_{p,0}$ is the measured concentrations of the tracer in the peeper prior to deployment (mg/L or µg/L)
- $Tr_{p,t}$ is the measured concentrations of the tracer in the peeper at time of retrieval (mg/L or µg/L)
- $Tr_{e,t}$ is the concentrations of the tracer in the external media (mg/L or µg/L) which for seawater was assumed to be 65 mg/L for bromide and 100 µg/L for lithium
- t is the deployment time (days)

In some cases, non-linear regression modeling was used to fit the data to a one-compartment first-order kinetic model. Non-linear modeling was conducted in Excel using the Solver function. Standard models included: 1) A model used to predict one-compartment first-order kinetic uptake (Equation 5); 2) A model used to predict elimination with an asymptote of zero (Equation 6);

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[5] Buffle et al. (2007) provides diffusion coefficients at 25°C. These were converted to values at 20°C using the dynamic viscosities of water at 20°C and 25°C (Potter and Wiggert, 2001). However, temperature at which the D values were measured does not affect the pre-equilibrium calculations as long as the D values being used are based on estimates from the same temperature. The ratio between the D values for the analyte and the tracer (lithium) is key to the pre-equilibrium equation, and it does not change with temperature. For example, the D value at 20°C for lithium is 1.7 times higher than that of chromium and the D value at 25°C for lithium is 1.7 times higher than that of chromium.

and 3) A model used to predict elimination with a constant non-zero asymptote determined by the model-data best fit (Equation 7):

$$C_t = C_{equil} \times (1 - e^{-K_i \times t}) \qquad \text{(Equation 5)}$$

$$C_t = C_{zero} \times e^{-K_i \times t} \qquad \text{(Equation 6)}$$

$$C_t = C_{zero} \times e^{-K_i \times t} + C_{equil} \qquad \text{(Equation 7)}$$

Where:

- C_t is the concentration of the tracer or analyte at time t in the peeper (mg/L or µg/L)
- C_{equil} is the concentration of the tracer or analyte at equilibrium in the peeper (mg/L or µg/L)
- C_{zero} is the concentration of the tracer or analyte at time zero (prior to deployment) in the peeper (mg/L or µg/L)
- K_i is the elimination rate of the analyte or tracer (K_t)
- t is the deployment time (days)

Figures presenting peeper data were generally one of three formats (unless otherwise specified in the figure captions):

- Bar charts depicting the arithmetic mean and error bars representing standard deviation (SD)
- Box and whisker plots depicting individual data points as circle symbols (red filled symbols indicate results below the MDL, with the value graphed equal to one-half the MDL), numerical labels depicting the arithmetic mean, boxes depicting the 25th, 50th, and 75th percentiles, whiskers depicting the 10th and 90th percentiles, and red "X" symbols depicting individual results that were considered outliers and not included in the calculation of the arithmetic mean or symbology (boxes and whiskers)
- In cases in which a significant (*P* less than 0.05) one-compartment first order kinetics model fit was detected in the kinetic studies (Experiment 5 and 6), model fit curves were plotted as solid lines, bounded by 95% confidence bands on the model (inner dashed-lined bands) and 95% confidence bands on the model predictions (outer dotted-lined bands)

3. EXPERIMENT-BY-EXPERIMENT DETAILS

This section describes the objectives, methods, results, and conclusions of each experiment. An overview of the experiments is provided in Table 3-1.

Table 3-1: Experiment goals and methods overview.

Experiment	Focus	Date	Peeper Types	Tracer	Peeper Water Deoxygenated?	Peeper Water Filling Method	Deployment matrix	Deployment times (days)	Processing	Analytes
1 Peeper Design	Optimal peeper design	August-September 2021	SP15, SP30, SP60	Potassium bromide, 100 mg/L	Yes	Sub-merged in bath	Standard sediment (aerated)	14, 28	Benchtop (air), immediately after retrieval	Target metals, bromide tracer
2 Peeper Deoxygenation	Effects of deoxygenation on peeper results	November 2021	SP15, SP60	Lithium bromide, 1000 mg/L	Yes and No	Sub-merged in bath	Standard sediment (aerated)	14	Benchtop (air), immediately after retrieval	Target metals, iron and manganese, bromide and lithium tracers
3 Peeper Sample Processing	Need to process peeper samples in anoxic conditions	<u>2 Studies:</u> January-February 2022 (aerated sediment); June 2022 (un-aerated sediment)	SP15	None for aerated sediment; lithium, 1000 mg/L for un-aerated sediment	No	Sub-merged in bath	Standard sediment (aerated); Spiked sediment (un-aerated)	14	Benchtop (air) and glove box (nitrogen), immediately after retrieval	Target metals, iron and manganese, lithium tracer
4 Peeper Storage - Oxygen	Storage methods with regards to peeper water oxygen	December 2021	SP15	None	No	Sub-merged in bath	None	None	None	Oxygen
5 Peeper Storage - Post Deployment	Storage methods with regards to peeper water metals	February 2023	SP15	Lithium bromide, 1000 mg/L	No	Pipette	Spiked sediment (un-aerated)	14	Benchtop (air), various periods, as long as 14 days after retrieval	Target metals, iron and manganese, lithium tracer
6 Tracers for Pre-equilibrium Deployments	Demonstrate and validate reverse tracers for pre-equilibrium deployments	<u>3 Studies:</u> March-May 2022 (water); April-May 2022 and October-December 2022 (sediment)	SP15	Lithium bromide, 100 mg/L (water) or 1000 mg/L (sediment)	No	Sub-merged in bath	Spiked water; Spiked sediment (aerated); Indian Head sediment (aerated)	Various (0.17 to 47 days)	Benchtop (air), immediately after retrieval	Target metals, bromide and lithium tracers (water); Target metals, iron and manganese, bromide and lithium tracers (sediment)
7 Peeper Water Salinity	Peeper water salinity effects on peepers in marine sediment	December 2022-January 2023	SP15	Lithium bromide, 1000 mg/L	No	Pipette	Spiked sediment, (aerated)	14	Benchtop (air), immediately after retrieval	Target metals, iron and manganese, bromide, and lithium tracers

3.1 Experiment 1: Peeper Design

3.1.1 Rationale and Methods for Experiment 1

Experiment 1 was conducted to identify an optimal peeper design to be used in the remainder of experiments as well as provide insight into the approximate time period over which the peepers equilibrate.

Peeper design is an aspect of significant variability in the passive sampling of sediments, and the success in standardizing the use of peepers to monitor inorganics in sediment depends on the identification of an optimal, cost-effective peeper design that collects representative samples and sufficient volumes for standard laboratory analyses in a minimized deployment time.

Three different peeper designs were built and tested for Experiment 1: SiREM's 60-mL HDPE peeper (SP60), a 30-mL polytetrafluoroethylene (PTFE) peeper with two membranes on each end of the sampler; and a 15-mL polypropylene peeper (SP15) (Figure 3-1). The "SP" designation for these three peeper designs may not be the official product name, and were used in this project to differentiate the peeper designs. All peeper caps were drilled with a 1.25-inch-diameter hole in the center to serve as an opening for the membrane. Additional design characteristics are detailed below in Table 3-2.

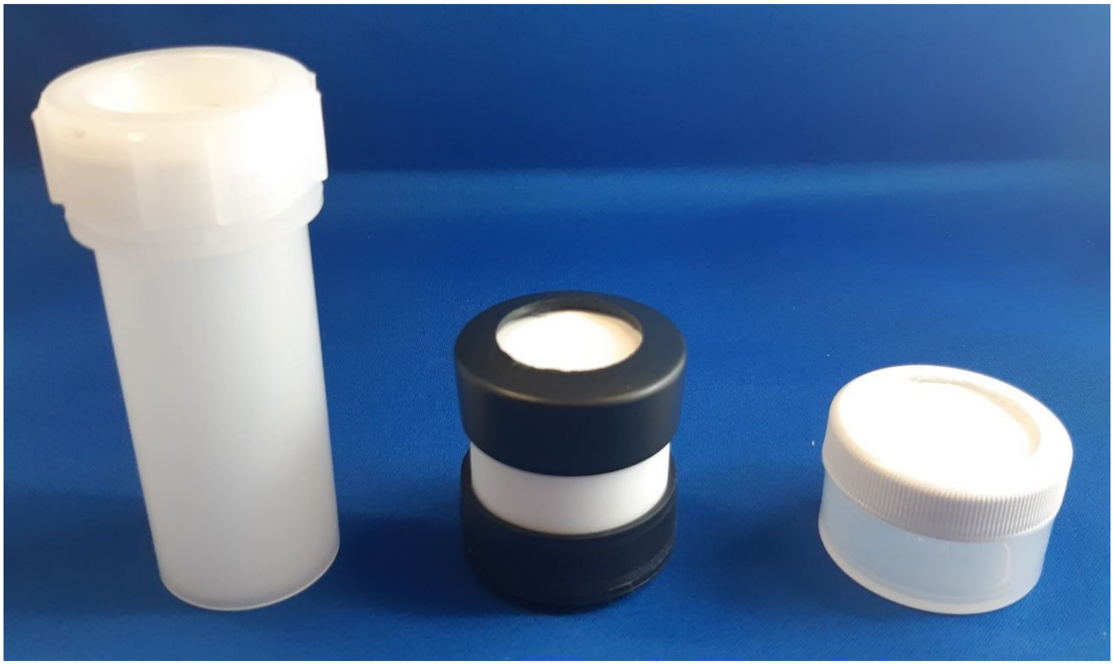


Figure 3-1: Peeper designs used in Experiment 1; from left to right, SP60, SP30, and SP15.

Table 3-2: Experiment 1 peeper design characteristics.

Peeper	Peepers per Chamber	Material	Nominal Volume (mL)	F Factor (mL per square centimeter)	Membrane material	Other considerations
SP60	1	HDPE	60	8.0	Polyethersulfone	
SP15	4	Polypropylene	15	2.8	Polyethersulfone	
SP30	2	PTFE	30	2.2	Polyethersulfone	One membrane on each end of sampler

Notes:
F Factor - volume ÷ surface area of the membrane(s) used on the peeper

Prior to deployment, the peepers underwent a decontamination process to minimize the presence of residual trace metals. This process included being cleaned with laboratory-grade detergent and rinsed with RO water, followed by a rinse with ultrapure DI water. Materials were then acid washed for 24 hours in a 5% trace metal grade nitric acid bath and rinsed five times with DI water. After a second acid bath and DI rinse and subsequent 24-hour DI bath, the materials were added to a preparation bath of ultrapure water and reverse tracer (potassium bromide, 100 mg/L). The preparation bath was bubbled with argon gas via diffuser stone to deoxygenate the water to DO levels of less than 0.1 mg/L. Vials were filled with the bath solution, and a membrane was fixed to the top and secured to the cap. Following assembly, peepers were kept in Mylar bags filled with preparation bath solution to ensure they remained wet and anoxic prior to deployment.

Peeper designs were deployed for 14 days and 28 days in test mesocosms containing 1.2 kilograms of sediment overlaid by 500 mL (2 inches) of water with 36 g/L Instant Ocean mix. One SP60, two SP30, and four SP15 peepers were placed in each mesocosm to obtain a sufficient volume for metal and bromide analysis. SP30s were deployed side by side, and SP15s were deployed in a ‘star’ pattern (Figure 2-6). During deployment, peepers were individually removed from the Mylar bag, which was then resealed to prevent oxygen diffusion. Water within mesocosms was kept aerated by bubbling air inside the water layer.

After the deployment period, peepers were retrieved and individually processed. Peepers were first washed with DI water, and the peeper water was extracted using a 25-mL pipette. The extraction process involves poking the pipette through the membrane and drawing up the water, which is then distributed to the metal analysis and bromide analysis sample containers. Total volume provided by all designs was approximately 60 mL: 40 mL for metals analysis and 20 mL for bromide analysis. Blanks for each sampler were also collected and analyzed to assess potential for contamination of each design, as well as initial bromide concentration.

3.1.2 Results and Discussion for Experiment 1

Raw data from Experiment 1 is provided in Table 3-3, and supporting laboratory analytical reports are provided in Appendix B. Statistical analyses were not conducted due to the low sample sizes, high numbers of potential outliers, and preliminary nature of the experiment. Overall, target metals data (Figure 3-2) indicated that for the target metals with sufficient detections (chromium, copper, nickel, lead, nickel, and zinc) concentrations in porewater were generally highest for the SP15 at day 14 and day 28 and the SP60 at day 28. These three groups (SP15 day 14, SP15 day 28, and SP60 day 28) were all approximately equal as well. This suggested that equilibrium may have been attained by the SP15 within 14 days and by the SP60 in the 14- to 28-day period. This result is not surprising given the SP15 has a higher F Factor (Table 3-2) compared to the SP60, which would facilitate more rapid kinetics.

The results for the SP30 were generally lower than the SP15 and SP60 results. The lower values in the SP30 were hypothesized to be because the SP30 sank lower in the mesocosm sediment after deployment, exposing the peeper to a deeper sediment layer that may have been purely anoxic and thus, exhibiting lower metal availability. The SP30 is comprised a very dense, heavy PTFE tube that was not supported by the soft test sediment (hence, the sinking of the SP30 to the bottom of the chamber). The SP30 day 14 and day 28 data were approximately equal for the metals except for zinc, indicating that equilibrium may have been attained by the SP30 within 14 days.

Bromide data was not evaluated because the bromide concentration used in the peeper water (100 mg/L) was very comparable to the concentration of bromide present in the Instant Ocean water used as the overlying water in the mesocosms. In future experiments, 1000 mg/L bromide was selected as the target concentration for the peeper water.

In addition to the analytical data, the level or effort (labor time) and materials required to fabricate and process the 1 SP60, 2 SP30, and 4 SP15 peepers was tabulated on a basis to estimate the approximate per-sample costs. The costs assumed as-purchased materials costs and per-hour technician costs at a default ($100 per hour) rate. The actual per-sample wholesale and retail costs would be much higher given the additional overhead and profit costs that would be applied, thus, the costs estimated provide only a rough comparison among the three peeper designs.

The estimated costs for the three peeper designs are shown in Figure 3-3, and indicate that the SP30 design was the most expensive, primarily due to the relatively higher materials cost (due to the PTFE). The SP60 was approximately half of the cost of the SP30. The SP15 was approximately 1.4 times higher in cost than the SP60, primarily because of the higher materials cost and longer preparation time associated with the 4 15-mL SP15 vials compared to the single 60-mL SP60 vial. Overall, however, the SP15 was selected for the remainder of the experiments because it was still relatively inexpensive, especially compared to the SP30. In addition, the SP15 attained equilibrium more rapidly (within 14 days) compared to the SP60, and this could present substantial overall cost savings to the project for field work in which deployment and retrieval could be conducted in a single mobilization (e.g., over a period of 7 to 10 days). A single field mobilization would not likely be feasible if a 14-day or 28-day deployment is required, which is suggested for the SP60.

Experiment 1 Lessons Learned and Recommendations

- The bromide tracer needs to be added to the peeper water at a concentration of 1000 mg/L when deploying peepers in marine sediment.
- The SP15 design offers the most optimal balance in low cost and rapid sampling times (i.e., 14 days or less).
- Deployment times for SP15 in future laboratory experiments should be approximately 14 days.

Table 3-3: Concentrations of target constituents for three candidate peeper designs (SP15, SP60, and SP30) following 14- and 28-day deployments in standard test sediment.

Time	Sampler Type	Sample ID	Concentration (µg/L)							Concentration (mg/L)	
			Cadmium	**Chromium**	**Copper**	**Lead**	**Mercury**	**Nickel**	**Zinc**	**Bromide**	**Chloride**
	Approximate Method Detection Limit		**0.22**	**1.5**	**0.63**	**0.13**	**0.13**	**0.34**	**32**	**2.7**	**710**
14 Days	SP15	EXP1-PP-14-1	ND	ND*	ND*	1.2*	ND	ND*	ND*	110	13,000
		EXP1-PP-14-2	ND	20	140	31	0.8	8.7	160	110	15,000
		EXP1-PP-14-3	ND	35	220	46	1	15	190	110	14,000
	SP60	EXP1-SP-14-1	0.8	3.7	56	4.8	ND	4.6	200	190	27,000
		EXP1-SP-14-2	ND	14	89	17	0.2	6.8	120	ND	11,000
		EXP1-SP-14-3	ND	10	83	12	0.26	4.4	98	ND	9,200
	SP30	EXP1-TP-14-1	ND	ND	5.6	1.1	ND	0.58	65	120	15,000
		EXP1-TP-14-2	ND	5.2	32	5.8	ND	2.5	67	150	22,000
		EXP1-TP-14-3	ND	14	81	17	0.31	5.6	140*	120	14,000
28 Days	SP15	EXP1-PP-28-1	ND	30	210	43	0.92	14	100	100	--
		EXP1-PP-28-3	ND	17	120	26	ND	9.7	94	180	--
	SP60	EXP1-SP-28-1	ND	7.4*	52*	11*	ND	3.7*	37*	110	--
		EXP1-SP-28-2	ND	26	190	39	0.83	14	130	110	--
		EXP1-SP-28-3	0.3	33	190	45	0.77	16	160	20	--
	SP30	EXP1-TP-28-1	ND	6.6	40	8.6	ND	3.1	30	140	--
		EXP1-TP-28-3	ND	6.4	46	8.9	ND	3.7	37	780	--
Blanks		EXP1-PP-28-BLANK	ND	ND	1.1	ND	ND	ND	16	86	--
		EXP1-SP-28-BLANK	11	ND	8	0.19	ND	ND	81	100	--
		EXP1-TP-28-BLANK	ND	ND	15	ND	ND	ND	89	99	--

Notes:

* - Identified as outlier

-- - Not sampled

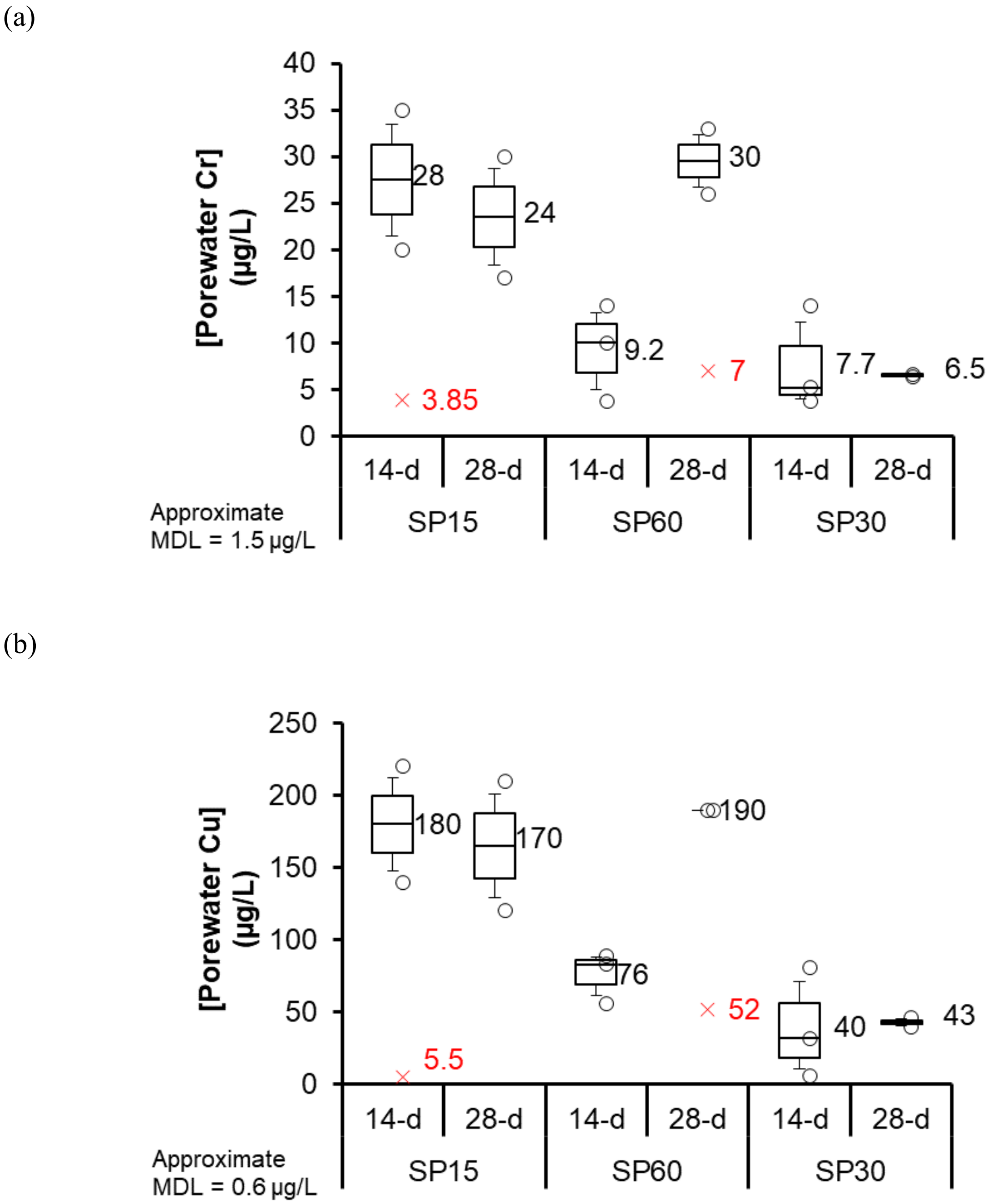
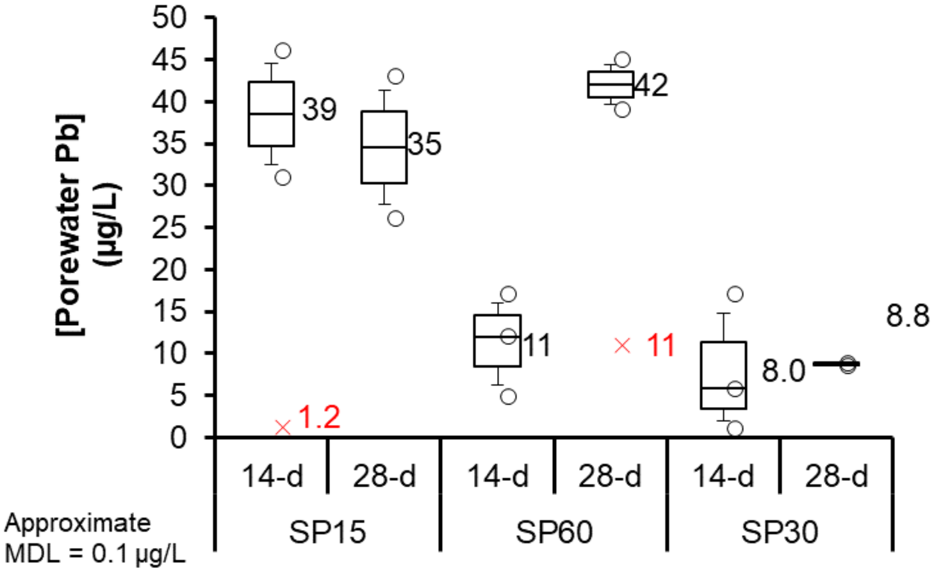


Figure 3-2: Concentrations of target metals in standard sediment-deployed peeper waters for three candidate peeper designs (SP15, SP60, and SP30) tested over two time periods (14 and 28 days). Data are not shown for mercury or cadmium due to the high number of ND results for these metals.

(c)



(d)

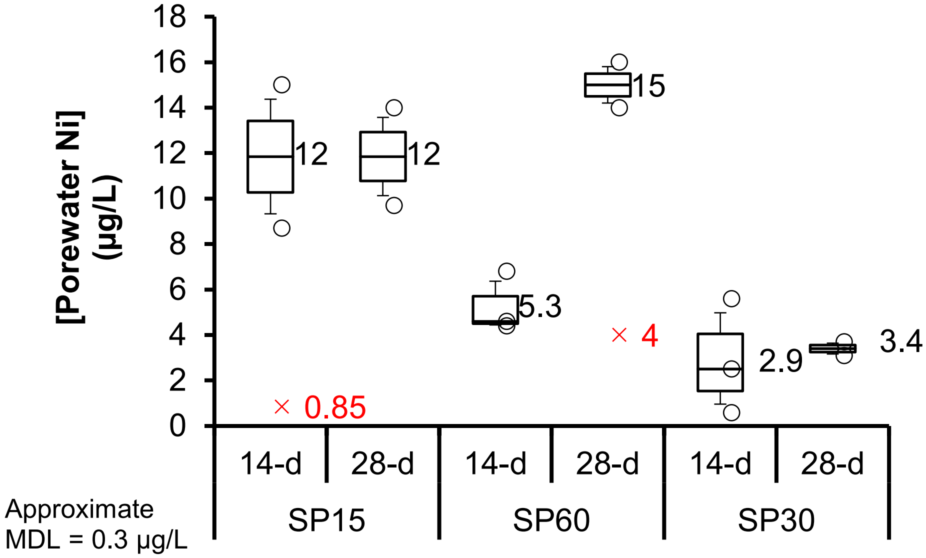


Figure 3-2: Continued.

(e)

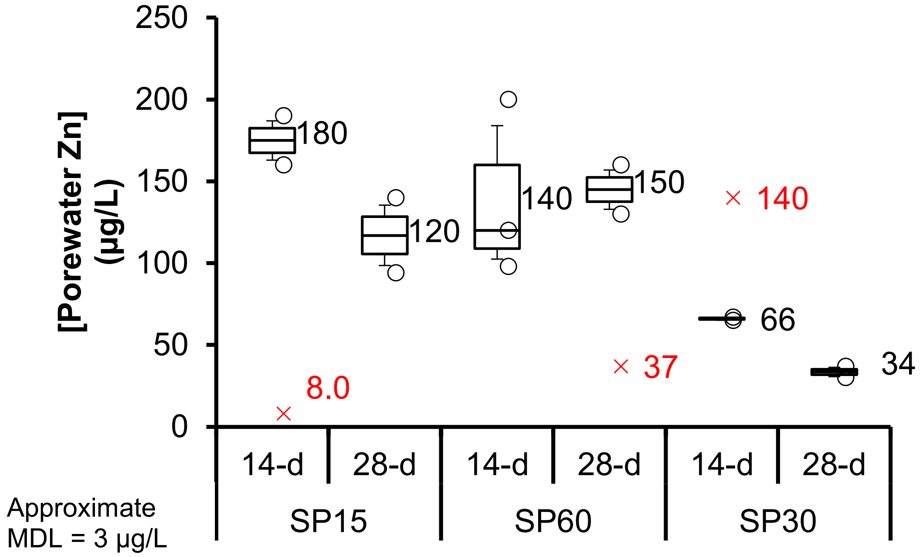


Figure 3-2: Continued.

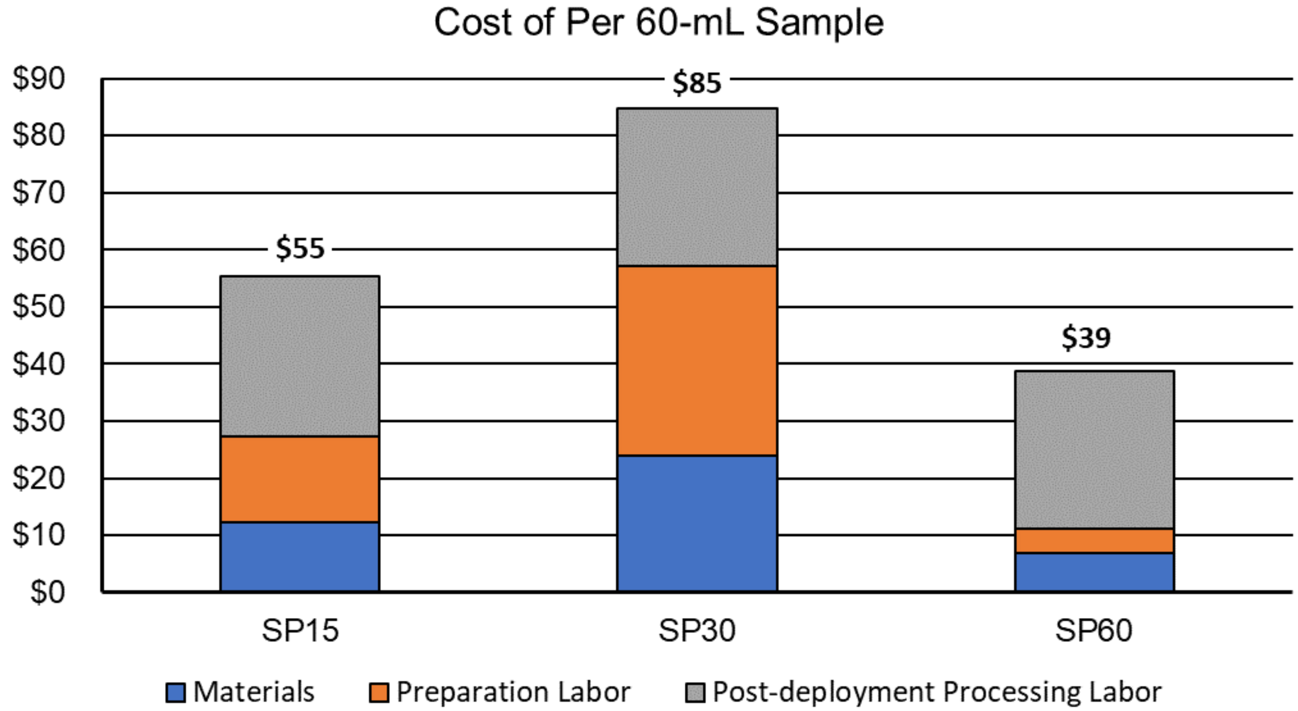


Figure 3-3: Cost breakdown for each of the three peeper designs to produce a 60-mL porewater sample. Cost values plotted are not intended to represent retail prices offered to passive sampling commercial customers, as the values do not include costs for overhead, research and development costs, profits, etc. These values are presented to represent relative differences in base cost among the three sampler designs.

3.2 Experiment 2: Peeper Deoxygenation

3.2.1 Rationale and Methods for Experiment 2

Experiment 2 was conducted to evaluate the need for deoxygenation of the peeper water prior to deployment.

Deoxygenation of peeper waters during manufacturing, preparation, and storage is a complicated process requiring specialized equipment such as anaerobic glove boxes/glove bags and compressed inert gases (typically nitrogen, argon, or helium). It is assumed that peeper waters need to be deoxygenated because most sediments in which peepers are deployed are partly or completely anoxic. As discussed in Risacher et al. (2023a), it is hypothesized that oxygen present in the peeper water prior to deployment could alter redox conditions in the sediment in which it is deployed, potentially affecting the availability of metals that are affected by the presence of oxygen (e.g., the target metals in this study, and manganese and iron). Thus, in previous investigations and studies, peepers are often deoxygenated when prepared and/or before being deployed in the field to ensure redox sensitive species are not affected by oxygen present in the peeper water or peeper plastic once inserted in the sediments (Risacher et al., 2023a). Deoxygenation of peepers before deployment has been inconsistently applied in prior peeper work, and no consensus has been reached on the importance of these procedures. Experiment 2 was conducted to compare the concentration of the target metals in peepers prepared with and without deoxygenation when deployed in sediment.

Peepers were prepared and cleaned via the standard method used Experiment 1, with the exception of the deoxygenation step. Only the SP15 design was used since it performed best in Experiment 1.

- Half of the peepers were prepared via standard deoxygenation procedure and half were prepared without deoxygenation. Deoxygenated peepers were prepared in a bath with 0.05 mg/L DO and stored in protective bag filled the tracer water to maintain anoxia. Each peeper was deployed one by one to limit oxygen ingress as much as possible. Each peeper was exposed to air for a maximum of 30 seconds between the bag storage and the deployment in sediments.
- Half of the peepers were prepared without the deoxygenation procedure. Oxygenated peepers were prepared the same manner as above, however, DO in the peeper water bath was 8.05 mg/L, as it was not purged with argon.

A lithium bromide salt was chosen as the tracer to provide additional tracer options, especially in sea water, where bromide is present at approximately 65 mg/L. Lithium bromide tracer concentration in the preparation bath was at 1000 mg/L.

Deployment of peepers were on the same day as peeper preparation to limit storage time. In total, 16 deoxygenated SP15s were deployed in four mesocosms while 16 oxygenated SP15s were deployed in four mesocosms. Four deoxygenated SP60 were deployed in four mesocosms as a way to confirm lithium and bromide tracer data between the two sampler designs, a confirmation of Experiment 1 results. Blank SP15 and SP60 were also produced for each preparation methods. Samplers were retrieved after 14 days and processed on the benchtop immediately after retrieval from sediment.

3.2.2 Results and Discussion for Experiment 2

Overall results are shown in Table 3-4, with supporting analytical chemistry reporting in Appendix B. As shown in Figure 3-4, 14-day deployment results for the SP15s indicated no significant differences ($P > 0.05$) between deoxygenated and oxygenated SP15 peepers for the seven metals that indicated a majority of results above the MDL (much of the cadmium and mercury data were ND). Individual figures for each metal are shown in Figure 3-5. This indicated that there were no differences in results between peepers prepared with or without the deoxygenation step. Thus, the small amount of oxygen in the of peeper water (8 mg/L DO in 60 mL of water per mesocosm) is unlikely to greatly influence DO in the surface sediment, redox reactions, and metals geochemistry over the 14-day equilibration period.

Although the overlying water was aerated in this experiment, DO levels in the sediment to which the peepers were exposed were likely hypoxic (e.g., < 2-3 mg/L). For example, average (SD) concentrations of DO as measured in water of peepers deployed 2 and 5 days in aerated sediment (side experiment) that received aeration were 1.2 (0.12) mg/L and 1.5 (0.13) mg/L, respectively. Concentrations of DO in an unaerated sediment (Experiment 3) were lower (0.1 to 0.4 mg/L; Table 3-5). Target metal availability is expected to be lower for sediments with lower concentrations of oxygen, whereas availability of iron and manganese is expected to be higher in sediments with lower concentrations of oxygen. Availability conditions were similar for most metals when evaluated in the aerated and unaerated sediment when evaluated as a part of Experiment 3 (Figure 3-10). This indicated that the sediment, even when the overlying water was aerated, was relatively low in oxygen for Experiment 2. Thus, if the presence of oxygen in the peeper water was able to cause a change in metal availability in a poorly oxygenated sediment, Experiment 2 would have been able to provide evidence of this process. However, there was no evidence of a difference between results of deoxygenated and oxygenated peepers (Figure 3-4). Overall, deoxygenation of peepers prior to deployment is considered to be unnecessary.

Figure 3-6 depicts the percentage to equilibration indicated by lithium and bromide tracers for deoxygenated SP15s, oxygenated SP15s, and deoxygenated SP60s. These results indicate that there was no difference ($P > 0.05$) in equilibration between the oxygenated and deoxygenated SP15s, as the percentage of equilibration was approximately 70% based on the lithium and bromide tracers, indicating no need to deoxygenate the peepers prior to deployment. There was also no difference ($P > 0.05$) between the percentage of equilibration indicated by bromide and lithium for the SP15s, indicating that the kinetics of lithium and bromide were basically identical. This observation was also found in a field deployment of the SP15 peepers (Risacher et al., 2023b). Given the lack of a difference between results estimated with bromide tracer versus the lithium tracer, the fact that bromide concentrations in seawater are likely much higher than concentrations lithium (resulting in some uncertainty regarding tracer elimination rates for bromide), and that fact that the analysis of bromide requires a separate sample preservation and analysis step (Table 2-2), the use of lithium as a single tracer was considered to be advantageous to measuring both bromide and lithium. Using lithium bromide as a tracer, but only quantifying the concentrations of lithium in the peepers, saves analytical costs (i.e., not having a separate analysis for bromide), simplifies the post-deployment peeper processing steps, and allows more peeper water sample volume to be devoted to the analysis of the target metal analytes, which will improve analytical precision and lower MDLs.

The bromide and lithium tracer results also confirmed the results of Experiment 1, which indicated more rapid equilibration for SP15s (approximately 70%) compared to SP60 (approximately 50%), as shown in Figure 3-6. Results for the percentage equilibration values based on bromide and lithium were not statistically significantly different between SP15s and SP60s. However, if the unusually high potential outlier value in the SP60 data (77% and 92% equilibration based on bromide and lithium, respectively) is removed, the percentages of equilibration based on both tracers is statistically lower in the SP60s (averages of 38% and 46%) compared to SP15s (approximately 70%).

Additionally, metal data from the SP60s also confirmed lower degrees of equilibration compared to SP15s. At least a few of the concentrations of the metals (e.g., manganese, copper, lead, etc.) were significantly ($P < 0.05$) different, with the mean concentrations in the SP15s being generally 2-4 times higher than concentrations indicated by the SP60s. For example, in Figure 3-7 (left), concentrations of manganese in the SP15s (data from both deoxygenated and oxygenated SP15s), concentrations in the peeper water were statistically different, with concentrations in the SP15s (210 µg/L) being approximately a factor of 2 higher than the SP60s (110 µg/L). However, when the data are corrected to equilibrium using the lithium tracer data (equations in Section 2.3), it is notable that the average concentrations of manganese for SP15s and SP60s are 400 µg/L and not statistically different (Figure 3-7, right). This provided initial support for the ability of the tracer to enable pre-equilibrium sampling. Additional verification of the pre-equilibrium sampling was conducted in Experiment 6.

Overall, the tracer and metal data further support the general observation that, at 14 days, the SP15 is more equilibrated than the SP60. However, SP60s would still be valid for use given the relatively high amount of equilibration attained in a 14-day deployment. SP60s provide more volume per peeper (60 mL instead of 15 mL), and this factor may be helpful for measurement programs that require more sample volume. For the remainder of this project, SP15s were used as the default peeper design.

Experiment 2 Lessons Learned and Recommendations

- Peepers do not need to be deoxygenated prior to deployment in sediment.
- Lithium can also be used as a tracer and indicated the same results as the bromide tracer.
- The use of lithium tracer is advantageous because lithium can be measured in the same sample as the target metals, unlike bromide, which requires a separate sample and analysis.

Table 3-4: Concentrations of target metals, concentrations of lithium and bromide tracers, and percentage equilibration for lithium and bromide tracers for two peeper designs (SP15 and SP60) deployed in standard sediment for 14 days. Peepers were oxygenated or deoxygenated prior to deployment.

		Concentration (µg/L)										[mg/L]	Lithium Equilibrium %	Bromide Equilibrium %
Sampler Type	**Sample ID**	**Cadmium**	**Chromium**	**Copper**	**Iron**	**Lead**	**Manganese**	**Mercury**	**Nickel**	**Zinc**	**Lithium**	**Bromide**		
Approximate Method Detection Limit		**0.22**	**1.5**	**0.63**	**20**	**0.13**	**0.87**	**0.13**	**0.34**	**3.2**	**34**	**2.7**		
SP15 Deoxygenated	EXP2-SP15-DO-1	ND	1.6	9.5	26000	1.8	220	ND	0.8	7.5	30000	290	66%	70%
	EXP2-SP15-DO-2	ND	ND	3.3	28000	0.55	200	ND	ND	8	26000	250	70%	74%
	EXP2-SP15-DO-3	ND	ND	3.5	28000	0.6	200	ND	0.35	ND	31000	340	64%	65%
	EXP2-SP15-DO-4	ND	1.6	8.4	31000	1.8	210	ND	0.81	7.6	30000	320	66%	67%
SP15 Oxygenated	EXP2-SP15-O-1	ND	ND	8.6	28000	1.8	220	ND	0.83	5.6	25000	290	71%	70%
	EXP2-SP15-O-2	ND	ND	5.4	27000	1.2	190	ND	0.56	4.4	27000	290	68%	70%
	EXP2-SP15-O-3	ND	1.5	5.8	29000	1.4	220	ND	0.67	4.9	27000	300	68%	69%
	EXP2-SP15-O-4	ND	ND	5.2	21000	1.1	230	ND	0.61	4.9	34000	340	60%	65%
SP60 Deoxygenated	EXP2-SP60-1	ND	ND	1.3	7400	0.22	81	ND	ND	ND	64000	670	26%	30%
	EXP2-SP60-2	ND	ND	1.3	11000	0.27	140	ND	ND	ND	47000	440	46%	54%
	EXP2-SP60-3	ND	ND	3.3	5300	0.73*	84	ND	0.43	6.4	52000	450	40%	53%
	EXP2-SP60-4	1.2	ND	38*	ND*	0.29	140	ND	2.9*	27*	6800	220	92%	77%
Blanks	EXP2-SP15-DO-BLK	ND	ND	1.3	ND	ND	ND	ND	ND	40	87000	980	NA	NA
	EXP2-SP15-O-BLK	ND	ND	1.8	20	0.13	ND	ND	ND	27	85000	40*	NA	NA
	EXP2-SP60-BLK	ND	2.2	0.75	20	ND	ND	ND	ND	5.3	87000	960	NA	NA

Notes:
* - Identified as outlier
NA - Not applicable

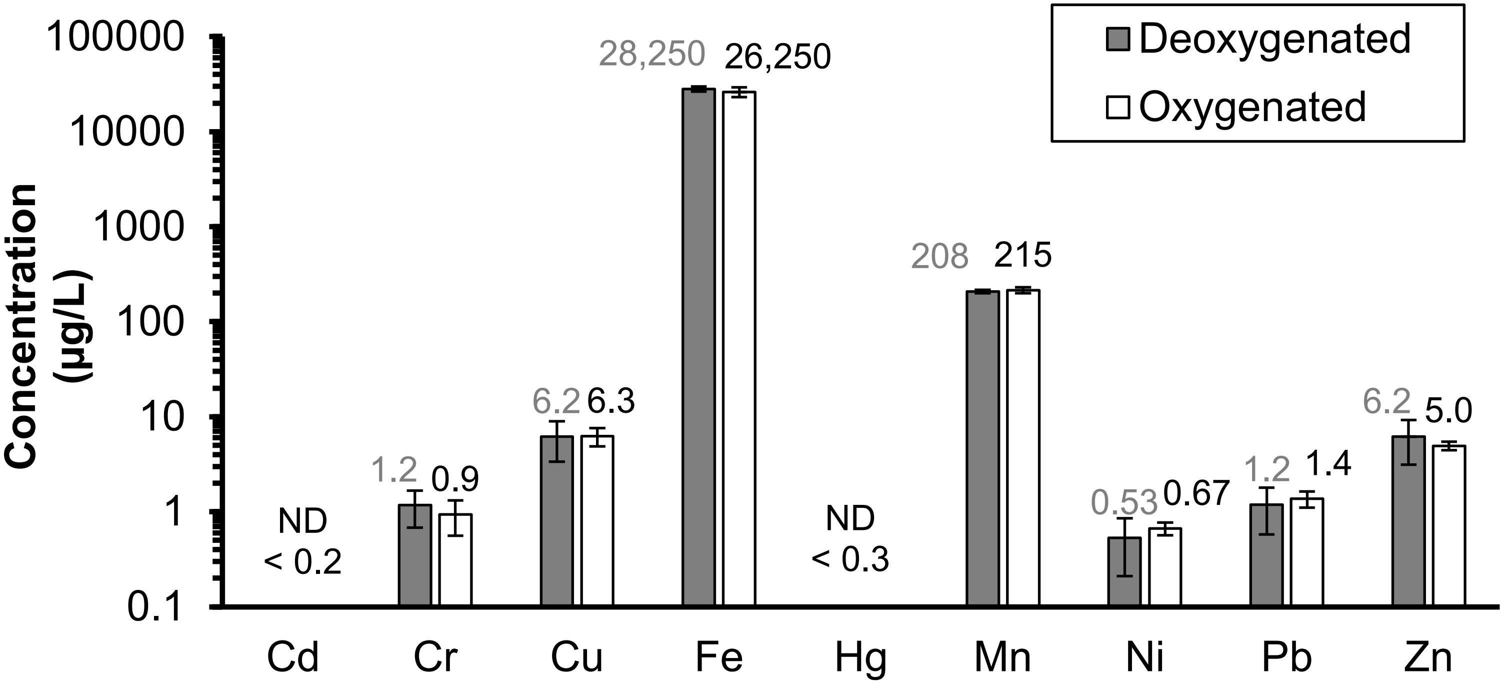
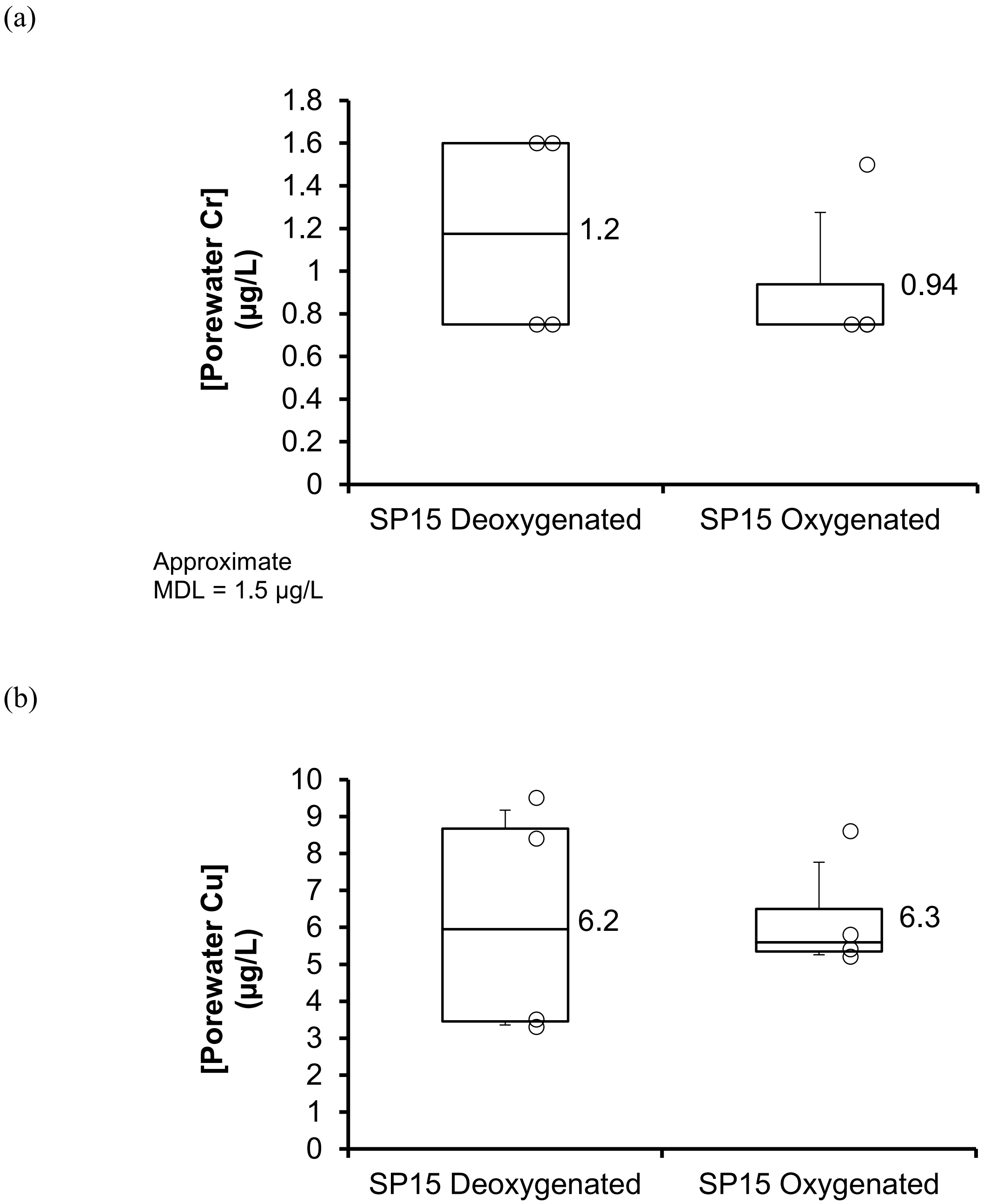


Figure 3-4: Mean concentrations (SD) of metals in standard sediment-deployed peeper waters for SP15 samplers that were either oxygenated or deoxygenated prior to deployment. Data is not shown for mercury or cadmium due to the high number of ND results.

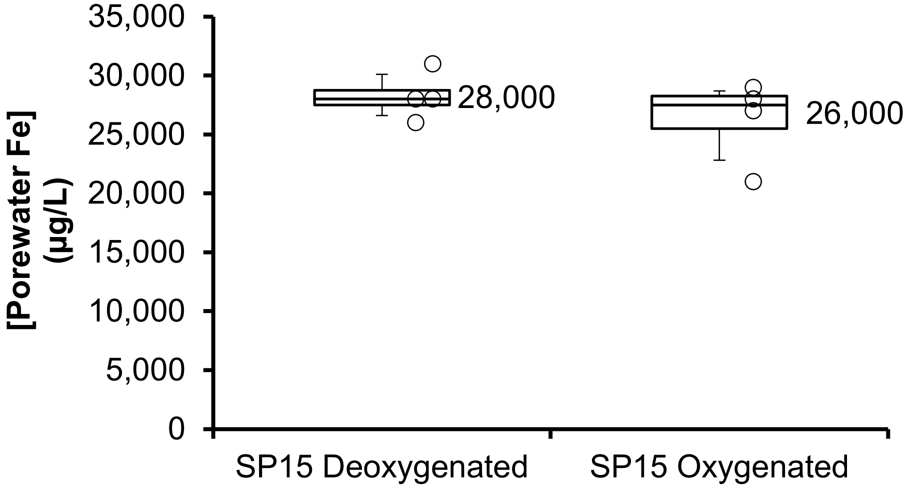


Approximate
MDL = 1.5 µg/L

Approximate
MDL = 0.6 µg/L

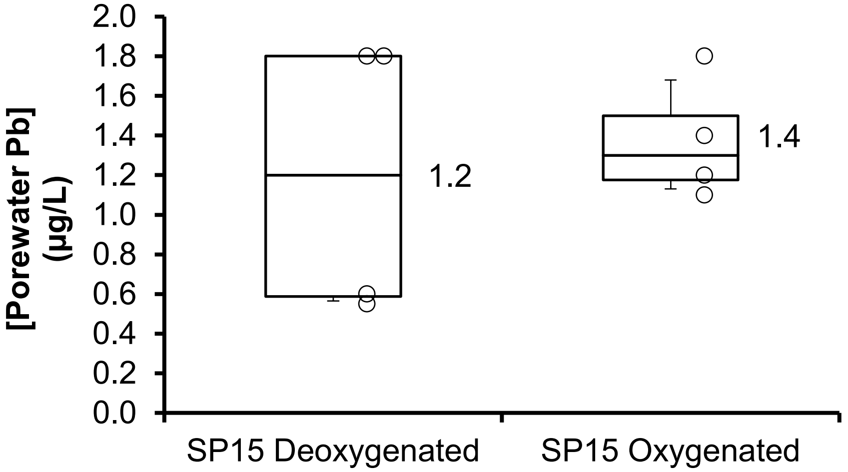
Figure 3-5: Concentrations of metals in standard sediment-deployed peeper waters for SP15 samplers that were either deoxygenated prior to deployment or left oxygenated. Data is not shown for mercury or cadmium due to the high number of ND results.

(c)



Approximate
MDL = 20 µg/L

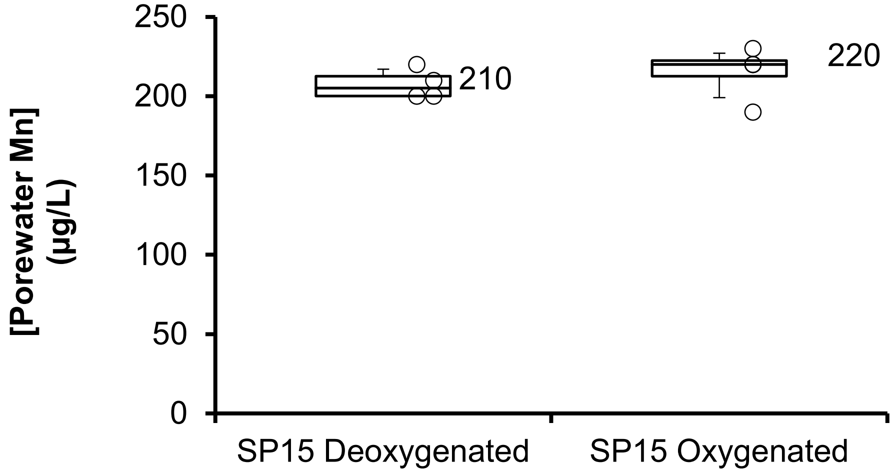
(d)



Approximate MDL =
0.13 µg/L

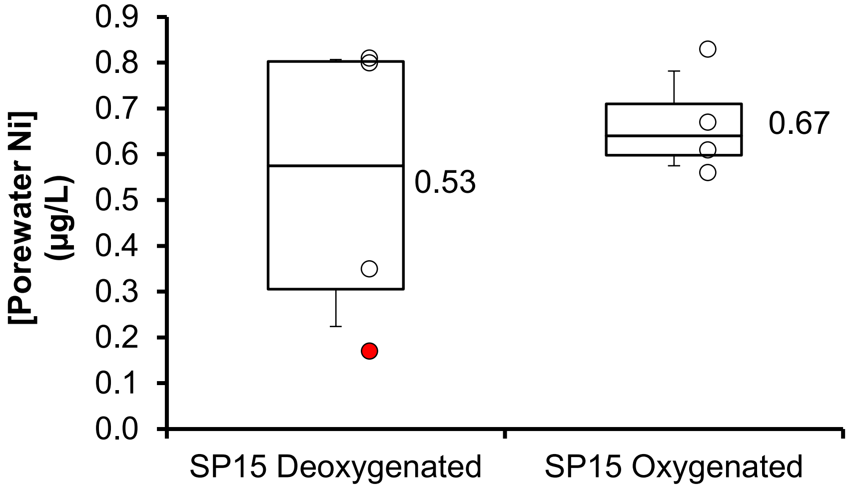
Figure 3-5: Continued.

(e)



Approximate
MDL = 0.87 µg/L

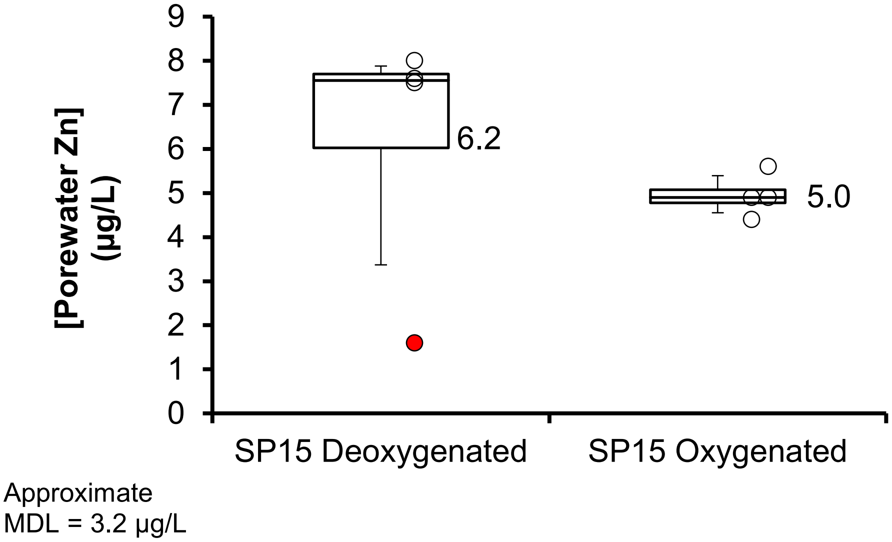
(f)



Approximate MDL =
0.34 µg/L

Figure 3-5: Continued.

(g)



Approximate
MDL = 3.2 µg/L

Figure 3-5: Continued.

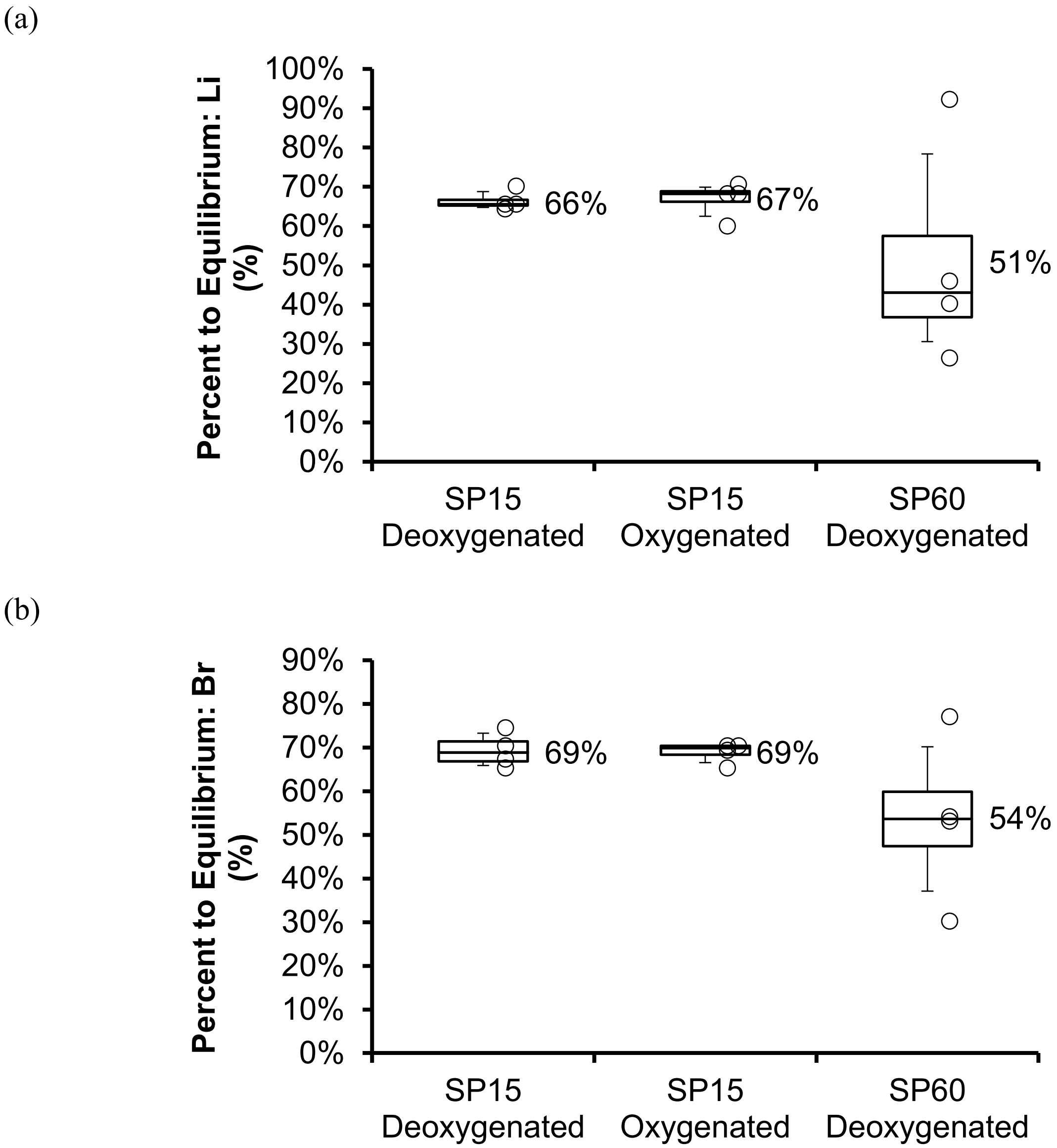


Figure 3-6: Percentage to equilibration indicated by lithium (a) and bromide (b) tracers for deoxygenated SP15, oxygenated SP15s, and deoxygenated SP60s deployed in standard sediment for 14 days.

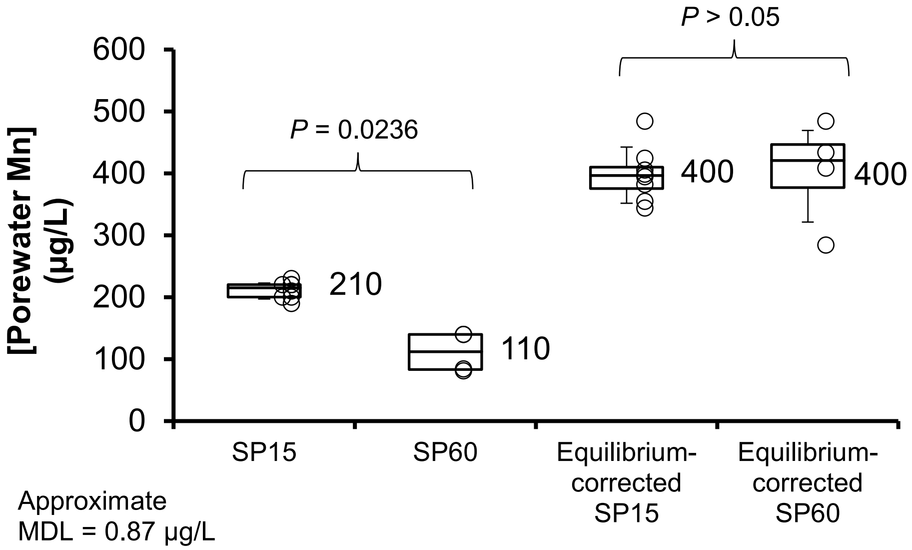


Figure 3-7: Concentrations of manganese peeper waters for SP15 samplers and SP60 deployed in standard sediment for 14 days. Data are shown as measured (left), which indicate a statistical difference between SP15s and SP60s. When data are corrected to the concentration expected at equilibrium using lithium tracer measurements (right), there is no statistical difference between SP15s and SP60s.

3.3 Experiment 3: Peeper Sample Processing

3.3.1 Rationale and Methods for Experiment 3

Experiment 3 was conducted to identify the need to process deployed peepers in an inert atmosphere versus air.

As with a lack of consensus with the need for deoxygenation of peepers prior to deployment, there is also a lack of consensus on the need to protect peeper samples from oxygen after they removed from a sediment low in oxygen. As discussed in Risacher et al. (2023a), it is hypothesized that oxygen could diffuse into the peeper water, altering redox conditions before or during the process of transferring the water to the sample storage bottle (in which it is preserved via acidification). One potential mechanism affecting samples is via oxygen contamination prior to acidification that could result in loss of metals via precipitation of iron oxides that scavenge dissolved metals from the water solution, followed by partitioning of the precipitates to the inside of the peeper chamber (preventing transfer of the metal mass to the sample storage container).

As a result of these hypotheses, some sample processing procedures have focused on transferring peeper waters to storage containers in anoxic atmospheres (e.g., nitrogen-filled glove boxes). However, no consensus has been reached for an optimum protocol for collecting porewater from peepers once recovered (Risacher et al., 2023a). Most methods have focused on maximizing the speed at which the peeper water can be extracted from the peeper and transferred to the sample storage container. However, faster transfer methods also carry a risk of particles or oxygen contamination. The goal of Experiment 3 was to evaluate multiple processing methods and compare the concentration of metals in peepers.

For Experiment 3, SP15 peepers were built and cleaned via the same standard method from Experiment 1, although without deoxygenation of the peeper water prior to deployment. The lithium bromide tracer was not added in this deployment. Two separate deployments were conducted. In the first deployment, peepers were deployed in the standard sediment for 14 days. This sediment received aeration, which resulted in hypoxic conditions in sediment (approximately 1 mg/L). After retrieval peepers were sampled using either one of three methods that were evaluated as part of this experiment:

- **Pipetting in air:** This is the same method that has been used in Experiments 1 and 2, where the peepers are retrieved one at a time, cleaned using DI water and pierced with a 25 mL pipette to collect the peeper water. The water is then dispensed into the sample storage bottle containing the nitric acid preservative. The entire processing procedure is performed on the benchtop in a normal ambient (air) atmosphere.
- **Pipetting in glove box:** This method is similar to the pipetting in air with the difference that peepers are removed from sediment and placed in a nitrogen-purged glove box. The entire processing procedure (as above) is performed in the inert nitrogen atmosphere. This allows the peepers water to avoid contact with oxygen, but adds a high degree of complexity to the processing procedure.
- **Open and pour in air:** This is the simplest method, where the peepers are retrieved one at a time, cleaned with DI water and then manually opened via unscrewing the plastic cap (ring) holding the membrane on to the peeper chamber. After the membrane is removed, the peeper water is poured into the sample bottle. The entire processing procedure is performed on the benchtop in a normal ambient (air) atmosphere. It was hypothesized that

this method could simplify the processing approach and avoid the need to use a pipette for transferring the peeper water.

In this aerated exposure with the standard sediment, 12 mesocosms were prepared and sampled with three peepers each for a total of 12 samples. Four samples were processed using the pipette method in air, 4 samples were processed by the pour method, and 4 samples were processed via pipetting in the glove box method. Blanks were processed using each of these 3 methods. Samples were analyzed for target metals, lithium, manganese, and iron.

A second deployment was also conducted to evaluate the Experiment 3 study questions. This second deployment was conducted because peepers deployed in sediment had low levels of oxygen (e.g., approximately 1 mg/L), representative of hypoxic sediments. It was hypothesized that a clearer difference would be evident if a purely anoxic sediment was tested, so the second experiment was conducted with sediment in mesocosms that were not aerated. This resulted in lower concentrations of oxygen in the peeper water, approximately 0.1 to 0.4 mg/L (Table 3-5). Additionally, the second deployment was conducted with the spiked sediment. This allowed an evaluation of several of the metals that yielded non-detect results in the first deployment of Experiment 3.

In the second deployment, peepers were prepared following the standard method from Experiment 1 with no deoxygenation. The lithium bromide tracer was added in this deployment. The mesocosms were not aerated to keep the sediments anoxic and contained spiked sediments. Four peepers were deployed for 14 days per mesocosms for a total of 6 mesocosms. Half of the peepers (three mesocosms) were processed using the pipetting in air method while the other half (three mesocosms) was processed using the pipetting in nitrogen method. Both methods were identical to the ones described above. The simple “open and pour” method was not used in the second deployment because of the potential for contamination and lack of control and precision with liquid transfer afforded by the pipette transfer method. Blanks were prepared and immediately processed using the pipetting in air method. Samples were analyzed for target metals, lithium, manganese, and iron.

3.3.2 Results and Discussion for Experiment 3

Overall results for the first deployment with the aerated, standard sediment (no tracer) are shown in Table 3-4 and overall results for the second deployment with the unaerated, spiked sediment (with tracer) are shown in Table 3-5. Supporting analytical chemistry reporting in Appendix B. In the first deployment, cadmium and mercury were not detected, but the 8 other metals were able to be used to evaluate differences between the processing methods.

Concentrations of metals in peepers that were processed by the “open and pour” method (conducted in air) were clearly higher than in peepers in which the water was transferred by pipette (Figure 3-8) in two of the eight metals. In the case of lead (Figure 3-8d), this was statistically significant ($P < 0.05$). In the case of chromium (Figure 3-8a), chromium was not detected (i.e., < 0.75 μg/L) in the samples transferred by pipette, but was detected (average 4.5 μg/L) in peeper waters processed by the “open and pour” method. This could be due to particle contamination encountered during the pouring approach. However, the data were not consistent. In the case of iron, manganese, and lithium (three of eight metals; Figure 3-8), it was clear that there was no such potential contamination due to the “open and pour” method. Over the course of the experiment, it was observed that the pipette method afforded a higher degree of control and precision with regards to the transfer of peeper water such that there was no substantial time savings in the “open and pour" method. Overall, although results in Figure 3-8 are mixed, it was concluded that the pipetting method is preferable to the "open and pour" method, simply due to the ease of liquid transfer. In cases in which a pipette is unavailable to aid in peeper processing, the "open and pour" method may be acceptable for processing, with the understanding that there may be a chance of particle contamination that could bias the results high.

With regards to the need to transfer the peeper water in air versus nitrogen, the results from the first deployment (aerated, standard sediment) were mixed:

- Concentrations of copper and zinc were approximately 5 to 6 times statistically higher ($P < 0.05$) in the peepers transferred in air compared to those transferred in nitrogen (Figures 3-8b and 3-8g). If processing peepers in air caused formation of iron precipitates that resulted in loss of metals to the interior surface of the peeper container, one would expect lower concentrations of affected metals in the peepers processed in air. However, the opposite was observed for copper and zinc.
- Concentrations of manganese and iron were not significantly different ($P > 0.05$) in the peepers transferred in air compared to those transferred in nitrogen (Figures 3-8c and 3-8e). There was also no significant difference for lithium (Figure 3-8h); however, as lithium availability is not affected by redox changes a difference was not expected.
- Results were unclear for chromium due to complete lack of detectable concentrations in peepers pipetted in nitrogen and peepers pipetted in air (Figure 3-8a).
- Results were unclear for lead due to a high number of non-detect data in peepers processed in nitrogen (Figure 3-8d). Results for peepers pipetted in air (0.18 to 0.86 µg/L) were just above the detection limit of 0.17 µg/L.
- Results were somewhat unclear for nickel. Although concentrations of nickel were not significantly different ($P > 0.05$) in the peepers transferred in air compared to those transferred in nitrogen (Figure 3-8f), three of the four results for peepers pipetted in nitrogen were non-detect, complicating the comparison.
- Results for cadmium and mercury were not evaluated because they were largely ND.

With regards to the need to transfer the peeper water in air versus nitrogen, the results from the second deployment (unaerated, standard sediment) were more consistent than the second deployment. For all metals except for mercury (which did not yield enough detections to be analyzed statistically), there were no statistically detectable differences ($P > 0.05$) in the concentrations of cadmium, chromium, copper, iron, lead, manganese, nickel, or zinc (Figure 3-9). Oxygen had the ability to affect the porewater, as oxygen does increase as a result of pipetting the peeper water in air on the benchtop. This was observed in the second deployment peepers. As shown in Table 3-5, simply pipetting in air increased the concentrations of oxygen by approximately 1 mg/L (from approximately 0.4 mg/L to approximately 1.5 mg/L).

Overall, Figures 3-8 and Figure 3-9 do not provide evidence of a clear difference with regards to processing via pipetting in air versus nitrogen. The most notable difference was found for copper and zinc in the first deployment, where concentrations increased by a factor of 5-6 as a result of pipetting the peeper water in air. However, this difference was not found in the second deployment. Given that the difference observed for copper and zinc was the reverse of the expected effect of pipetting in air, and was not observed in the second deployment, or for other metals, it was concluded that pipetting in air, when conducted in the manner as described in the methods of this study, is acceptable.

Additionally, the concentrations of copper, zinc, manganese, and iron in the peepers for the first and second deployments were compared (Figure 3-10). Only copper, zinc, manganese, and iron were compared because other target metals were added to the sediment after the first aerated (hypoxic) sediment deployment, but before the second unaerated (anoxic) sediment deployment. Overall, concentrations indicated little differences in availability between the hypoxic and anoxic sediments, with the exception of manganese, which was a factor of approximately 2 higher in the anoxic sediment when compared to the aerated (hypoxic) sediment. This is expected given that the availability of manganese would be expected to be higher at lower concentrations of oxygen. It is notable that the difference in manganese availability between the hypoxic and anoxic was detected by peepers processed in air and peepers processed in nitrogen. This provides further support that indicates that the effects of pipetting in air or nitrogen do not affect results.

Overall, the results of Experiment 3 indicate that pipetting peeper water is preferable to pouring. Pipetting in an inert atmosphere, even for peepers water that are anoxic, is not required, as there were no consistent differences in results of peepers processed in air versus peepers processed in nitrogen. The ability to process peepers in air greatly simplifies the peeper processing approach, as processing in nitrogen requires a specialized setup with compressed gases (e.g., nitrogen) and a glove box or glove bag. In addition to the additional costs and complications of the setup, processing in the nitrogen glove bag required much more labor time for a technician to process each sample, increasing costs and processing time.

Experiment 3 Lessons Learned and Recommendations

- If particles are thoroughly removed from peepers, peeper water may be simply poured from the peeper into the sample storage container; however, pipetting is recommended due to the added control and precision of liquid transfer.
- There is no need to process exposed peepers in an inert atmosphere – peeper water can be transferred (via pipette) from the peeper to the sample storage and preservation container in air without affecting results.

Table 3-5: Oxygen concentration in peeper water before and after pipetting in air or nitrogen. Peepers were deployed in unaerated (anoxic) sediment for 14 days prior to samples being extracted.

Processing Method	Pre-pipetting concentration of oxygen in peeper (mg/L)	Post-pipetting concentration of oxygen in peeper (mg/L)
Pipette in Air	0.44	1.20
	0.42	1.88
	0.33	1.40
Pipette in Nitrogen (Glove Box)	0.13	0.15
	0.15	0.14
	0.17	0.18

Table 3-6: Concentrations of metals and lithium for three different processing methods used to extract samples from peepers. Peepers were deployed in aerated (hypoxic) sediment for 14 days prior to samples being extracted. Lithium tracer was not spiked into the peeper water.

Processing Method	**Sample ID**	**Concentration (µg/L)**									
		Cadmium	**Chromium**	**Copper**	**Iron**	**Lead**	**Manganese**	**Mercury**	**Nickel**	**Zinc**	**Lithium**
Approximate Method Detection Limit		**0.22**	**1.5**	**1.1**	**28**	**0.17**	**1.3**	**0.13**	**0.52**	**2.9**	**0.83**
Pipette in Nitrogen (Glove Box)	EXP3-SP15-GB-1	ND	ND	5.1	28000	1	210	ND	0.55	4.1	160
	EXP3-SP15-GB-2	ND	ND	1.2	23000	ND	210	ND	ND	ND	160
	EXP3-SP15-GB-3	ND	ND	ND	26000	ND	220	ND	ND	ND	160
	EXP3-SP15-GB-4	ND	ND	ND	17000	ND	210	ND	ND	ND	160
Pipette in Air	EXP3-SP15-SE-1	ND	ND	5.5	22000	0.86	200	ND	ND	7.9	160
	EXP3-SP15-SE-2	ND	ND	15	3300	0.33	300	ND	1.7	24	160
	EXP3-SP15-SE-3	ND	ND	11	14000	0.18	220	ND	1.1	12	170
	EXP3-SP15-SE-4	ND	ND	9.1	15000	0.41	230	ND	0.93	9.9	140
Open and Pour in Air	EXP3-SP15-P-1	ND	4.8	25	18000	5.4	200	ND	2	19	180
	EXP3-SP15-P-2	ND	6.3	76	17000	9.4	410	0.16	3.7	36	210
	EXP3-SP15-P-3	ND	1.5	13	27000	1.8	200	ND	0.89	7.4	170
	EXP3-SP15-P-4	ND	5.4	12	31000	2.1	240	ND	0.9	9.6	170
Blanks	EXP3-SP15-GB-BLK	ND	ND	ND	ND	ND	ND	ND	ND	14	ND
	EXP3-SP15-SE-BLK	ND	ND	ND	ND	ND	ND	ND	ND	13	ND
	EXP3-SP15-P-BLK	ND	ND	ND	ND	ND	ND	ND	ND	13	ND

Table 3-7: Concentrations of metals and lithium tracer for three different processing methods used to extract samples from peepers. Peepers were deployed in unaerated (anoxic) sediment for 14 days prior to samples being extracted. Lithium tracer was spiked into the peeper water.

Processing Method	Sample ID	Concentration (µg/L) Cadmium	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Zinc	Lithium
Approximate Method Detection Limit		**0.22**	**1.5**	**1.1**	**28**	**0.17**	**1.3**	**0.13**	**0.52**	**2.9**	**21**
Pipette in Nitrogen (Glove Box)	EXP5A-SP15-PA-1	1.1	14	8.4	16000	3.9	430	0.38	140	26	37000
	EXP5A-SP15-PA-2	0.48	3.8	4.8	14000	1.6	420	ND	130	21	36000
	EXP5A-SP15-PA-3	0.67	7.5	5.4	20000	2.5	510	0.14	150	15	33000
Pipette in Air	EXP5A-SP15-PN-1	0.51	5.3	4.3	14000	2.9	470	ND	160	21	36000
	EXP5A-SP15-PN-2	0.36	3.5	3.9	20000	1.5	500	ND	110	15	31000
	EXP5A-SP15-PN-3	ND	2.1	2.4	11000	1.9	400	ND	130	24	39000
Blank	EXP5A-SP15-PA-BLANK	ND	ND	ND	ND	ND	ND	ND	ND	99	67000

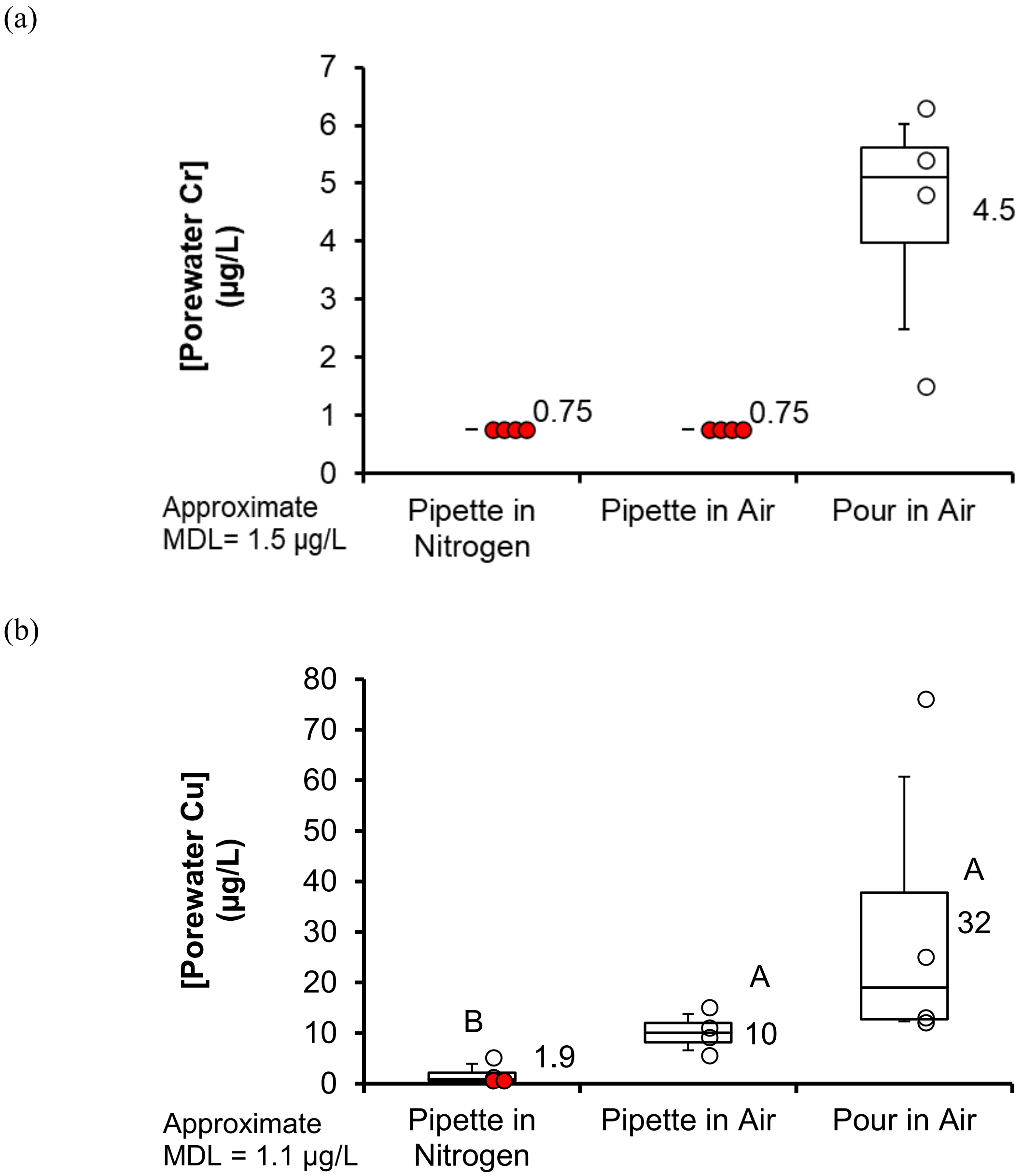


Figure 3-8: Concentrations of metals in standard sediment-deployed peeper waters extracted using three different methods. Peepers were deployed in <u>aerated (hypoxic)</u> standard sediment for 14 days prior to sample extraction. Red-filled symbols are raw data that are plotted (and included in calculation of average) that are below the MDL, with the value being used representing 1/2 of the MDL. Data are not shown for cadmium and mercury due to the high number of ND results.

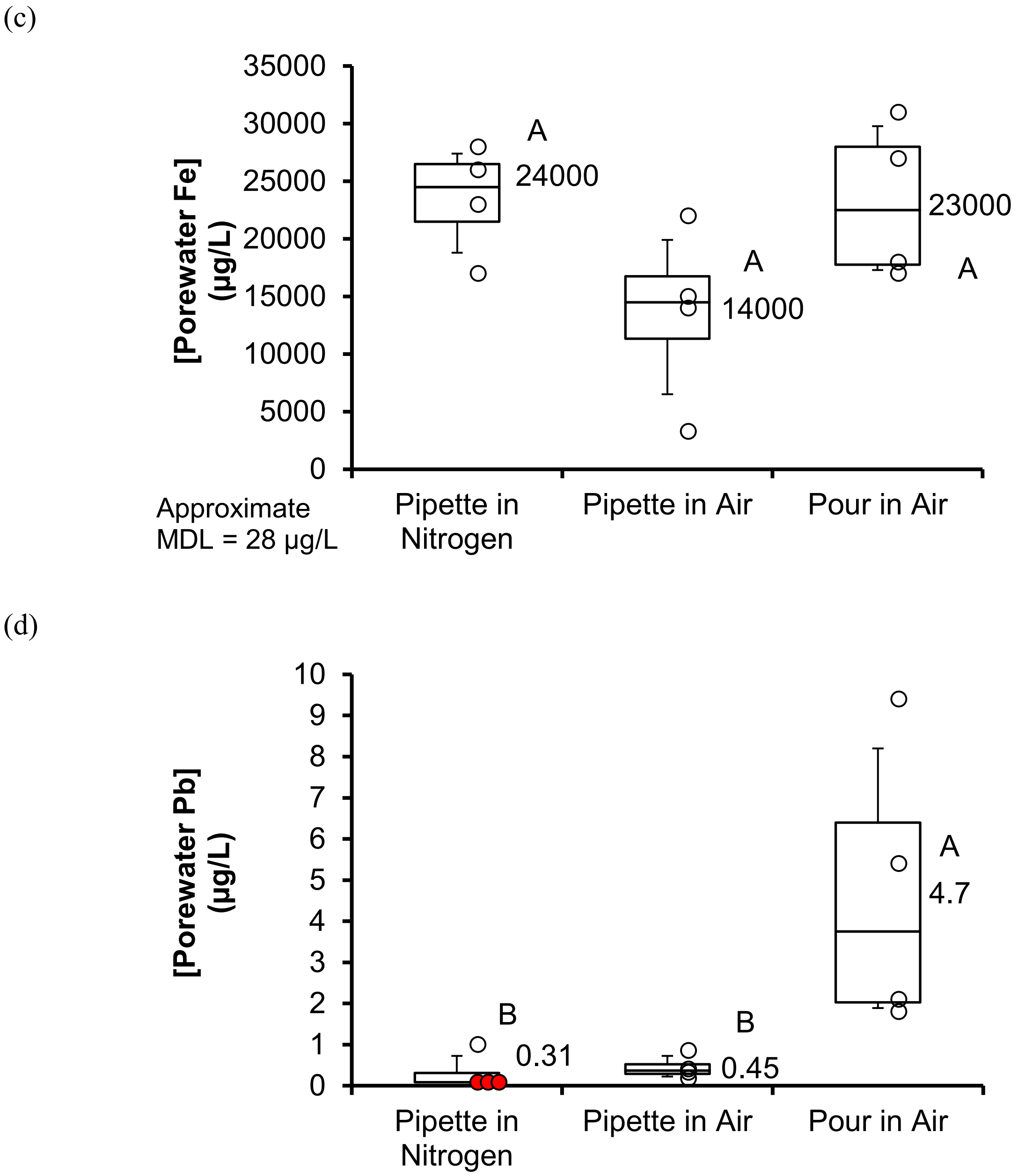
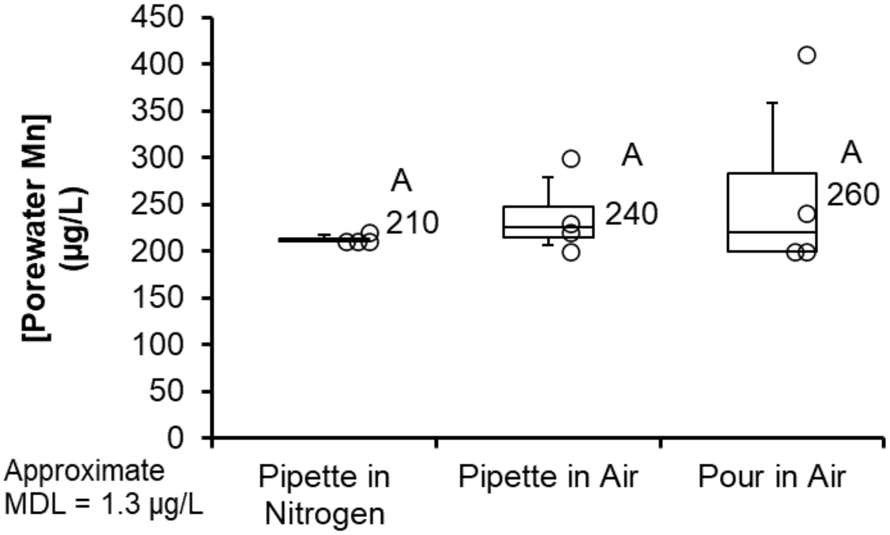


Figure 3-8: Continued.

(e)



(f)

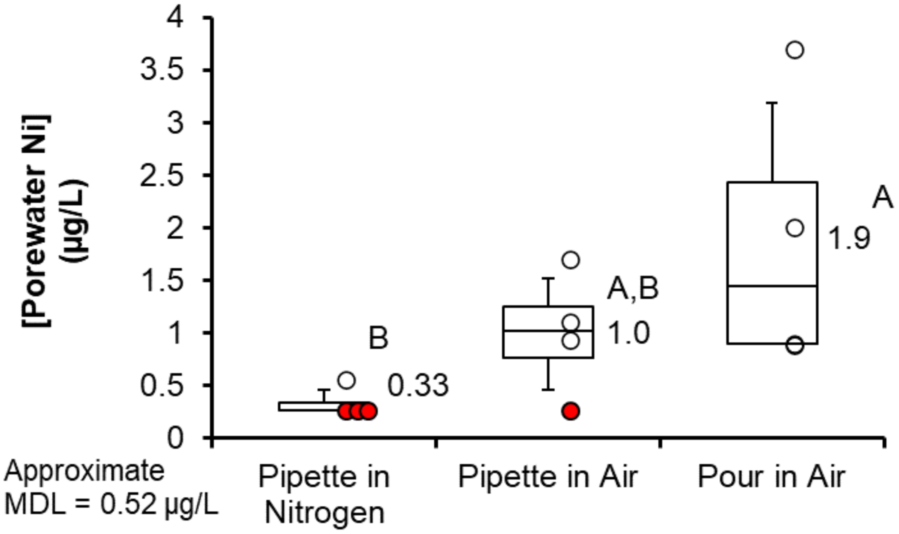
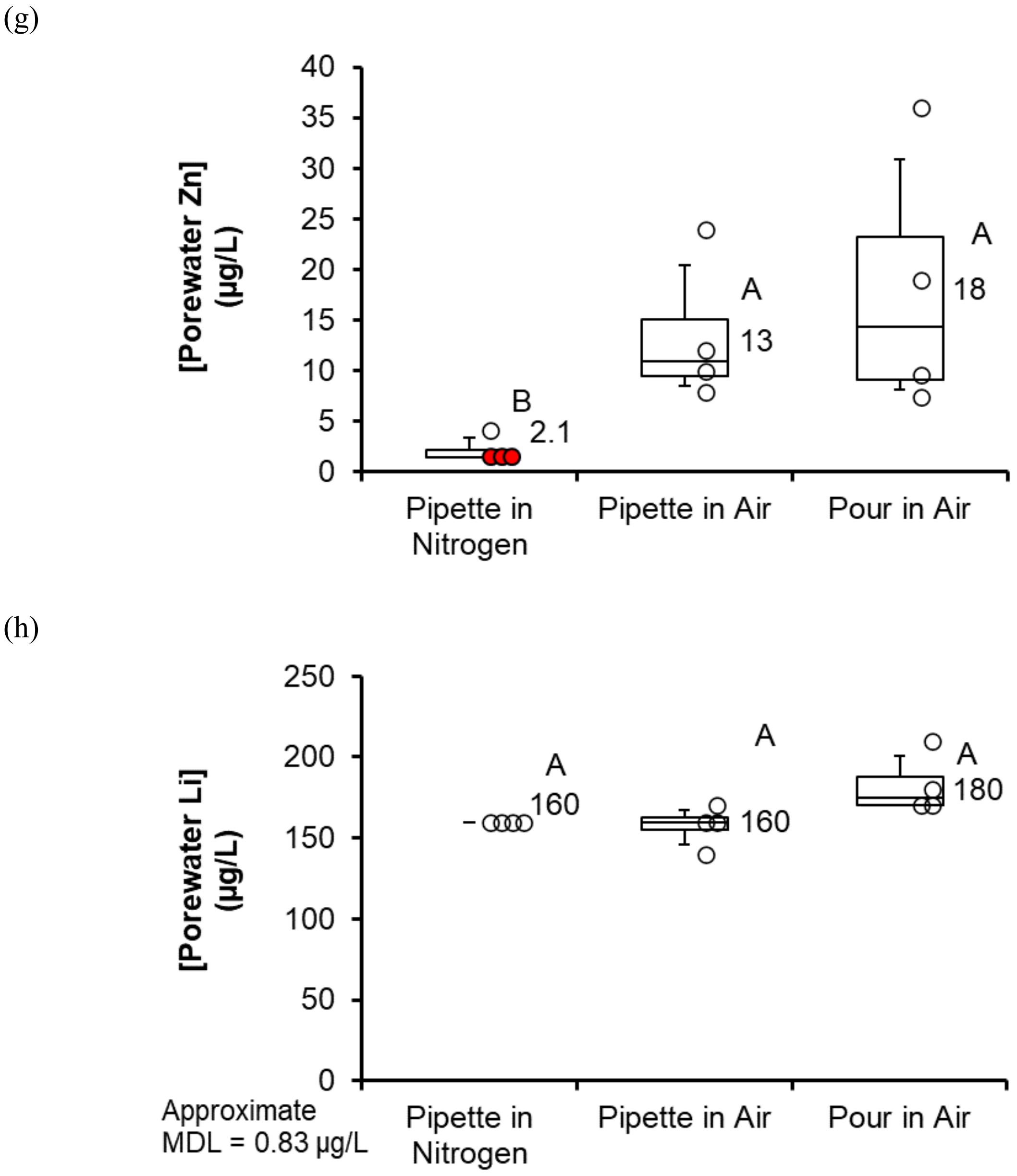


Figure 3-8: Continued.



Approximate MDL = 0.83 µg/L

Figure 3-8: Continued.

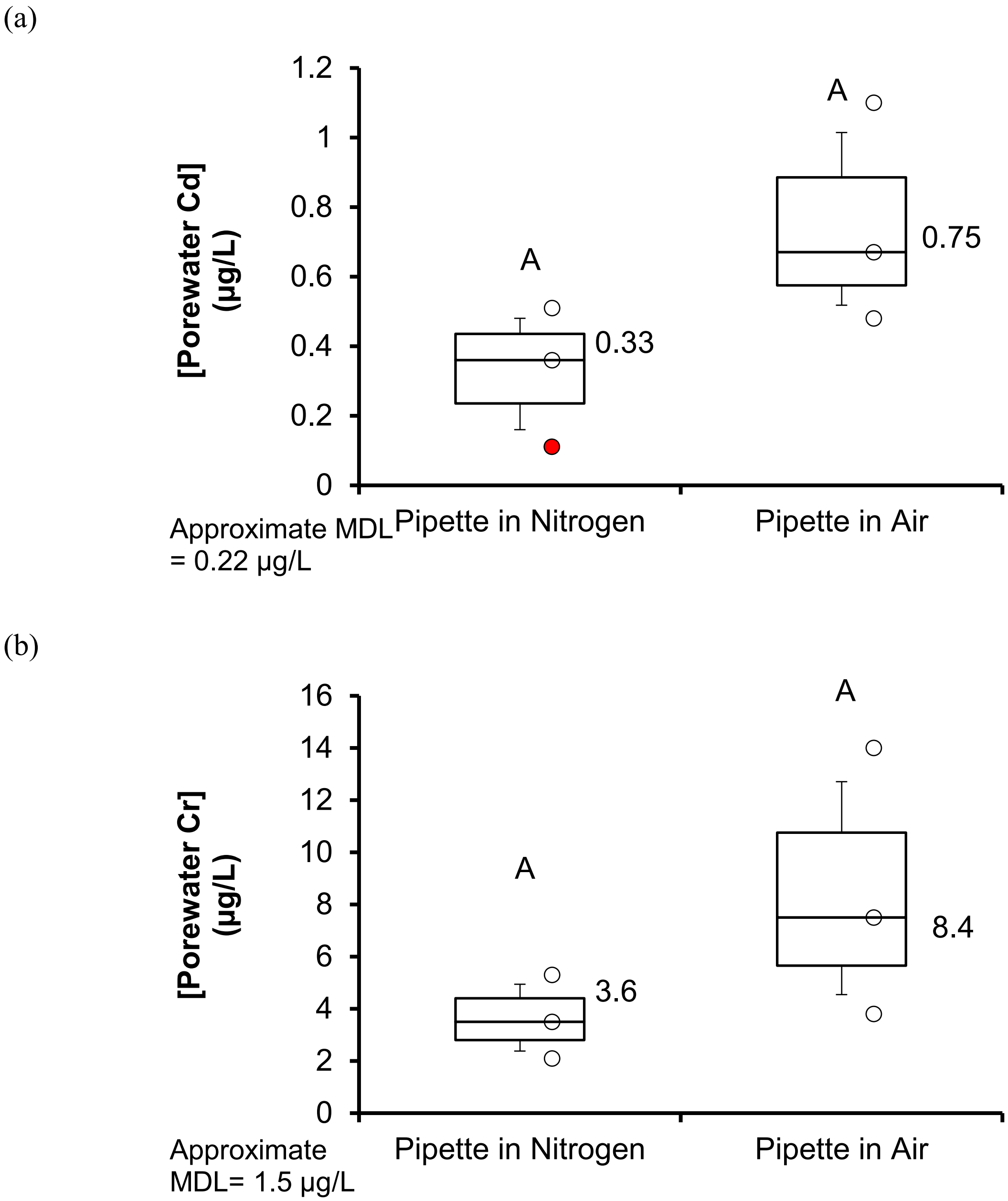


Figure 3-9: Concentrations of metals and lithium tracer in sediment-deployed peeper waters extracted using two different methods. Peepers were deployed for 14 days in unaerated (anoxic) sediment for 14 days prior to sample extraction. Red-filled symbols are raw data that are plotted (and included in calculation of average) that are below the MDL, with the value being used representing 1/2 of the MDL. Data are not shown for mercury due to the high number of ND results.

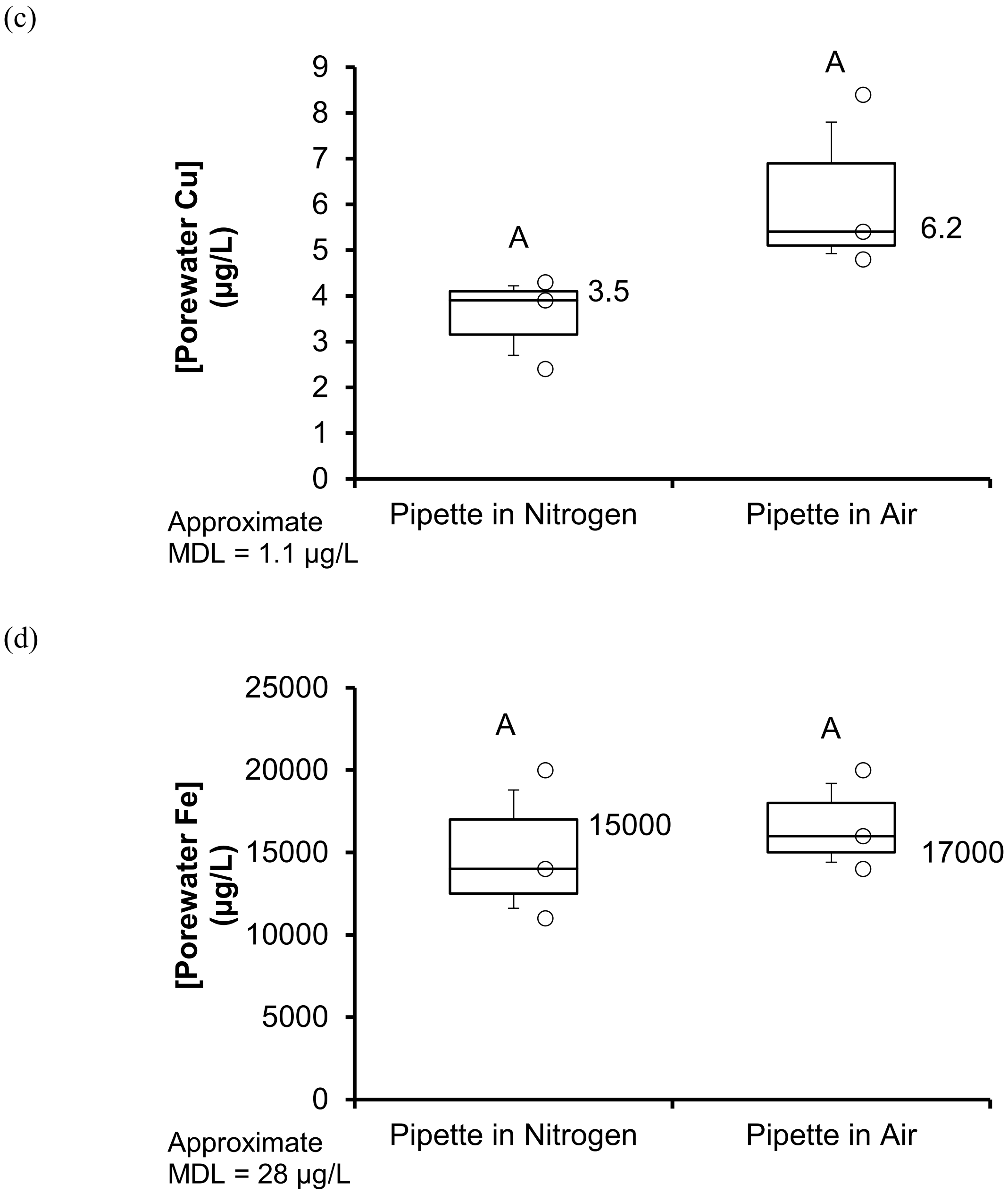
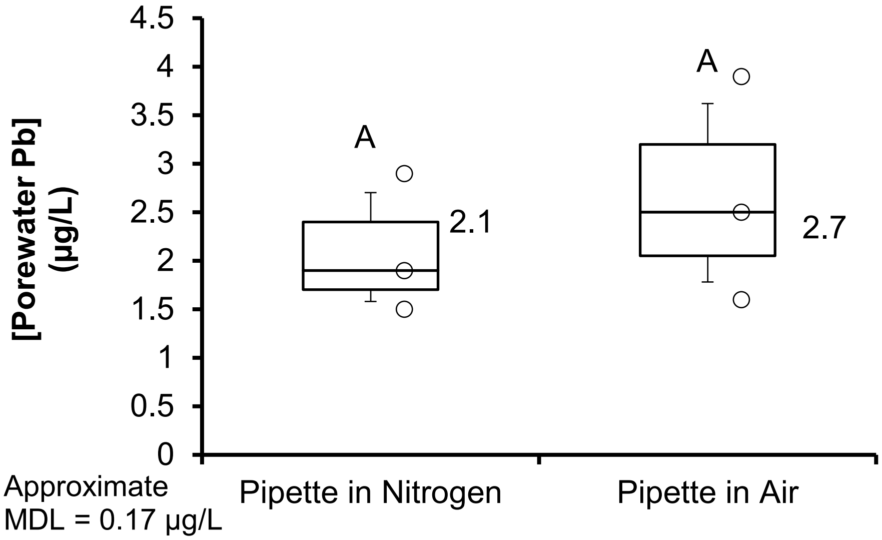


Figure 3-9: Continued.

(e)



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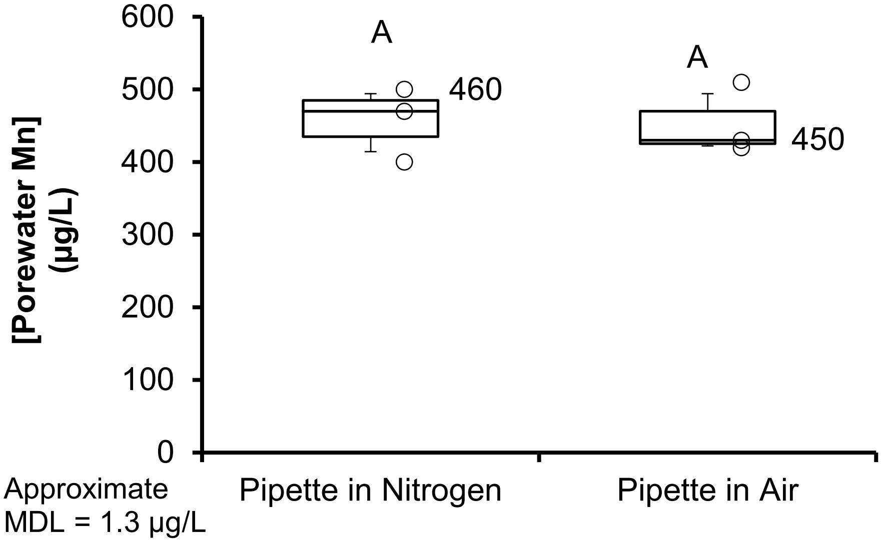
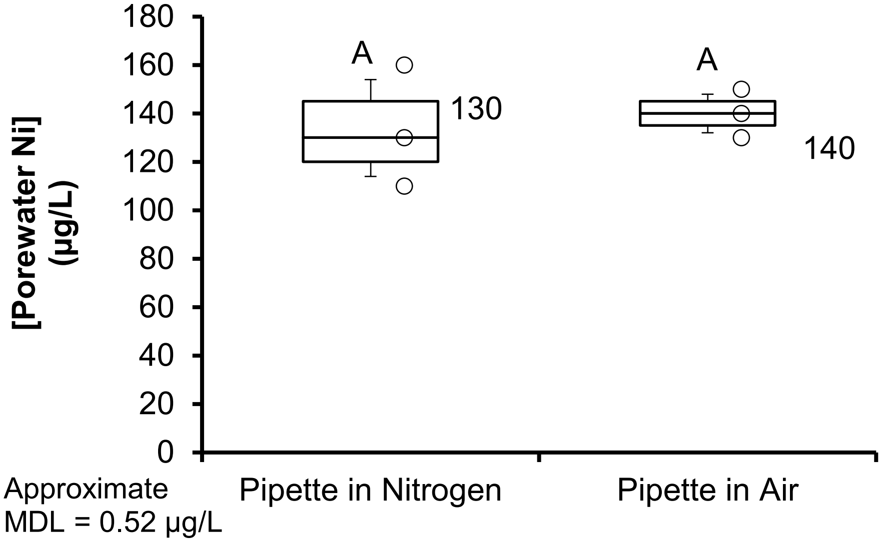


Figure 3-9: Continued.

(g)



(h)

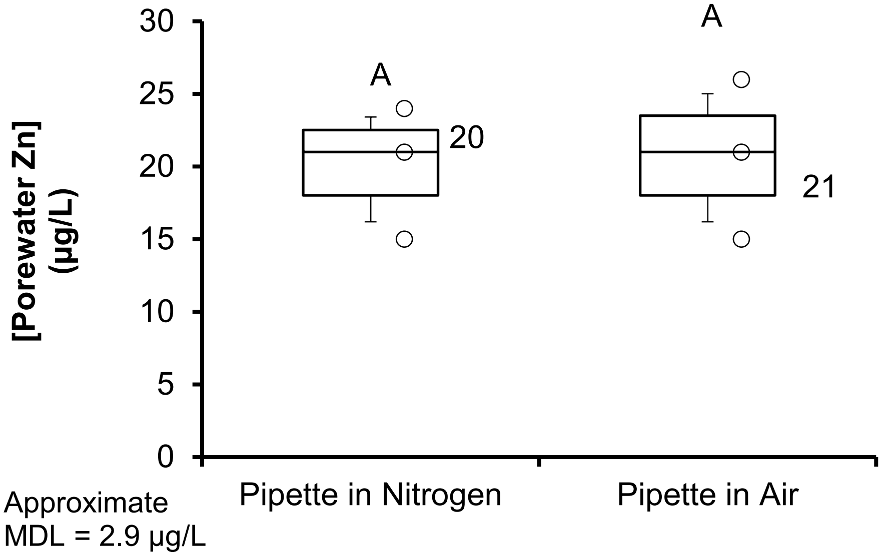


Figure 3-9: Continued.

(i)

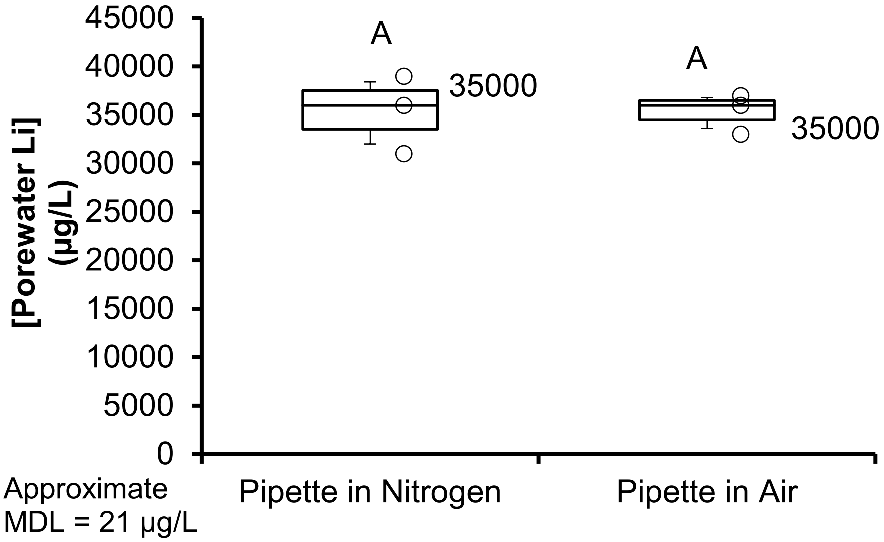
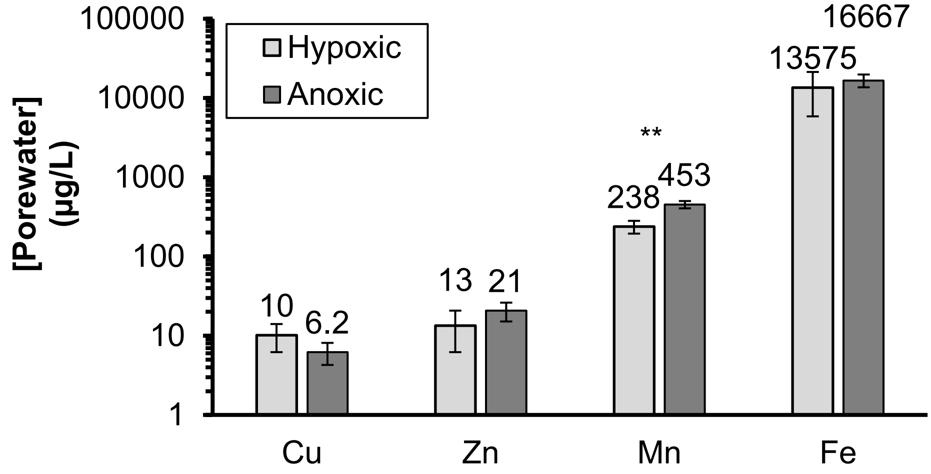


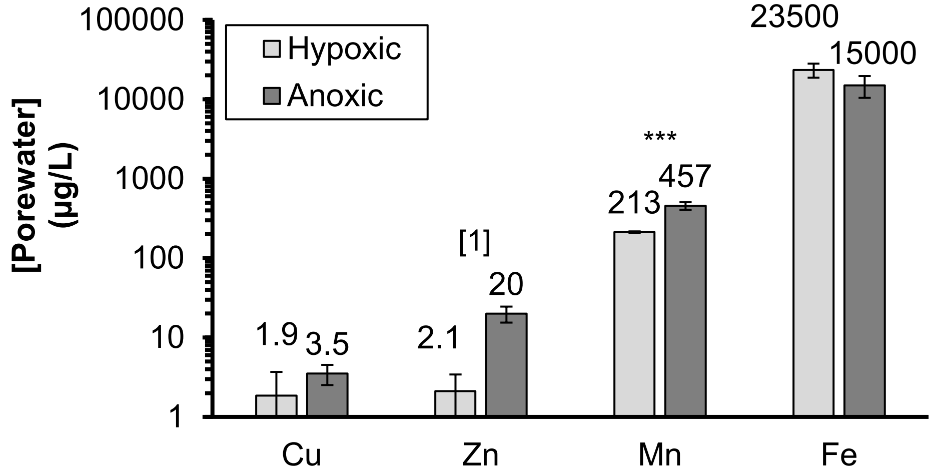
Figure 3-9: Continued.

(a)



**: P < 0.01

(b)



[1]: Not compared statistically due to high number of NDs in hypoxic data. ***: P < 0.001

Figure 3-10: Concentrations of copper, zinc, manganese, an iron in sediment-deployed peeper waters pipetted in air (a) or nitrogen (b). Peepers were deployed in either aerated (hypoxic) standard sediment or unaerated (anoxic) spiked sediment for 14 days prior to sample extraction. Data shown only for copper, zinc, manganese, and iron because other target metals were added to the sediment after the aerated (hypoxic) sediment test, but before the unaerated (anoxic) sediment test.

3.4 Experiment 4: Peeper Storage – Oxygen

3.4.1 Rationale and Methods for Experiment 4

Experiment 4 was conducted to identify an optimal approach to prevent oxygen contamination for storage, for use when peepers cannot be processed immediately after removal from sediment.

Experiment 3 demonstrated that peepers could be processed in air without the effects of oxygen compromising metals results. Peepers in Experiment 3 were processed fairly quickly (within approximately 5 minutes) of removal from sediment. However, it was not clear if the same results would be observed for peepers left in contact with air for a longer time period, as oxygen would likely continue to increase beyond the approximate 1.5 mg/L value observed in peepers processed in air during Experiment 3 (Table 3-5). Processing peepers in the field within minutes of removal from sediment is not always feasible or practical, so peepers are often preserved in an inert gas to maintain anoxia of peeper waters prior to processing (Risacher et al., 2023a). This often requires the use of inert gases, which can be impractical in many field situations, particularly on marine vessels, where heavy and unstable cannisters of inert gases can represent an additional health and safety issue that must be addressed.

The goal of Experiment 4 was to simulate the anoxic state of peepers after retrieval and store them using a method that could be used in the field for maintaining low concentrations of oxygen (e.g., below approximately 1.5 mg/L). Experiment 4 was conducted using peepers that were prepared using the methods of Experiment 1 (i.e., they were deoxygenated). The peepers were not deployed in sediment, and the concentration of oxygen in the peeper waters after being prepared in the deoxygenated water bath was approximately 0.2 to 0.6 mg/L. Immediately after removal from the peeper water preparation bath, peepers were preserved using one of six methods:

- **Air:** Peepers were placed on a laboratory workbench in the open (ambient) atmosphere. This treatment represents a complete lack of storage or protection from oxygen.
- **Mylar - Air:** Peepers were placed in a Mylar zipseal storage bag (just large enough to contain four peepers) and stored on a laboratory workbench.
- **Mylar - Food-preservation Nitrogen/Argon Gas:** Peepers were placed in a Mylar zipseal storage bag (just large enough to contain four peepers), then the bags were purged for approximately 5 seconds with a commercially available food-preservation gas consisting of a mixture of argon and nitrogen (Private Preserve Wine Preservation System).[6] The bags were then stored on a laboratory workbench. This approach was evaluated because the cannisters are small and available to be ordered and shipped relatively easily to project sites.
- **Mylar - Oxygen Muncher**: Peepers were placed in a Mylar zipseal storage bag (just large enough to contain four peepers) containing two “500cc” oxygen absorbing packets (oxygen munchers). An example oxygen muncher packet is shown below:

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[6] https://privatepreserve.com/

The bags were then stored on a laboratory workbench. This option was explored because it completely avoids the use of compressed gases. However, the muncher (active ingredient - iron) takes time to consume the oxygen present in the Mylar bag.

- **Mylar - Nitrogen:** Peepers were placed in a Mylar zipseal storage bag (just large enough to contain four peepers) and purged with nitrogen gas for approximately 5 seconds. The bags were then stored on a laboratory workbench. This approach was evaluated because it was assumed to provide the most robust preservation approach.

For most of the treatments, peepers were stored for 13 different time points (0 minutes, 10 minutes, 30 minutes, 1 hour, 2 hours, 8 hours, 12 hours, 1 day, 2 days, 4 days, 7 days, 14 days and 28 days). For the Mylar - Food-preservation Nitrogen/Argon Gas method, peepers were stored for 7 time points (0 minutes, 1 hour, 6 hours, 12 hours, 1 day, 4 days and 7 days). For the Mylar - Oxygen Muncher method, peepers were stored for 6 time points (0 minutes, 15 minutes, 30 minutes, 2 hours, 4 hours and 76 hours). Following the storage time, the peepers were removed from the Mylar bags and the oxygen probe was immediately inserted through the membrane to measured oxygen.

3.4.2 Results and Discussion for Experiment 4

Concentrations of dissolved oxygen in the peeper waters for the various preservation methods are shown in Table 3-8 and Figure 3-11. No method was perfect, as all methods were unable to maintain the initial concentrations of oxygen (0.2 to 0.6 mg/L). The best preservation methods were storage of the peepers in Mylar bags after preservation with nitrogen or oxygen munchers. Both of these methods maintained oxygen levels below the 1.5 mg/L concentration in the long term (Figure 3-11). This was demonstrated to be from 3 to 11 days, and, as long as the zip seal or bag is not compromised, there is no reason to assume that the low concentrations would not be maintained for much longer time periods. The 1.5 mg/L was selected as a reasonable threshold, as Experiment 3 indicated that the effects of oxygen on metals results did not appear to be an issue for peeper water of approximately 1.5 mg/L (although this oxygen threshold could be higher).

Given that oxygen muncher packets are inexpensive (< $ 0.20 per packet) and are much less logistically challenging than the use of compressed gases (e.g., nitrogen, argon, etc.) in the field, the results of Experiment 4 indicate oxygen munchers are the most efficient approach for maintaining low oxygen in peepers exposed to sediment.

It was notable that the accumulation of oxygen into the peepers exposed to the atmosphere ("Air": no storage) followed one-compartment, first order kinetics (Figure 3-12). The model indicated that 0.5, 1, and 1.5 mg/L is reached within 10, 21, and 32 minutes, respectively. This indicates that peepers should be placed in storage as soon as possible after removal from sediment, ideally within 10 to 30 minutes.

Experiment 4 Lessons Learned and Recommendations

- Oxygen contamination of peepers can be best managed by storing the peepers in a small Mylar zipseal bag containing 2 or more "500-cc" oxygen muncher packets.
- Oxygen contamination can be avoided under proper storage conditions for many days; likely indefinitely if the storage container is not compromised.
- Peepers should be stored as soon as possible after removal from sediment (within 10 to 30 minutes of removal from sediment).

Table 3-8: Oxygen concentrations in peepers stored using various methods.

Treatment	Time (hours)	Oxygen Concentration (mg/L)
Air	0	0.2
	0.17	1.0
	0.5	1.6
	1	2.8
	2	4.0
	8	8.1
	12	8.6
	24	8.2
	48	8.2
	96	8.3
	168	8.7
Mylar - Air	0	0.2
	0.17	1.2
	0.5	1.8
	1	2.1
	2	3.4
	8	6.4
	12	7.4
	24	6.6
	48	8.2
	96	8.3
	168	8.5
	360	8.4
	672	8.4
Mylar – Food-preservation Nitrogen/Argon Gas	0	0.2*
	1	1.3
	6.75	1.6
	20.75	3.8
	24.5	3.4
	59	7.4
	158	8.4
Mylar - Oxygen Muncher	0	0.6
	0.25	1.2
	0.5	1.5
	2	2.0
	4	1.6
	76	1.0
Mylar - Nitrogen	0	0.2
	0.17	1.9
	0.5	0.9
	1	0.5
	2	1.1
	8	0.9
	12	1.0
	24	1.0
	48	0.6
	96	0.8
	168	0.8
	360	1.0
	672	1.1

Notes:
* - Not Measured; Assumption based on other peepers.

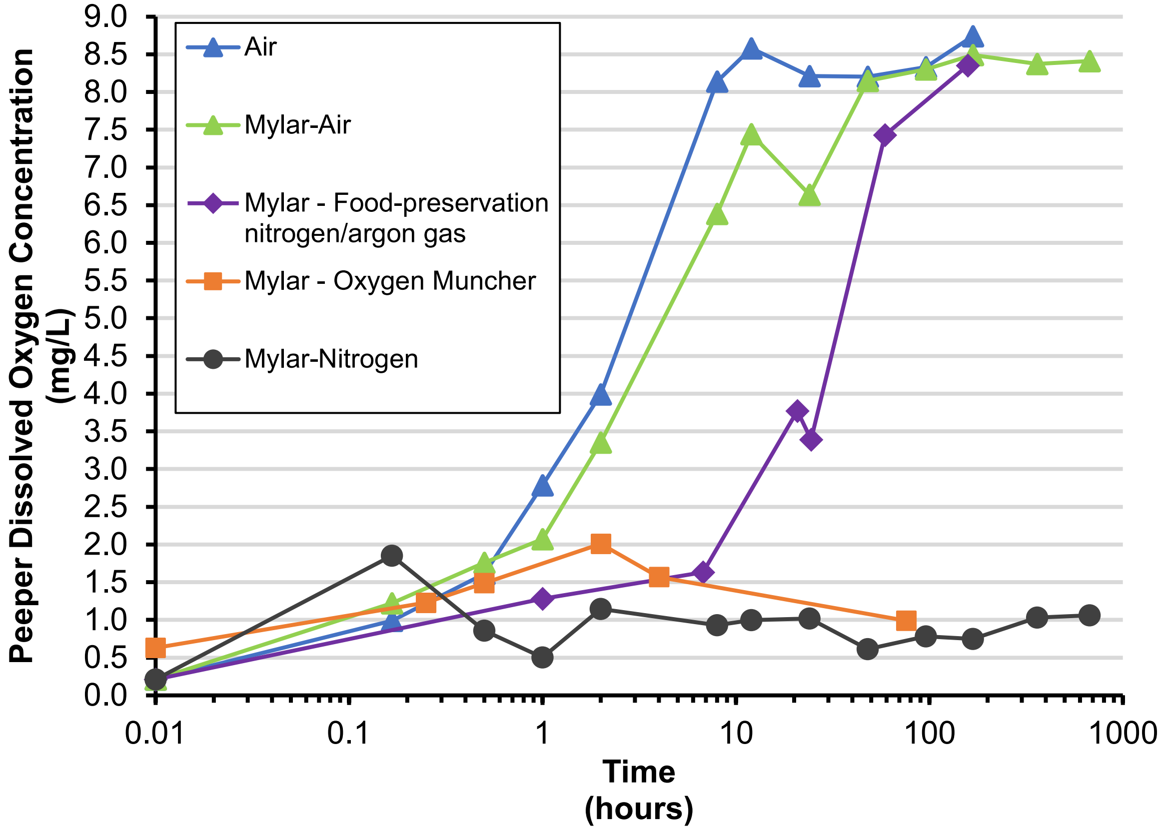


Figure 3-11: Oxygen concentrations in peepers stored using various methods, graphed over time (note Log_{10}-scale x-axis).

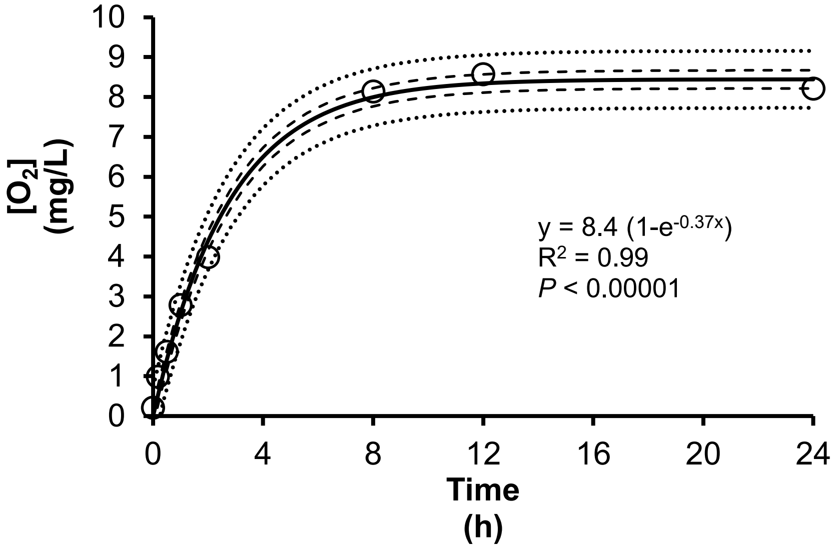


Figure 3-12: Concentration of oxygen in peepers left exposed to the ambient atmosphere.

3.5 Experiment 5: Peeper Storage – Post Deployment

3.5.1 Rationale and Methods for Experiment 5B

Experiment 5 was conducted to confirm the optimal storage approach (storage of peepers in Mylar bags with oxygen munchers) and storage time, using metals data from peepers deployed in sediment.

Experiment 5 is a follow-up to Experiment 4. Experiment 5 was used to evaluate post-retrieval storage time and preservation approach for peepers. Experiment 4 only measured oxygen to calculate oxygenation rates using three preservation methods whereas, in this experiment, preservation methods were tested with peepers deployed in sediment to examine the effects of different methods on concentrations of the target metals.

Similarly to Experiment 4, Experiment 5 was conducted to test the impact of the preservation time and method on the concentration of metals in peepers after retrieval. Peepers were prepared following the standard method with no deoxygenation of the peeper water prior to deployment. Approximately one week prior to the deployment, 15 sediment mesocosms were prepared with spiked sediment. Mesocosms were prepared with no aeration, and these mesocosms were not aerated during the 14-day peeper exposure to ensure an anoxic sediment. At the beginning of the peeper exposure, three peepers were deployed in each mesocosm and were exposed for 14 days. After exposure, peepers were retrieved from the sediment, and rinsed. Peepers each of the 15 mesocosm were separated into five treatment groups (i.e., three sets of three peepers per treatment) and treated as follows:

- **Processed Immediately:** Peepers from one treatment group were immediately processed (within several minutes of retrieval), to represent peepers that would be processed immediately at the location of the retrieval in the field.
- **Oxygen Muncher 8 h:** Peepers from one treatment group were placed in a mylar storage bag containing three “500-cc” oxygen muncher packets, stored for 8 hours at 4°C, and then processed. This treatment simulated a hypothetical scenario in which peepers were preserved in the field and processed at the end of the field day.
- **Oxygen Muncher 5 d:** Peepers from one treatment group were placed in a mylar storage bag containing three “500-cc” oxygen muncher packets, stored for five days at 4°C, and then processed. This treatment simulated a hypothetical scenario in which peepers were preserved in the field and processed at the end of the field event (week of retrieval effort).
- **Oxygen Muncher 14 d:** Peepers from one treatment group were placed in a mylar storage bag containing three “500-cc” oxygen muncher packets, stored for 14 days at 4°C, and then processed. This treatment simulated a hypothetical scenario in which peepers were placed in storage with the oxygen muncher packets in the field, shipped to an analytical laboratory, and processed by the analytical laboratory (instead of processing in field conditions).
- **No preservation 14 d:** Peepers from one treatment group were placed in a mylar storage bag, stored for 14 days at 4°C, and then processed. This treatment simulated a hypothetical scenario in which peepers were placed in storage without the oxygen muncher packets in the field, shipped to an analytical laboratory, and processed by the analytical laboratory (instead of processing in field conditions).

Peepers were processed using the pipetting method in air as described in the general methods section. Each sample consisted of water composited from the three peepers in each sediment chamber (approximately 45 mL), which was preserved with nitric acid—this sample was analyzed for target metals, iron, lithium, and manganese. A separate un-acidified 15-mL sample was not generated for analysis of bromide in this experiment. One additional set of three peepers that were not exposed to sediments was processed and analyzed as a blank.

3.5.2 Results and Discussion for Experiment 5

Raw data for Experiment 5 are shown in Table 3-9, with supporting analytical chemistry reporting in Appendix B. A high proportion of ND results precluded evaluation of the effects of storage approaches on mercury results. Outliers were limited to anomalously high values for cadmium, copper, nickel, and zinc one sample in the "Processed immediately" treatment group. It is hypothesized that the sample may have been contaminated by sediment particles.

Overall, as shown in Figure 3-13, there was no consistent difference in results among the storage approaches. The only clear differences suggesting a potential effect of storage approaches was for cadmium (Figure 3-13a), where average concentrations in the samples stored for 5 days and 14 days were approximately 10 to 20 times lower (and statistically different from) than the average concentration of the samples that were processed immediately. The concentration of the oxygen muncher-preserved sample stored for 8 hours was approximately 2 times lower than the average concentration of the sample processed immediately, although it was not statistically significantly different. For iron, the average results for the samples stored for 8 hours and 5 days were statistically higher than the immediately processed samples by a factor of 15, however, there was high variation in the results for the samples stored for 8 hours and 5 days. For the other 6 metals evaluated, there were no statistically detectable effect of storage approach on metals (comparing the immediately processed result to the stored samples), and no indication that sample storage affected the concentrations of the metals.

Overall, there appears to be no clear and consistent effects on storage time, and the differences observed could be due to high variation in sample results rather than a clear effect of storage approach or time. The best evidence for an effect of storage time on sample results was found for cadmium. The results of the immediately processed sample group were affected by high variability and exclusion of an outlier, so results are uncertain, and additional research could be conducted to see if this result was repeatable. Taken at face value, the cadmium results suggest that if samples are processed within 8 hours (with inclusion of an oxygen muncher in the storage bag), there should not be a difference from processing the sample immediately. However, there is no clear reason why a demonstrable effect of storage time was only noted for cadmium, and not for any other redox-sensitive divalent metals such as copper, lead, zinc, or nickel. If the cadmium results were a function of chance, it could suggest peepers could be safely stored longer periods of time.

In terms of the need to include oxygen munchers for sample preservation, results were inconsistent. Results of the samples preserved with the oxygen munchers and stored for 14 days as well as the samples that did not receive oxygen munchers (stored for 14 days) were statistically compared. In general, with the exception of copper, average concentrations for the samples stored with the oxygen munchers were slightly higher than those stored without the oxygen munchers. In the case of three of the eight metals (manganese, nickel, and zinc), average concentrations of the samples stored with the oxygen muncher for 14 days were 1.4 to 2.7 times higher (statistically significant) than average concentrations of samples stored without oxygen munchers for 14 days (Figure 3-13).

For the other five metals, there were no statistical differences between these two storage types ($P > 0.05$). As noted above, only in the case of cadmium did results of the storage approaches differ significantly from the immediately processed result in a consistent manner. In the case of cadmium, the oxygen muncher samples stored for 14 days and the unpreserved sample stored for 14 days differed significantly from the results of the sample processed immediately, so there was no clear advantage to adding the oxygen munchers.

Given the low cost (less than $0.20 per oxygen muncher packet) and ease of using oxygen muncher packets, and general observations for a few differences, it is recommended that oxygen absorbing packets be used when peeper waters are stored prior to processing. Additional research would be useful to evaluate the effect of using oxygen absorbing packets, perhaps repeating this experiment with additional replication and with peepers deployed in oxygenated sediment (i.e., having peeper water with slightly oxygenated water).

Experiment 5 Lessons Learned and Recommendations

- Peepers should be processed within approximately 8 hours after collection, and they should be stored at 4 °C in an airtight bag with 2 or more “500-cc” oxygen muncher packets.
- Tentative evidence suggests that samples could be stored for up to 14 days, perhaps with without an oxygen muncher packet; additional research would be needed to confirm this approach.

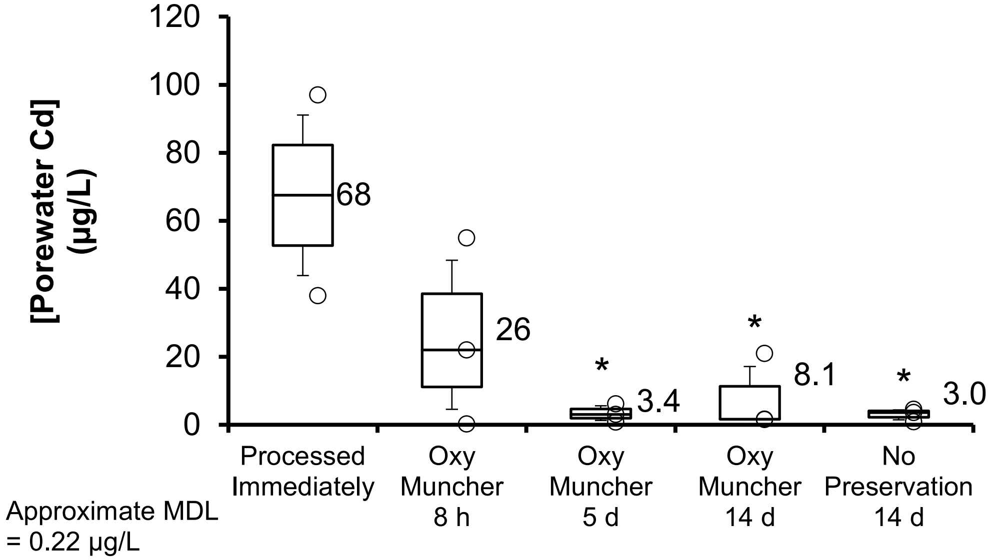
Table 3-9: Concentrations of metals and lithium for five different storage methods in peepers. Peepers were deployed in unaerated (anoxic) spiked sediment for 14 days prior to samples being extracted.

Treatment	**Sample ID**	**Concentration (µg/L)**									
		Cadmium	**Chromium**	**Copper**	**Iron**	**Lead**	**Manganese**	**Mercury**	**Nickel**	**Zinc**	**Lithium**
Approximate Method Detection Limit		**0.22**	**1.5**	**1.1**	**280**	**0.38**	**1.3**	**0.13**	**0.52**	**60**	**130**
Blank	EXP5B-BLANK	ND	ND	12	ND	ND	ND	ND	ND	120	58000
Processed immediately	EXP5B-SP15-A14-1	38	4.7	20	1800	1.2	990	0.2	140	160	48000
	EXP5B-SP15-A14-2	97	1.9	19	200	0.75	1600	ND	190	210	54000
	EXP5B-SP15-A14-3	6500*	1.7	600*	ND	1.9	2100	0.32	560*	560*	55000
Oxygen muncher 8 h	EXP5B-SP15-O-1	55	3.7	74	7600	4.5	900	0.29	160	300	63000
	EXP5B-SP15-O-2	0.23	1.5	3.9	16000	1.3	1100	ND	89	140	56000
	EXP5B-SP15-O-3	22	1.7	30	7600	5	1700	ND	210	220	56000
Oxygen muncher 5 d	EXP5B-SP15-OM0.3-1	0.85	9.5	10	14000	3.5	1100	0.35	110	140	56000
	EXP5B-SP15-OM0.3-2	3.1	3.7	20	13000	1.9	1200	0.15	100	130	44000
	EXP5B-SP15-OM0.3-3	6.2	4.6	14	8800	5.9	1800	0.2	200	150	54000
Oxygen muncher 14 d	EXP5B-SP15-OM3-1	1.6	3	4.3	4600	7.3	1800	ND	210	180	59000
	EXP5B-SP15-OM3-2	1.7	2.2	3.9	1900	0.39	1900	ND	210	140	55000
	EXP5B-SP15-OM3-3	21	1.8	15	2900	0.4	1700	ND	240	190	57000
No preservation 14 d	EXP5B-SP15-OM14-1	4.6	1.8	16	2800	0.41	1100	0.15	83	120	51000
	EXP5B-SP15-OM14-2	0.93	ND	16	520	ND	1200	ND	77	120	55000
	EXP5B-SP15-OM14-3	3.6	ND	14	860	ND	820	ND	83	110	54000

Notes:

* - Identified as an outlier.

(a)



(b)

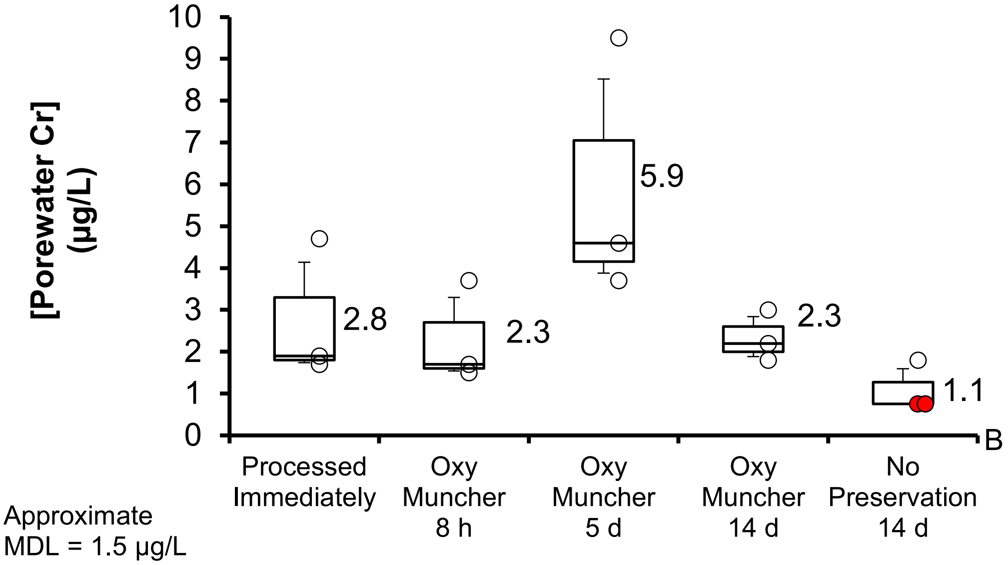
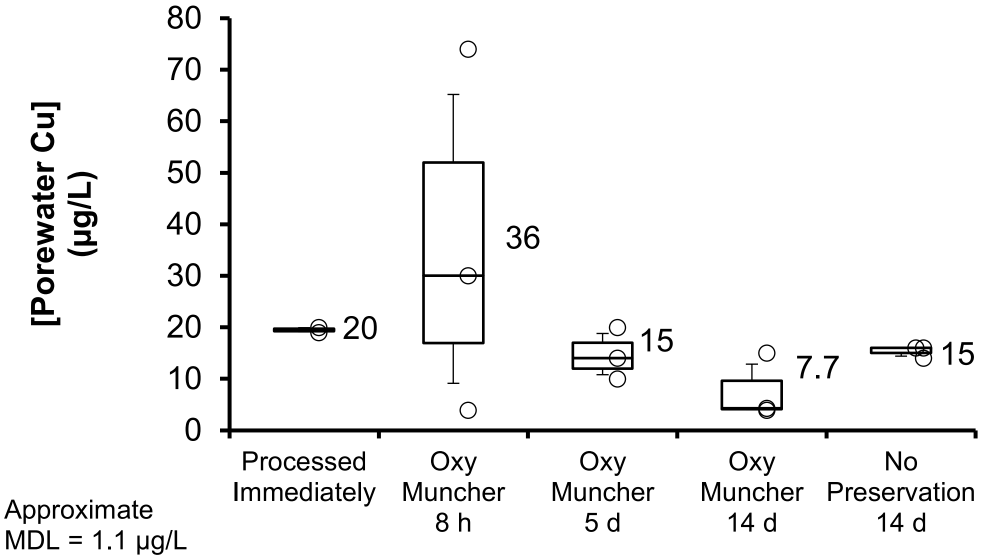


Figure 3-13: Concentrations of metals in spiked sediment-deployed peeper waters stored in various approaches with oxygen munchers and time periods prior to sample preservation. Data are not shown for mercury due to the high number of ND results. "*" symbols indicate results that differ significantly ($P < 0.05$) from peepers processed immediately. Outliers are not shown in the cadmium, copper, and nickel figures because they would distort the figure scale.

(c)



(d)

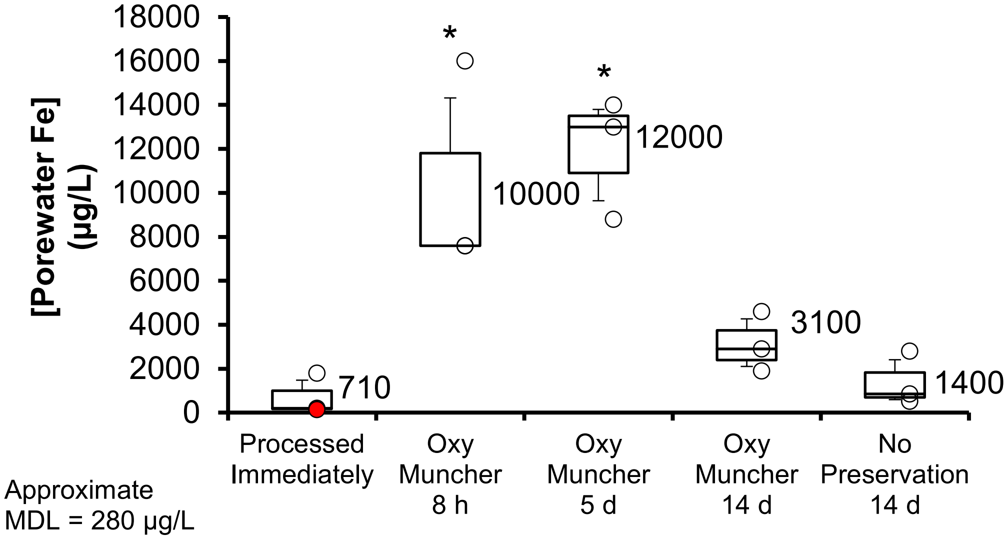
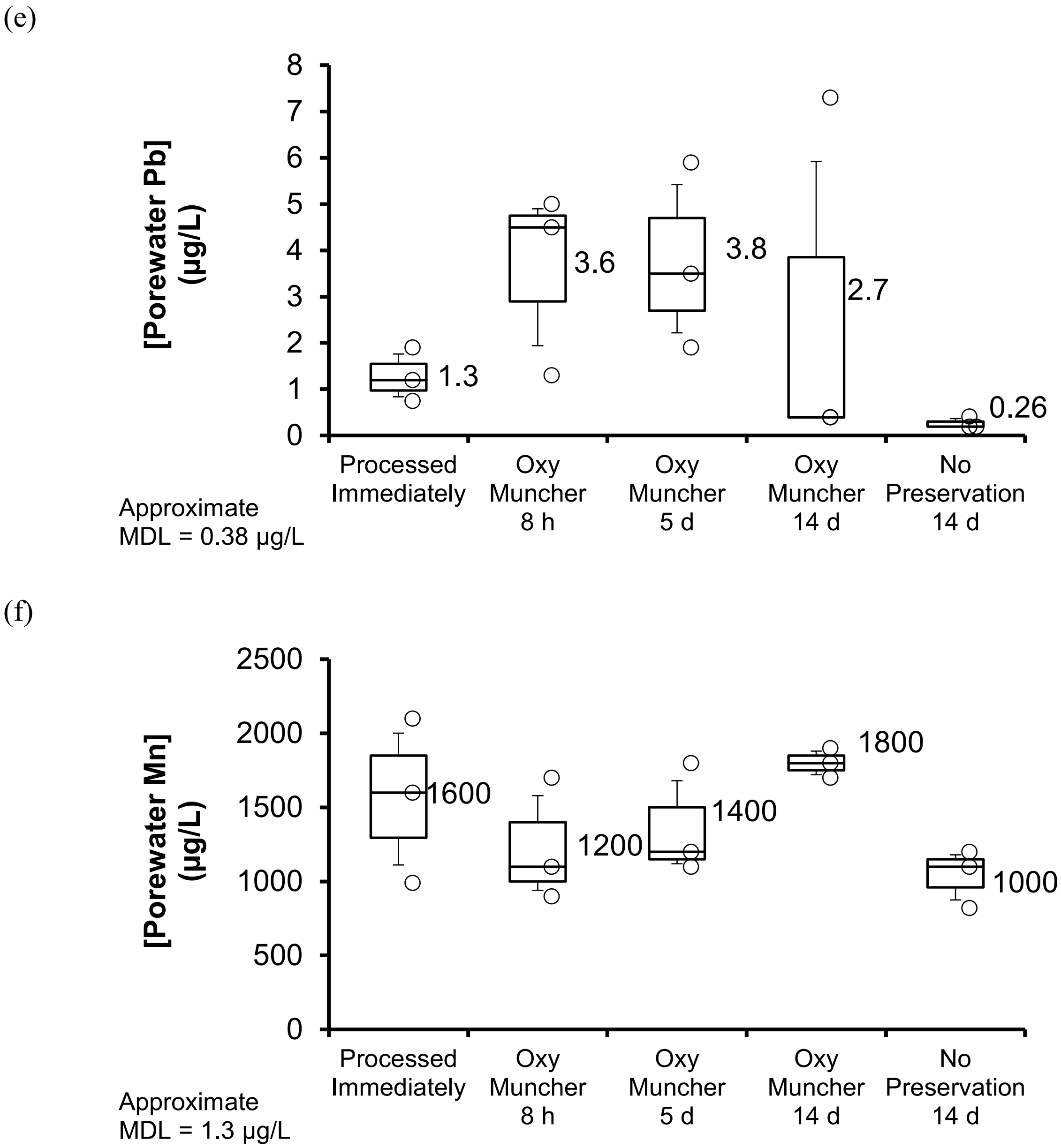


Figure 3-13: Continued.



Approximate
MDL = 0.38 μg/L

Approximate
MDL = 1.3 μg/L

Figure 3-13: Continued.

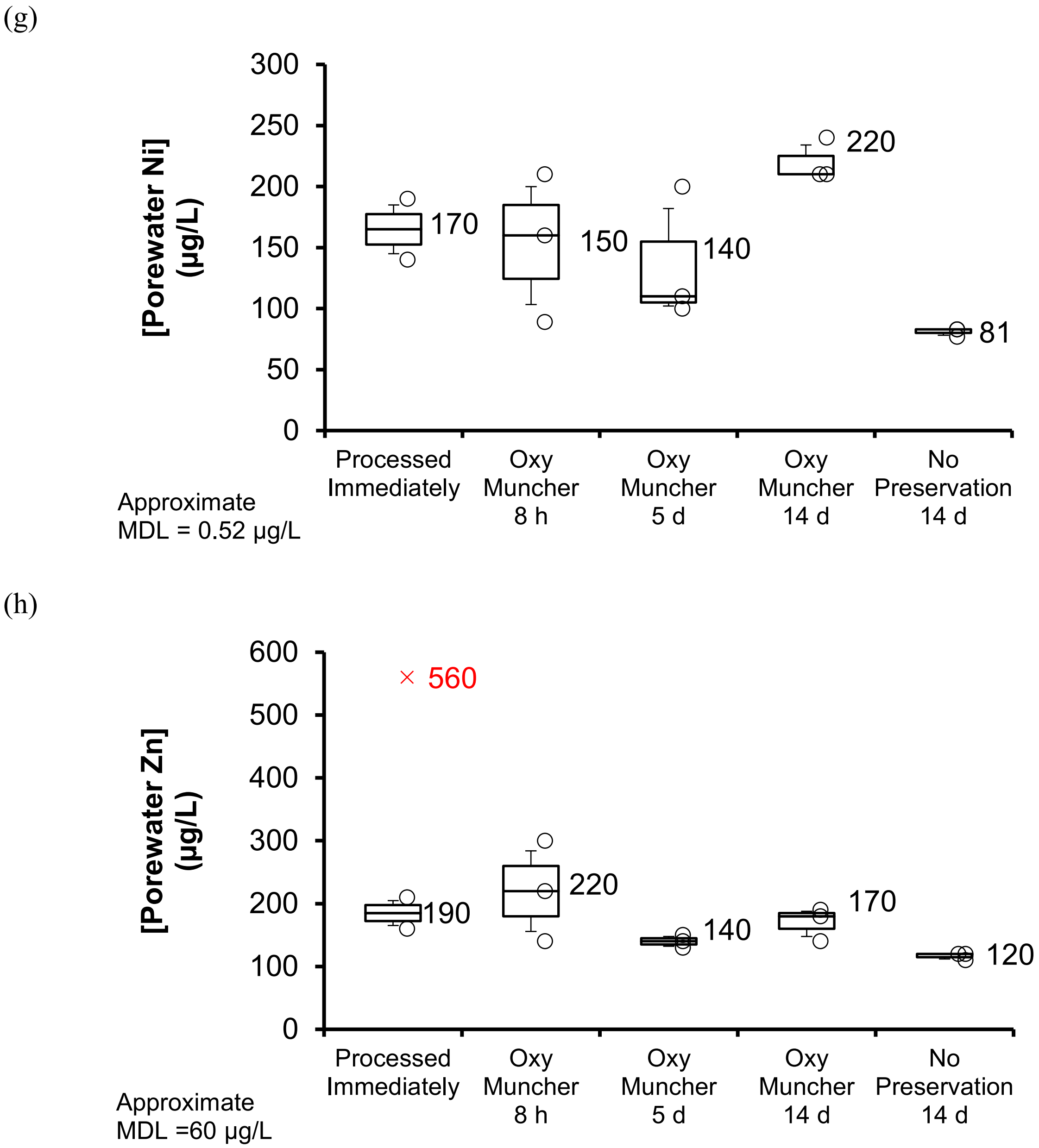


Figure 3-13: Continued.

3.6 Experiment 6: Tracers for Pre-equilibrium Deployments

3.6.1 Rationale and Methods for Experiment 6

Experiment 6 was conducted to validate the use of the lithium tracer to predict concentrations of target metals at equilibrium for peepers deployed in water and sediment.

Passive sampling with peepers relies on the passive diffusion of ions to achieve equilibrium between the sediment porewater and the peeper water inside the peeper. However, equilibrium can take several days or weeks to reach under some conditions, and equilibration can vary depending on sampling conditions. For example, as shown in Experiment 2 (Figure 3-6), only approximately 70% of equilibrium was achieved by lithium tracers in peepers deployed in sediment for 14 days in the laboratory. In Experiment 3, which also consisted of testing peepers for 14 days in sediment in the laboratory, only approximately 47% of equilibrium (on average) was achieved by lithium tracers (as calculated from lithium data in Table 3-7). In a field deployment in San Diego Bay (Risacher et al., 2023b), peepers deployed in sediment and water for 10 days indicated the lithium tracer achieved (on average) 87% and more than 99% of equilibrium, respectively.

One important aspect to consider in the use of the lithium tracer (and bromide tracer) is that the target metals diffuse more slowly than tracers, based on their literature-derived diffusion coefficients (Table 2-3). Thus, the percentage of equilibration estimated for the target metals is expected to be less than that for the lithium tracer. For example, in the case of the slowest diffusing target metal in this study (chromium), the percentage of equilibration for chromium will be approximately a factor of 1.5 times less than that indicated by the lithium tracer when lithium equilibration is approximately 50% achieved (i.e., 50% for lithium, 33% for chromium). However, it is possible that the solid phases of sediment may be able to quickly react (e.g., via desorption and dissolution) to maintain concentrations in the porewater, which could increase apparent diffusivity rates. This would decrease the equilibrium time of the species compared to the conservative tracer.

In addition to evaluating the relative degree of equilibration attained by target metals, the use of a reverse tracer allows the use of diffusion equations (Equations 1 to 4) to calculate the concentrations of metals at equilibrium for deployments that are not of sufficient duration to achieve equilibrium. This pre-equilibrium sampling approach is useful in ensuring accurate measurements, enabling rapid field programs for passive sampling, but has seen limited use for peepers in the literature (Risacher et al., 2023a).

Experiment 6 was conducted to evaluate the application of pre-equilibrium sampling approaches using the lithium tracer. This experiment was conducted in three deployments:

- In the first deployment, peepers were deployed in water with known concentrations of metals over variable lengths of time
- In the second deployment, peepers were deployed in the standard spiked sediment over variable lengths of time
- In the third deployment, peepers were deployed again in the standard spiked sediment as well as in an additional field collected sediment (Indian Head Sediment) over variable lengths of time

The water deployment portion of Experiment 6 was conducted with peepers prepared via the same procedure as Experiment 1, albeit with no deoxygenation, and a lower concentration of the lithium bromide tracer (100 mg/L—recommended for deployments in freshwater). A metal-spiked water solution was created in carboy with target metal salts (**Error! Reference source not found.**) and deionized water. Nominal concentrations were confirmed via measurement of samples collected from experimental beakers at 3 time points (Table 3-11) and were within 18% (on average) of measured values. The solution was adjusted to pH 2 using a small amount of nitric acid so that metals in the solution would be present in a 100% dissolved form. The prepared metal-spiked water was allocated into 18 beakers (1.3 L per beaker), and four peepers were deployed per beaker. As shown in Table 3-11, concentrations of target metals in the water to which peepers did not change over the course of the 28-day experiment, although the concentration of lithium and bromide were detected at approximately 150 µg/L and 1.1 mg/L, respectively, at the end of the experiment, likely due to diffusion of lithium and bromide tracers from the peepers into the surrounding water. Two beakers were prepared per time point, and peepers were left to equilibrate for 4 hours, 8 hours, 12 hours, 24 hours, 36 hours, 2 days, 7 days, 14 days and 28 days. After each deployment period, peepers were retrieved, processed using a pipette (in air), and submitted for target metals, lithium, and bromide analysis. Blanks were also prepared and processed immediately and submitted for analysis of target metals, lithium and bromide analysis.

Table 3-10: Preparation of metal-spiked water for the Experiment 6 water deployment.

Metal	Nominal Concentration in Water (µg/L)	Salt Form
Cadmium	70	$CdCl_2$
Chromium	60	$CrCl_2$
Copper	370	$CuCl_2$- $2H_20$
Mercury	50	$HgCl_2$
Lead	700	$PbCl_2$
Nickel	60	$NiCl_2$- $6H_2O$
Zinc	780	$ZnCl_2$

The second deployment portion of Experiment 6 (standard spiked sediment deployment) was conducted with peepers prepared via the same procedure as Experiment 1, albeit with no deoxygenation. Fifteen mesocosms were filled with the standard spiked sediment, and four peepers were deployed in each mesocosm, which were aerated for the duration of the experiment. Three mesocosms were prepared per time point and peepers were left to equilibrate for 24 hours, 3 days, 7 days, 14 days, and 28 days. After the deployment period, peepers were retrieved, immediately processed using a pipette in air and submitted for analysis of target metals, manganese, iron, lithium and bromide. Blanks were also prepared and processed immediately and analyzed for target metals, manganese, iron, lithium and bromide analysis.

The third deployment portion of Experiment 6 (standard spiked and Indian Head sediment deployment) was conducted to confirm the unexpected results observed in the second deployment. The third deployment was conducted with peepers prepared via the same procedure as Experiment 1, albeit with no deoxygenation. A limited experimental design consisting of 12 mesocosms was used: six mesocosms containing the standard spiked sediment and six mesocosms containing Indian Head sediment. Four peepers were deployed in each mesocosm, which were aerated for the duration of the experiment. One mesocosm was prepared per time point and peepers was left to equilibrate for 2 days, 5 days, 7 days, 14 days, 28 days, and 47 days. After the deployment period, peepers were retrieved, immediately processed using a pipette in air and submitted for analysis of target metals, manganese, iron, lithium and bromide. Blanks were also prepared and processed immediately and analyzed for target metals, manganese, iron, lithium and bromide analysis.

3.6.2 Results and Discussion for Experiment 6

Raw data for the three deployments of Experiment 6 are shown in Tables 3-12, 3-13, and 3-14, with supporting analytical chemistry reporting in Appendix B.

The first Experiment 6 deployment in metal spiked water confirmed that uptake of target metals by the peepers followed one-compartment first-order kinetics. Robust uptake curve model fits (Equation 5) were applied to each of the target metals (Figure 3-14). Zinc was present in the blank peepers from this experiment (34-52 µg/L), its presence did not affect the model fit (Figure 3-14g). Concentrations indicated by the model fits (Figure 3-14) were within 8% to 14% of the values measured in water samples obtained from the beaker at 28 days (Table 3-11), indicating that the peeper-beaker system was fully equilibrated and well-described by the models.

Model-estimated elimination rates for the target metals (K_i values) and the times to 90% of equilibrium (calculated using the elimination rates) are provided in Table 3-15. Elimination rates for the target metals indicated that chromium was the slowest metal, while zinc was the fastest metal. Elimination rates for the target metals (based on overlap of 95% confidence intervals [CIs]) were represented by three partially overlapping groups:

- Slower equilibrating metals: chromium and mercury
- Medium equilibrating metals: nickel, cadmium, and copper
- Faster equilibrating metals: lead, and zinc

The first Experiment 6 deployment in metal spiked water confirmed one-compartment first-order kinetics elimination of the bromide and lithium tracers into the surrounding water of the beakers in which the peepers were deployed. Robust elimination curve model fits were applied to the tracers (Figure 3-15). Although both elimination models were considered (Equations 6 and 7), the Equation 7 elimination model, which assumes a constant non-zero asymptote determined by the best fit of the model to the data, performed better than Equation 6 in terms of model fit (i.e., higher r^2 values). Model-estimated elimination rates for the tracers (K_t values) and the times to 90% of equilibrium (calculated using the elimination rates) are provided in Table 3-15. The lithium tracer was found to be slightly more rapid than bromide, although the difference was only 18%. As shown in Figure 3-16, the lithium tracer had almost fully equilibrated in water by day 7 of the exposure (average of 87% equilibration). On day 14 of the exposure, equilibration averaged 91%, which was similar to equilibration values (87% to more than 99%) observed in sediment and water in the 10-day San Diego Bay field deployment (Risacher et al., 2023b). However, lithium equilibration in water over the 14 days in this experiment was much higher than observed in the sediment laboratory experiments in this study (i.e., approximately 50% to 70%). This is likely because diffusion in laboratory water is less hindered by solids associated with sediment, and diffusion in sediments in the field is facilitated by dynamic water movements near, into, and out of surface sediments.

The water uptake data (Table 3-12) provided a robust approach for evaluating the accuracy of the pre-equilibrium sampling approach. Using Equations 1 to 4 and the target metal and lithium tracer results for each sample in Table 3-12, the calculation of the concentrations of target metals at equilibrium was conducted (Table 3-16). The "equilibrium-corrected" values were calculated for each sample at the various time points (0.17 to 28 days) and then each value was divided by the average concentrations of the 4 water samples obtained from the beakers over the course of the deployment (Table 3-11). These values were graphed for the various time points (Figure 3-17). In general, values for most of the target metals were below 1 in the initial measurements. This was due to relatively low equilibration values of the lithium tracer. Lower equilibration of the tracer results in higher uncertainty and variability with regards to accurately predicting the concentration at equilibrium. However, with the exception of mercury, values at the day 1 and later time points were approximately 0.6 or higher (Figure 3-17), indicating that the equilibrium-corrected values were within 40% of measured values. At day 2, on average, the values shown in Figure 3-15 were 0.71 (range 0.54 to 0.85), indicating that at day 2, equilibrium values were within a 29% agreement (on average) with measured values. At day 2, lithium was approximately 40% equilibrated (Figure 3-16). In contrast, all values (except for one nickel value) at the day 7 and later time points were within 0.8 to 1.2 (Figure 3-17), indicating that the equilibrium-corrected values were within 20% of measured values. At day 7, on average, the values shown in Figure 3-15 were 0.93 (range 0.87 to 1.02), indicating that at day 7, equilibrium values were within a 7% (on average) agreement with measured values. Lithium was 87% equilibrated on average on day 7 (Figure 3-16). This data suggests between day 2 and day 7, equilibrium-corrected concentrations of target metals likely approach within 20% of measured values. For environmental decision-making purposes, measurements that are plus or minus 20% in accuracy are likely to be considered reasonable by most stakeholders. With that consideration, it the pre-equilibrium sampling approach described in Equations 1 to 4 is reasonably accurate for predicting concentrations at equilibrium, and performs best as long as the deployment is at least approximately 4 to 7 days in field surface water or field surface sediment when the lithium tracer has achieved at least 50% to 75% equilibrium.

The second Experiment 6, deployment in the standard metal-spiked sediment, did not indicate robust one-compartment first-order uptake curves for the target metals (Figure 3-18). The reasoning for this was unclear, but it could indicate that geochemical conditions were not favorable for the availability of the target metals. It is possible that the sediments were too anoxic (despite aeration) or that equilibrium with regards to metal availably in the sediment was not present.

Only statistically significant ($P < 0.05$) models were generated for iron and manganese (Figures 3-18d and 3-18f), with model fits indicating 90% of equilibrium would be reached in 37 and 13 days, respectively. This suggests manganese and iron were available, which would be expected in a more anoxic sediment.

In this sediment deployment, zinc displayed an elimination relationship (Figure 3-18h) that was likely due to the presence of zinc in the peeper water (as an unintended contaminant) at the beginning of the deployment. zinc was in the blank at 48 μg/L, and the model fit shown in Figure 3-18h indicates that concentrations of zinc in the peeper reached a plateau concentration of 8.6 μg/L by approximately 14 days. This indicated that the trace zinc contamination present in the peeper eliminated from the peeper, and that equilibration was evident in approximately 14 days. Thus, in cases where zinc (or another metal) is detected in the blank at a higher concentration than in observed in the sample, it is recommended that the sampling duration be sufficient to allow a relatively high degree of equilibration. For reference, lithium equilibration in sediment at 14 days was 65% (Figure 3-19), thus, deployment periods should be long enough to achieve approximately 50% or more of lithium equilibration to minimize the influence of metal presence in undeployed peepers. In the field, this is likely less than 14 days given that equilibration in a static sediment in the laboratory is a worst case (i.e., slow) scenario.

It is notable to emphasize that diffusion was occurring during the deployment in the standard metal-spiked sediment. One-compartment first-order kinetics elimination of the bromide and lithium tracers into the surrounding sediment in which the peepers were deployed was confirmed, and robust elimination curve model fits were applied to the tracers (Figure 3-20). Although both elimination models were considered (Equations 6 and 7), the Equation 7 elimination model, which assumes a constant non-zero asymptote determined by the best fit of the model to the data, performed better than Equation 6 in terms of model fit (i.e., higher r^2 values). Lithium equilibration in sediment at 14 days was 65%, within the 50% to 70% range observed in previous laboratory experiments with this sediment. At 28 days, lithium equilibration was 74% (on average). As shown in Figure 3-20, lithium and bromide plateaued at a concentration that was 28% and 31% of the measured concentration in the peeper at time zero (Table 3-13). This may suggest that the volume of porewater with which the peeper was equilibrating was somewhat constrained by the volume of the "sink" external to the peeper.

The sediment uptake data (Table 3-13) from the Experiment 6 second deployment was used to evaluate the accuracy of the pre-equilibrium sampling approach for manganese and iron. Using Equations 1 to 4 and the manganese, iron, and lithium tracer results for each sample in Table 3-13 allowed the calculation of the concentrations of target metals at equilibrium. The "equilibrium-corrected" values were calculated for each sample at the various time points (1 to 28 days), and then each value was divided by the equilibrium concentrations of manganese (700 µg/L) and iron (28000 µg/L) estimated by the one-compartment first-order kinetics models (Figures 3-18d and 3-18f). These values were graphed for the various time points (Figure 3-21). For iron, the most accurate estimates using the pre-equilibrium approach were found in the peepers deployed for 14 days and 28 days, which were, on average 3% and 25%, respectively, different that the model-predicted value estimated in Figure 3-18d. This is a reasonable amount of error given the 95% CI of the estimate of the equilibrium concentration of iron (28000 µg/L) ranges plus or minus approximately 30%. In contrast, the pre-equilibrium approach overestimated the equilibrium concentration of manganese by approximately 50% (on average) for all samples collected at 4, 7, 14, and 28 days (Figure 3-21b). This is a less than optimal amount of error given the 95% CI of the estimate of the equilibrium concentration of manganese (700 µg/L) ranges plus or minus approximately 6%. Manganese was overestimated because it reached equilibrium more quickly (time to 90% of equilibrium of 13 days) compared the lithium tracer, which was only at 65% of equilibrium at 14 days. Yet, based on the D values shown in Table 2-3, manganese should have equilibrated more slowly (by a factor of 1.3) in sediment compared to lithium. This may indicate some uncertainty in the D values or their applicability in a sediment matrix involving solid phases that may be able to replenish ions in porewater as they diffuse into the peeper, effectively increasing diffusion speed. In contrast, using un-corrected measurements from day 14 and day 28 were only 8% and 1% different from the model-estimated equilibrium concentration of manganese. Overall, the pre-equilibrium tracer sampling approach appeared to work acceptably (on average) for iron, but not as well for manganese, where the pre-equilibrium approach overestimates Cfree.

Given the unusual results of the second Experiment 6 deployment in the standard metal-spiked sediment, a third deployment in the standard spiked sediment and the Indian Head sediment was conducted. This third deployment yielded highly variable data for target metals, iron, and manganese that did not appear to follow one-compartment first-order kinetic uptake (Figure 3-22).

The results shown in this repetition of the uptake experiment with the standard spiked sediment and a completely different sediment provided further evidence that the conditions in the laboratory mesocosms did not appear to provide stable equilibrium conditions with respect to metal availability. This lack of stability hindered our ability to evaluate diffusion with respect to time.

As in the second deployment (standard spiked sediment), the lithium and bromide data did indicate diffusive exchange between the peeper and surrounding sediment matrix was occurring (Table 3-14). Lithium kinetics in the standard spiked sediment in the Experiment 6 third deployment was similar to that of the other sediment laboratory experiments, and one-compartment models (Equation 7) indicated 90% of equilibrium was reached in 14 days (Figure 3-23a). A one-compartment model indicated 90% of equilibrium for lithium in the Indian Head sediment was also reached in a similar time scale (10 days; Figure 3-23b).

Overall, the laboratory sediment mesocosms, as designed, may have not been able to provide a simulation of metals uptake in peepers in sediment under field conditions. As such, the sediment mesocosms were not considered to provide a thorough assessment of the pre-equilibrium approach in sediment. However, the water deployments provided a basic proof of concept for the ability of the pre-equilibrium approach to predict equilibrium concentrations in peepers using data from peepers sampled prior to equilibrium. It is reasonable to assume this finding may apply to field sediments, although this remains uncertain. In field sediments, equilibration is much more rapid than stagnant laboratory sediments tested in this experiment, and equilibrium in geochemical conditions over shorter time periods are likely to enable observations of one-compartment first-order kinetics. The available data for iron and manganese in sediment suggests that the pre-equilibrium approach may overestimate Cfree at equilibrium due to the possibility that diffusive flux in sediment may be higher than default (water-derived) values would indicate. A time series field experiment in sediment would be recommended to fully validate the pre-equilibrium approach in sediment. Until the pre-equilibrium approach can be further evaluated, we recommend the user consider using one of the following approaches when deploying peepers in sediment[7]:

1. Deploy the peeper in sediment for approximately 4 to 7 days and apply the pre-equilibrium sampling approach (Equations 1 to 4). In this case, lithium will be approximately 50% to 75% equilibrated in field sediment. At this level of equilibration, it is hypothesized that Cfree for the slowest diffusing metals (e.g., chromium) could be overestimated by the pre-equilibrium sampling approach by as much as 2 to 3 times.
2. Deploy the peeper in sediment for approximately 10 to 14 days. In this case, lithium will be approximately 85% to 95% equilibrated in field sediment. Application of the pre-equilibrium sampling approach (Equations 1 to 4) is not likely needed, but could be considered. At this level of equilibration, it is hypothesized that Cfree for the slowest diffusing metals (e.g., chromium) could be overestimated by the pre-equilibrium sampling approach by as much as 1.2 to 1.5 times (i.e., 20% to 50% difference), which is a relatively reasonable level range of measurement uncertainty for many sediment data quality objectives.

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[7] The time periods and percentages of equilibration noted below are specific to the general design of the peeper used in these laboratory experiments (15-mL volume, F Factor of 2.8 milliliters per square centimeter). Peepers with higher F Factors would be expected to require longer deployments to achieve similar levels of equilibration and measurement certainties.

3. Deploy the peeper in sediment for approximately 21 days or longer. In this case, lithium will be more than 99% equilibrated in field sediment. Application of the pre-equilibrium sampling approach (Equations 1 to 4) is not needed.

Experiment 6 Lessons Learned and Recommendations

- Uptake of target metals and elimination of lithium and bromide tracers follow one-compartment, first order kinetics, as demonstrated in water.
- The pre-equilibrium approach with the lithium tracer performs best when the lithium tracer indicates at least 50% equilibration, which occurs in approximately 4 to 7 days in stagnant water or field sediment.
- Assessment of the pre-equilibrium approach with the lithium tracer in sediment was limited, likely due to a lack of equilibrium conditions affecting metals geochemistry in the test sediments within the laboratory. A time series field sediment experiment would provide the best demonstration of the pre-equilibrium approach.
- Overall, the use of the lithium tracer enables pre-equilibrium short-term deployments of peepers. Some uncertainty remains for sediment, and this can be managed by increasing deployment time.

Table 3-11: Concentrations of target metals in metal-spiked water for various time periods.

Time (days)	Sample ID	Concentration (µg/L)								[mg/L]
		Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Zinc	Lithium	Bromide
Approximate Method Detection Limit		**0.22**	**1.5**	**1.1**	**0.17**	**0.13**	**0.52**	**2.9**	**0.83**	**0.053**
0	EXP6A-0H-METALS WATER	86	58	370	610	92	95	730	5.4	NM
2	EXP6A-48H-METALS WATER	84	57	360	600	96	93	710	3.8	NM
7	EXP6A2-7D-METAL WATER	84	54	350	610	95	88	690	170	1.1
28	EXP6A2-28D-METAL WATER	83	57	350	610	90	91	700	150	1.1

Notes:
NM - not measured

Table 3-12: Concentrations of target metals, concentrations of lithium and bromide tracers, and percentage equilibration for lithium and bromide tracers for peepers deployed in metal-spiked water for various time periods.

Time (days)	Sample ID	Concentration (µg/L)								[mg/L]	Lithium Equilibrium %	Bromide Equilibrium %
		Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Zinc	Lithium	Bromide		
Approximate Method Detection Limit		0.22	1.5	1.1	0.17	0.13	0.52	2.9	0.83	0.053		
0	EXP6A-SP15-BLK	ND	ND	ND	ND	ND	ND	52	8500	100	-	-
	EXP6A2-SP15-28D-BLANK	ND	ND	ND	ND	ND	ND	34	8300	95	-	-
0.17	EXP6A-SP15-4H	5	3	22	40	2	5.3	92	7300	96	14%	4%
	EXP6A-SP15-4H-DUP	5	2.9	22	40	1.9	5.3	94	7300	91	14%	9%
0.33	EXP6A-SP15-8H	7.6	3.8	34	61	4	8.6	110	6900	89	19%	11%
	EXP6A-SP15-8H-DUP	8.9	4.9	38	68	4.7	8.9	120	6800	86	20%	14%
0.5	EXP6A-SP15-12H	14	7.6	59	110	9.5	15	140	5300	79	38%	21%
	EXP6A-SP15-12H-DUP	13	7.4	56	100	10	14	140	5300	68	38%	32%
1	EXP6A-SP15-24H	16	8.3	70	130	12	17	170	5000	71	41%	29%
	EXP6A-SP15-24H-DUP	18	10	77	140	13	19	180	4900	68	42%	32%
1.5	EXP6A-SP15-36H	24	13	100	190	21	27	230	4100	53	52%	47%
	EXP6A-SP15-36H-DUP	24	13	100	190	19	26	230	4200	51	51%	49%
2	EXP6A-SP15-48H	27	15	120	210	25	30	250	3800	47	55%	53%
	EXP6A-SP15-48H-DUP	27	15	120	210	25	29	260	3700	45	56%	55%
7	EXP6A2-SP15-7D-1	57	33	250	450	75	64	530	1200	9.1	86%	91%
	EXP6A2-SP15-7D-2	61	36	260	470	73	67	540	950	12	89%	88%
14	EXP6A2-SP15-14D-1	71	48	320	540	74	83	650	800	9.9	91%	90%
	EXP6A2-SP15-14D-2	72	48	330	530	79	94	630	770	9.1	91%	91%
28	EXP6A2-SP15-28D-1	73	49	300	530	81	78	620	780	8.8	91%	91%
	EXP6A2-SP15-28D-2	75	50	310	550	77	79	640	780	9.1	91%	91%

Table 3-13: Concentrations of target metals, concentrations of lithium and bromide tracers for peepers deployed in standard spiked sediment for various time periods.

Time (days)	Sample ID	Concentration (µg/L)										[mg/L]
		Cadmium	**Chromium**	**Copper**	**Iron**	**Lead**	**Manganese**	**Mercury**	**Nickel**	**Zinc**	**Lithium**	**Bromide**
Approximate Method Detection Limit		**0.22**	**1.5**	**1.1**	**28**	**0.17**	**1.3**	**0.13**	**0.52**	**2.9**	**0.83**	**0.053**
0	EXP6B-SP15-BLANK	0.66	ND	ND	64	0.39	2.3	ND	1.3	48	79000	820
1	EXP6B-SP15-1D-1	31	4.1	3	310	1.4	150	ND	80	28	55000	650
	EXP6B-SP15-1D-2	96	ND	3.6	50	1.6	140	ND	120	39	53000	610
	EXP6B-SP15-1D-3	100	2.5	5	75	1.2	120	ND	100	43	54000	700
3	EXP6B-SP15-3D-1	15	9.3	6.6	1700	3.7	370	0.22	130	51	45000	520
	EXP6B-SP15-3D-2	5.4	2.4	1.4	3100	0.57	350	ND	100	33	48000	550
	EXP6B-SP15-3D-3	4.5	1.6	2.2	2500	1.8	290	ND	120	30	47000	520
7	EXP6B-SP15-7D-1	0.71	5.6	4.3	7700	2.3	420	ND	160	19	39000	340
	EXP6B-SP15-7D-2	ND	2.7	2.8	21000	0.72	490	ND	170	8.9	39000	420
	EXP6B-SP15-7D-3	7.4	ND	3.6	8800	1.2	420	ND	150	21	32000	380
14	EXP6B-SP15-14D-1	ND	ND	2.2	22000	0.41	500	ND	120	5.8	27000	250
	EXP6B-SP15-14D-2	160	ND	19	9900	15	750	ND	260	67*	29000	330
	EXP6B-SP15-14D-3	0.34	1.9	4.7	15000	1.6	690	ND	150	20	27000	280
28	EXP6B-SP15-28D-1	ND	ND	2.7	24000	0.54	670	ND	38	6.7	22000	230
	EXP6B-SP15-28D-2	0.49	1.6	32	25000	1.4	780	ND	71	15	18000	240
	EXP6B-SP15-28D-3	0.82	7.6	5.1	21000	2.6	680	0.14	110	8	21000	270

Notes:

* - Identified as outlier

Table 3-14: Concentrations of target metals, concentrations of lithium and bromide tracers for peepers deployed in standard spiked sediment and Indian Head sediment for various time periods.

Sediment	Time (days)	Sample ID	Concentration (µg/L)										[mg/L]
			Cadmium	**Chromium**	**Copper**	**Iron**	**Lead**	**Manganese**	**Mercury**	**Nickel**	**Zinc**	**Lithium**	**Bromide**
Approximate Method Detection Limit			**0.22**	**1.5**	**1.1**	**28**	**0.17**	**1.3**	**0.13**	**0.52**	**2.9**	**83**	**0.053**
	0	EXP6D-BLANK	ND	3.2	ND	ND	ND	ND	ND	ND	29	79000	930
Standard Spiked Sediment	2	EXP6D-SP15-2D-SS	930	3	14	ND	0.44	80	ND	140	39	47000	400
	5	EXP6D-SP15-5D-SS	600	2.8	160	34	1.7	700	ND	250	230	43000	440
	7	EXP6D-SP15-7D-SS	1900	3	63	62	4.8	420	ND	360	150	30000	420
	14	EXP6D-SP15-14D-SS	810	2.6	170	36	2.7	540	ND	290	160	24000	360
	28	EXP6D-SP15-28D-SS	370	5.9	36	140	2.2	59	0.3	160	75	14000	270
	47	EXP6D-SP15-47D-SS	1.1	ND	2.7	140	9.5	7600	ND	10	230	6200	370
Indian Head Sediment	2	EXP6D-SP15-2D-IH	ND	4.1	1.9	340	2.8	570	ND	1.9	30	49000	370
	5	EXP6D-SP15-5D-IH	0.3	ND	1.9	14000	1.9	5800	ND	7.6	88	28000	270
	7	EXP6D-SP15-7D-IH	1	4.4	11	2900	44	6100	ND	13	190	34000	280
	14	EXP6D-SP15-14D-IH	0.72	ND	2.3	2700	6.1	4200	ND	10	140	14000	190
	28	EXP6D-SP15-28D-IH	2	ND	3.9	12000	68	8600	ND	9.3	150	10000	240
	47	EXP6D-SP15-47D-IH	320	36	79	1100	14	230	2.1	160	150	10000	270

Table 3-15: Kinetic summary (model estimate with 95% CI in parenthesis) for target metals, lithium tracer, and bromide tracer, as estimated from measurements in the Experiment 6 water deployment.

Target Metal / Tracer	K_i (target metals) or K_t (tracers) (d^{-1})	Time to Reach 90% Equilibrium (d)
Cadmium	0.25 (0.23-0.27)	9.1 (8.4-9.8)
Chromium	0.19 (0.17-0.21)	12.3 (11.2-13.4)
Copper	0.26 (0.24-0.28)	8.9 (8.1-9.7)
Lead	0.28 (0.26-0.30)	8.2 (7.3-8.8)
Mercury	0.22 (0.20-0.26)	10.3 (8.9-11.6)
Nickel	0.24 (0.22-0.28)	9.4 (8.2-10.6)
Zinc	0.31 (0.27-0.36)	7.5 (6.5-8.5)
Lithium	0.53 (0.47-0.60)	4.4 (3.8-4.9)
Bromide	0.45 (0.42-0.50)	5.1 (4.6-5.5)

Table 3-16: Calculation of equilibrium-corrected concentrations of target metals using the lithium tracer data for each of the samples obtained in the Experiment 6 water deployment.

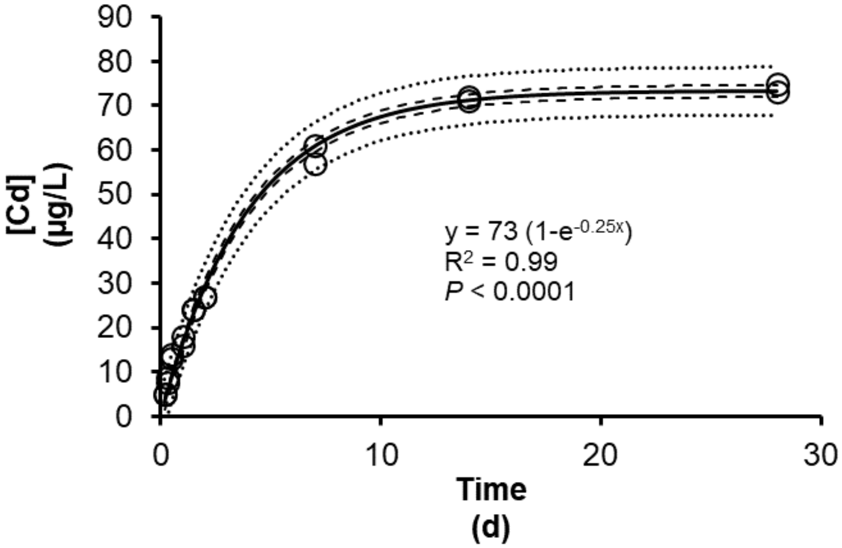
Sample ID	Chemical Name	Measured Concentration in Peeper	Result Unit	Initial Lithium Concentration (µg/L)	Deployment Time (days)	Assumed Lithium Concentration External to Peeper (µg/L) (days)	Sample-specific Elimination Rate for Lithium (Kt) (day^{-1})	Elimination Rate Constant for Metal (D, x10^{-5} cm^2/s)	$D_i \div D_t$	Sample-specific Elimination Rate for Analytes (K_i)	Percent Equilibrium Reached (%)	Equilibrium Corrected Result (µg/L)
EXP6A-SP15-4H	Lithium	7300	µg/L	8500	0.17	0	0.895	0.9	1.00	0.895	14	**--**
	Cadmium	5	µg/L		0.17			0.63	0.70	0.627	10	**49**
	Chromium	3	µg/L		0.17			0.52	0.58	0.517	8	**36**
	Copper	22	µg/L		0.17			0.62	0.69	0.617	10	**220**
	Lead	40	µg/L		0.17			0.83	0.92	0.826	13	**310**
	Mercury	2	µg/L		0.17			0.74	0.82	0.736	12	**17**
	Nickel	5.3	µg/L		0.17			0.62	0.69	0.617	10	**53**
	Zinc	92	µg/L		0.17			0.61	0.68	0.607	10	**940**
EXP6A-SP15-4H-DUP	Lithium	7300	µg/L	8500	0.17	0	0.895	0.9	1.00	0.895	14	**--**
	Cadmium	5	µg/L		0.17			0.63	0.70	0.627	10	**49**
	Chromium	2.9	µg/L		0.17			0.52	0.58	0.517	8	**34**
	Copper	22	µg/L		0.17			0.62	0.69	0.617	10	**220**
	Lead	40	µg/L		0.17			0.83	0.92	0.826	13	**310**
	Mercury	1.9	µg/L		0.17			0.74	0.82	0.736	12	**16**
	Nickel	5.3	µg/L		0.17			0.62	0.69	0.617	10	**53**
	Zinc	94	µg/L		0.17			0.61	0.68	0.607	10	**960**
EXP6A-SP15-8H	Lithium	6900	µg/L	8500	0.33	0	0.632	0.9	1.00	0.632	19	**--**
	Cadmium	7.6	µg/L		0.33			0.63	0.70	0.442	14	**56**
	Chromium	3.8	µg/L		0.33			0.52	0.58	0.365	11	**33**
	Copper	34	µg/L		0.33			0.62	0.69	0.435	13	**250**
	Lead	61	µg/L		0.33			0.83	0.92	0.583	17	**350**
	Mercury	4	µg/L		0.33			0.74	0.82	0.520	16	**25**
	Nickel	8.6	µg/L		0.33			0.62	0.69	0.435	13	**64**
	Zinc	110	µg/L		0.33			0.61	0.68	0.428	13	**830**
EXP6A-SP15-8H-DUP	Lithium	6800	µg/L	8500	0.33	0	0.676	0.9	1.00	0.676	20	**--**
	Cadmium	8.9	µg/L		0.33			0.63	0.70	0.473	14	**62**
	Chromium	4.9	µg/L		0.33			0.52	0.58	0.391	12	**41**
	Copper	38	µg/L		0.33			0.62	0.69	0.466	14	**270**
	Lead	68	µg/L		0.33			0.83	0.92	0.624	19	**370**
	Mercury	4.7	µg/L		0.33			0.74	0.82	0.556	17	**28**
	Nickel	8.9	µg/L		0.33			0.62	0.69	0.466	14	**62**
	Zinc	120	µg/L		0.33			0.61	0.68	0.458	14	**850**
EXP6A-SP15-12H	Lithium	5300	µg/L	8500	0.5	0	0.945	0.9	1.00	0.945	38	**--**
	Cadmium	14	µg/L		0.5			0.63	0.70	0.661	28	**50**
	Chromium	7.6	µg/L		0.5			0.52	0.58	0.546	24	**32**

Sample ID	Chemical Name	Measured Concentration in Peeper	Result Unit	Initial Lithium Concentration (µg/L)	Deployment Time (days)	Assumed Lithium Concentration External to Peeper (µg/L) (days)	Sample-specific Elimination Rate for Lithium (Kt) (day^{-1})	Elimination Rate Constant for Metal (D, x10^{-5} cm^2/s)	$D_i \div D_t$	Sample-specific Elimination Rate for Analytes (K_i)	Percent Equilibrium Reached (%)	Equilibrium Corrected Result (µg/L)
	Copper	59	µg/L		0.5			0.62	0.69	0.651	28	**210**
	Lead	110	µg/L		0.5			0.83	0.92	0.871	35	**310**
	Mercury	9.5	µg/L		0.5			0.74	0.82	0.777	32	**30**
	Nickel	15	µg/L		0.5			0.62	0.69	0.651	28	**54**
	Zinc	140	µg/L		0.5			0.61	0.68	0.640	27	**510**
EXP6A-SP15-12H-DUP	Lithium	5300	µg/L	8500	0.5	0	0.945	0.9	1.00	0.945	38	**--**
	Cadmium	13	µg/L		0.5			0.63	0.70	0.661	28	**46**
	Chromium	7.4	µg/L		0.5			0.52	0.58	0.546	24	**31**
	Copper	56	µg/L		0.5			0.62	0.69	0.651	28	**200**
	Lead	100	µg/L		0.5			0.83	0.92	0.871	35	**280**
	Mercury	10	µg/L		0.5			0.74	0.82	0.777	32	**31**
	Nickel	14	µg/L		0.5			0.62	0.69	0.651	28	**50**
	Zinc	140	µg/L		0.5			0.61	0.68	0.640	27	**510**
EXP6A-SP15-24H	Lithium	5000	µg/L	8500	1.0	0	0.531	0.9	1.00	0.531	41	**--**
	Cadmium	16	µg/L		1.0			0.63	0.70	0.371	31	**52**
	Chromium	8.3	µg/L		1.0			0.52	0.58	0.307	26	**31**
	Copper	70	µg/L		1.0			0.62	0.69	0.366	31	**230**
	Lead	130	µg/L		1.0			0.83	0.92	0.489	39	**340**
	Mercury	12	µg/L		1.0			0.74	0.82	0.436	35	**34**
	Nickel	17	µg/L		1.0			0.62	0.69	0.366	31	**56**
	Zinc	170	µg/L		1.0			0.61	0.68	0.360	30	**560**
EXP6A-SP15-24H-DUP	Lithium	4900	µg/L	8500	1.0	0	0.551	0.9	1.00	0.551	42	**--**
	Cadmium	18	µg/L		1.0			0.63	0.70	0.386	32	**56**
	Chromium	10	µg/L		1.0			0.52	0.58	0.318	27	**37**
	Copper	77	µg/L		1.0			0.62	0.69	0.379	32	**240**
	Lead	140	µg/L		1.0			0.83	0.92	0.508	40	**350**
	Mercury	13	µg/L		1.0			0.74	0.82	0.453	36	**36**
	Nickel	19	µg/L		1.0			0.62	0.69	0.379	32	**60**
	Zinc	180	µg/L		1.0			0.61	0.68	0.373	31	**580**
EXP6A-SP15-36H	Lithium	4100	µg/L	8500	1.5	0	0.486	0.9	1.00	0.486	52	**--**
	Cadmium	24	µg/L		1.5			0.63	0.70	0.340	40	**60**
	Chromium	13	µg/L		1.5			0.52	0.58	0.281	34	**38**
	Copper	100	µg/L		1.5			0.62	0.69	0.335	39	**250**
	Lead	190	µg/L		1.5			0.83	0.92	0.448	49	**390**
	Mercury	21	µg/L		1.5			0.74	0.82	0.400	45	**47**
	Nickel	27	µg/L		1.5			0.62	0.69	0.335	39	**68**
	Zinc	230	µg/L		1.5			0.61	0.68	0.329	39	**590**

Sample ID	**Chemical Name**	**Measured Concentration in Peeper**	**Result Unit**	**Initial Lithium Concentration (µg/L)**	**Deployment Time (days)**	**Assumed Lithium Concentration External to Peeper (µg/L) (days)**	**Sample-specific Elimination Rate for Lithium (Kt) (day^{-1})**	**Elimination Rate Constant for Metal (D, x10^{-5} cm^2/s)**	**$D_i \div D_t$**	**Sample-specific Elimination Rate for Analytes (K_i)**	**Percent Equilibrium Reached (%)**	**Equilibrium Corrected Result (µg/L)**
EXP6A-SP15-36H-DUP	Lithium	4200	µg/L	8500	1.5	0	0.470	0.9	1.00	0.470	51	**--**
	Cadmium	24	µg/L		1.5			0.63	0.70	0.329	39	**62**
	Chromium	13	µg/L		1.5			0.52	0.58	0.272	33	**39**
	Copper	100	µg/L		1.5			0.62	0.69	0.324	38	**260**
	Lead	190	µg/L		1.5			0.83	0.92	0.433	48	**400**
	Mercury	19	µg/L		1.5			0.74	0.82	0.386	44	**43**
	Nickel	26	µg/L		1.5			0.62	0.69	0.324	38	**68**
	Zinc	230	µg/L		1.5			0.61	0.68	0.319	38	**610**
EXP6A-SP15-48H	Lithium	3800	µg/L	8500	2	0	0.403	0.9	1.00	0.403	55	**--**
	Cadmium	27	µg/L		2			0.63	0.70	0.282	43	**63**
	Chromium	15	µg/L		2			0.52	0.58	0.233	37	**40**
	Copper	120	µg/L		2			0.62	0.69	0.277	43	**280**
	Lead	210	µg/L		2			0.83	0.92	0.371	52	**400**
	Mercury	25	µg/L		2			0.74	0.82	0.331	48	**52**
	Nickel	30	µg/L		2			0.62	0.69	0.277	43	**70**
	Zinc	250	µg/L		2			0.61	0.68	0.273	42	**590**
EXP6A-SP15-48H-DUP	Lithium	3700	µg/L	8500	2	0	0.416	0.9	1.00	0.416	56	**--**
	Cadmium	27	µg/L		2			0.63	0.70	0.291	44	**61**
	Chromium	15	µg/L		2			0.52	0.58	0.240	38	**39**
	Copper	120	µg/L		2			0.62	0.69	0.286	44	**280**
	Lead	210	µg/L		2			0.83	0.92	0.384	54	**390**
	Mercury	25	µg/L		2			0.74	0.82	0.342	50	**50**
	Nickel	29	µg/L		2			0.62	0.69	0.286	44	**66**
	Zinc	260	µg/L		2			0.61	0.68	0.282	43	**600**
EXP6A2-SP15-7D-1	Lithium	1200	µg/L	8500	7	0	0.280	0.9	1.00	0.280	86	**--**
	Cadmium	57	µg/L		7			0.63	0.70	0.196	75	**76**
	Chromium	33	µg/L		7			0.52	0.58	0.162	68	**49**
	Copper	250	µg/L		7			0.62	0.69	0.193	74	**340**
	Lead	450	µg/L		7			0.83	0.92	0.258	84	**540**
	Mercury	75	µg/L		7			0.74	0.82	0.230	80	**94**
	Nickel	64	µg/L		7			0.62	0.69	0.193	74	**86**
	Zinc	530	µg/L		7			0.61	0.68	0.190	73	**720**
EXP6A2-SP15-7D-2	Lithium	950	µg/L	8500	7	0	0.313	0.9	1.00	0.313	89	**--**
	Cadmium	61	µg/L		7			0.63	0.70	0.219	78	**78**
	Chromium	36	µg/L		7			0.52	0.58	0.181	72	**50**
	Copper	260	µg/L		7			0.62	0.69	0.216	78	**330**
	Lead	470	µg/L		7			0.83	0.92	0.289	87	**540**

Sample ID	Chemical Name	Measured Concentration in Peeper	Result Unit	Initial Lithium Concentration (µg/L)	Deployment Time (days)	Assumed Lithium Concentration External to Peeper (µg/L) (days)	Sample-specific Elimination Rate for Lithium (Kt) (day^{-1})	Elimination Rate Constant for Metal (D, x10^{-5} cm^2/s)	$D_i \div D_t$	Sample-specific Elimination Rate for Analytes (K_i)	Percent Equilibrium Reached (%)	Equilibrium Corrected Result (µg/L)
	Mercury	73	µg/L		7			0.74	0.82	0.257	83	**87**
	Nickel	67	µg/L		7			0.62	0.69	0.216	78	**86**
	Zinc	540	µg/L		7			0.61	0.68	0.212	77	**700**
EXP6A2-SP15-14D-1	Lithium	800	µg/L	8500	14	0	0.169	0.9	1.00	0.169	91	**--**
	Cadmium	71	µg/L		14			0.63	0.70	0.118	81	**88**
	Chromium	48	µg/L		14			0.52	0.58	0.098	74	**64**
	Copper	320	µg/L		14			0.62	0.69	0.116	80	**400**
	Lead	540	µg/L		14			0.83	0.92	0.156	89	**610**
	Mercury	74	µg/L		14			0.74	0.82	0.139	86	**86**
	Nickel	83	µg/L		14			0.62	0.69	0.116	80	**100**
	Zinc	650	µg/L		14			0.61	0.68	0.114	80	**810**
EXP6A2-SP15-14D-2	Lithium	770	µg/L	8500	14	0	0.172	0.9	1.00	0.172	91	**--**
	Cadmium	72	µg/L		14			0.63	0.70	0.120	81	**88**
	Chromium	48	µg/L		14			0.52	0.58	0.099	75	**64**
	Copper	330	µg/L		14			0.62	0.69	0.118	81	**410**
	Lead	530	µg/L		14			0.83	0.92	0.158	89	**590**
	Mercury	79	µg/L		14			0.74	0.82	0.141	86	**92**
	Nickel	94	µg/L		14			0.62	0.69	0.118	81	**120**
	Zinc	630	µg/L		14			0.61	0.68	0.116	80	**780**
EXP6A2-SP15-28D-1	Lithium	780	µg/L	8500	28	0	0.085	0.9	1.00	0.085	91	**--**
	Cadmium	73	µg/L		28			0.63	0.70	0.060	81	**90**
	Chromium	49	µg/L		28			0.52	0.58	0.049	75	**65**
	Copper	300	µg/L		28			0.62	0.69	0.059	81	**370**
	Lead	530	µg/L		28			0.83	0.92	0.079	89	**600**
	Mercury	81	µg/L		28			0.74	0.82	0.070	86	**94**
	Nickel	78	µg/L		28			0.62	0.69	0.059	81	**97**
	Zinc	620	µg/L		28			0.61	0.68	0.058	80	**770**
EXP6A2-SP15-28D-2	Lithium	780	µg/L	8500	28	0	0.085	0.9	1.00	0.085	91	**--**
	Cadmium	75	µg/L		28			0.63	0.70	0.060	81	**92**
	Chromium	50	µg/L		28			0.52	0.58	0.049	75	**67**
	Copper	310	µg/L		28			0.62	0.69	0.059	81	**380**
	Lead	550	µg/L		28			0.83	0.92	0.079	89	**620**
	Mercury	77	µg/L		28			0.74	0.82	0.070	86	**90**
	Nickel	79	µg/L		28			0.62	0.69	0.059	81	**98**
	Zinc	640	µg/L		28			0.61	0.68	0.058	80	**800**

(a)



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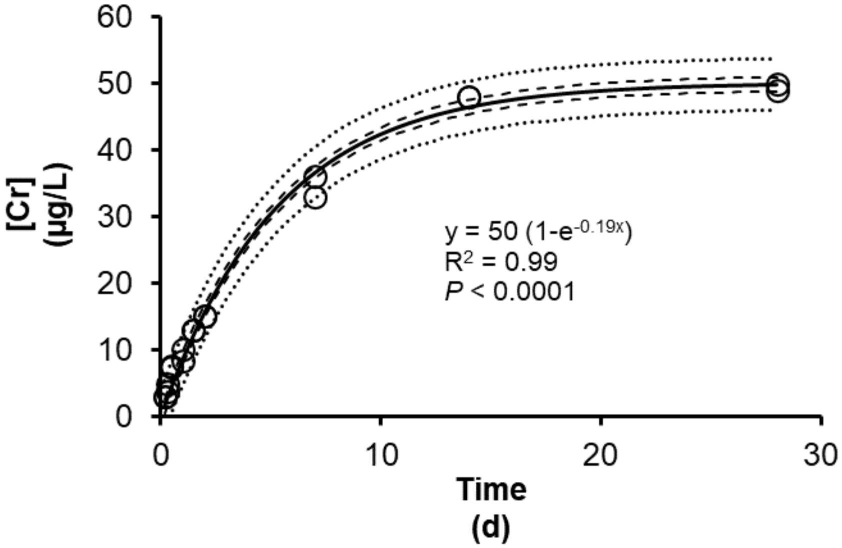
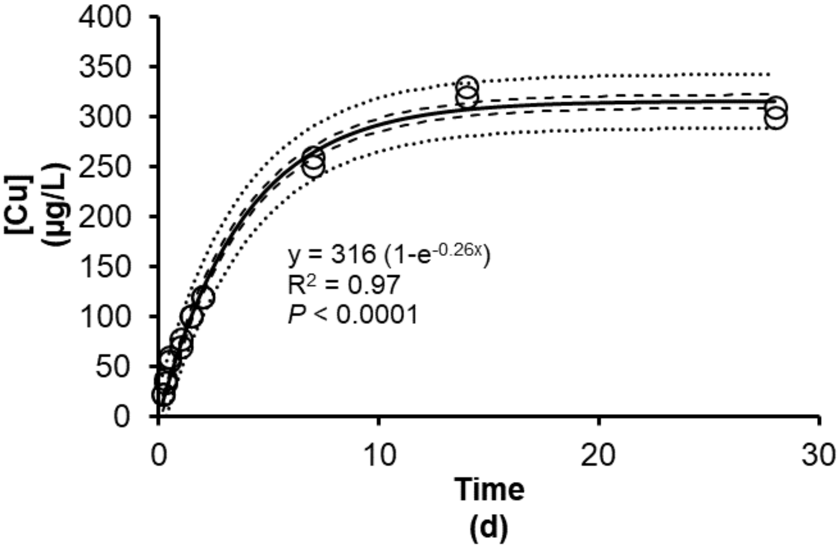


Figure 3-14: One-compartment first-order uptake models applied to concentrations of target metals for peepers deployed in metal-spiked water for various time periods.

(c)



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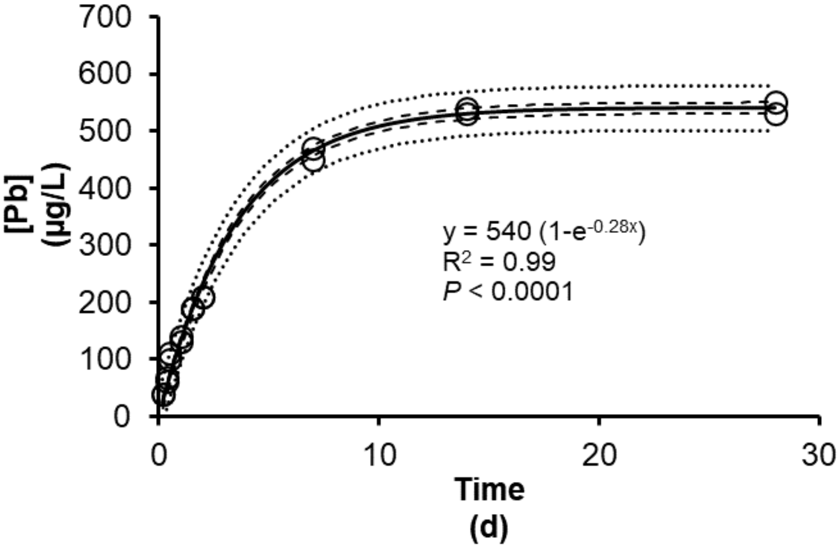

Figure 3-14: Continued.

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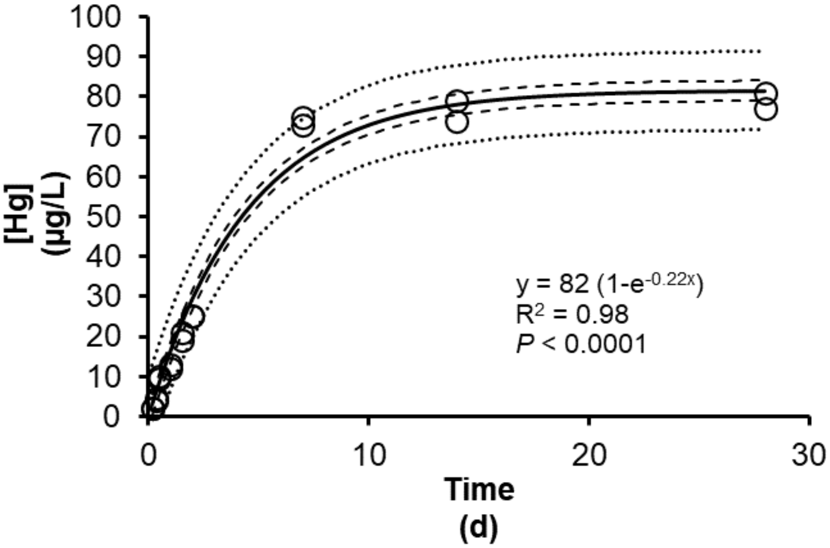

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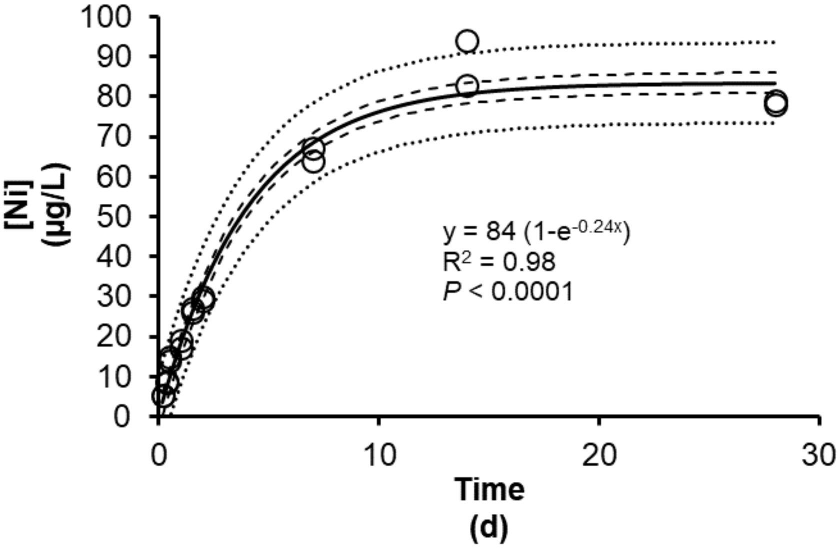


Figure 3-14: Continued.

(g)

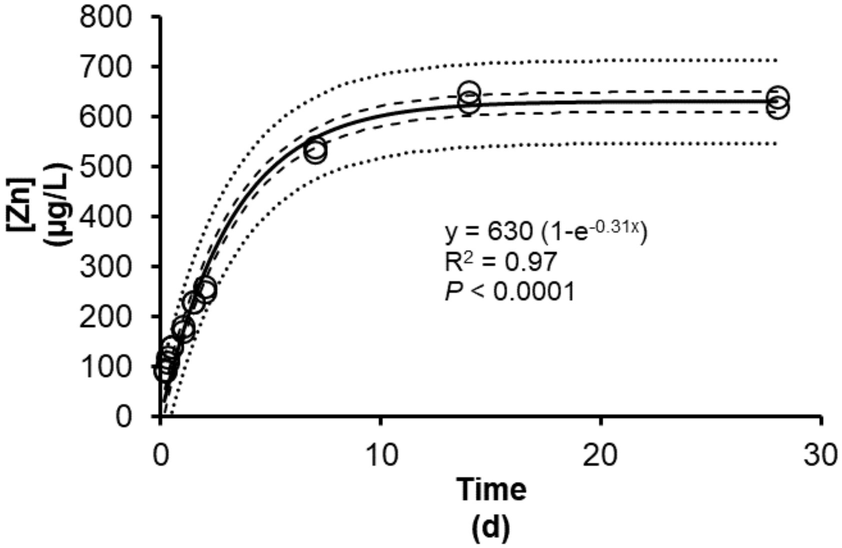
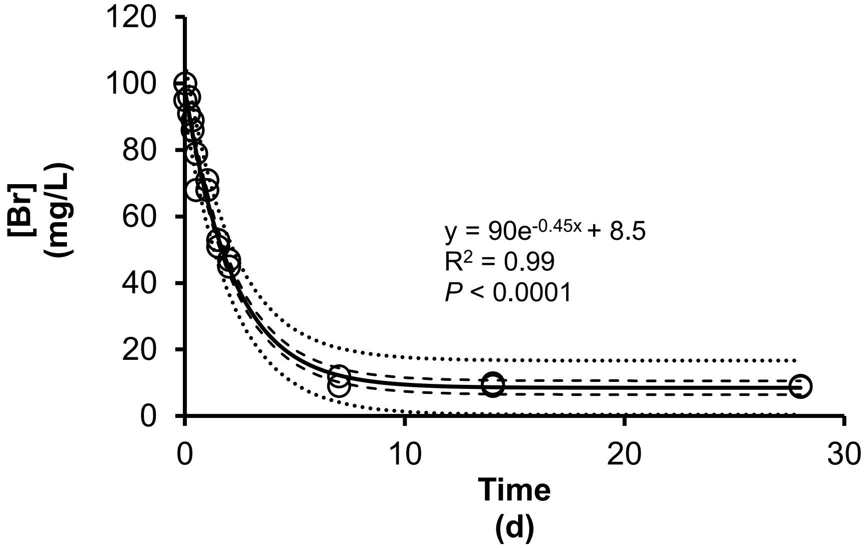


Figure 3-14: Continued.

(a)



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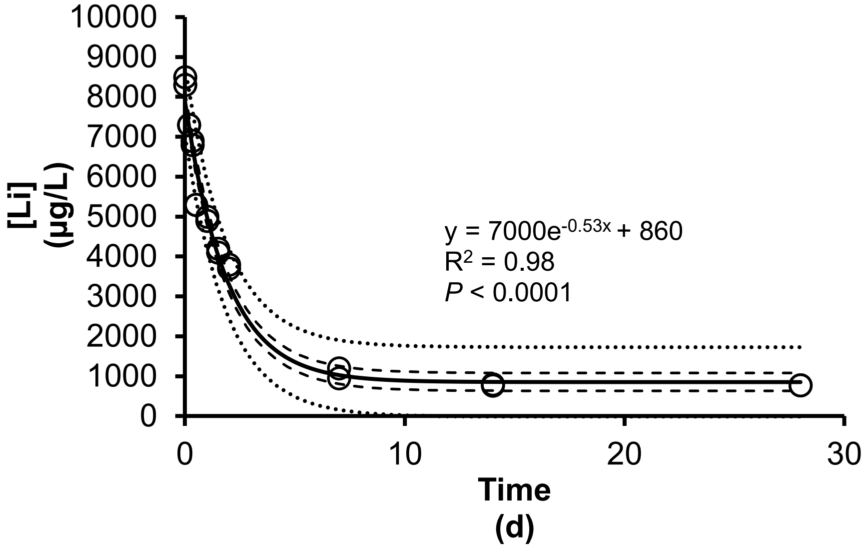


Figure 3-15: One-compartment first-order elimination models applied to concentrations of lithium and bromide tracers for peepers deployed in metal-spiked water for various time periods.

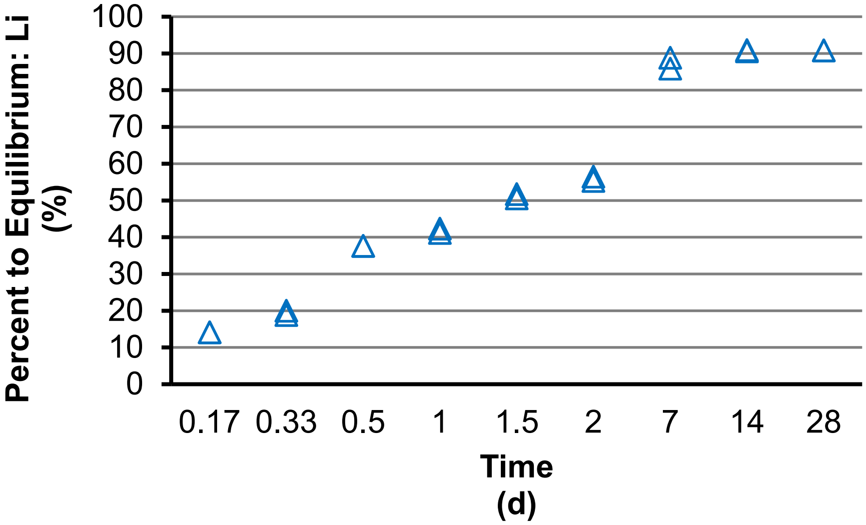
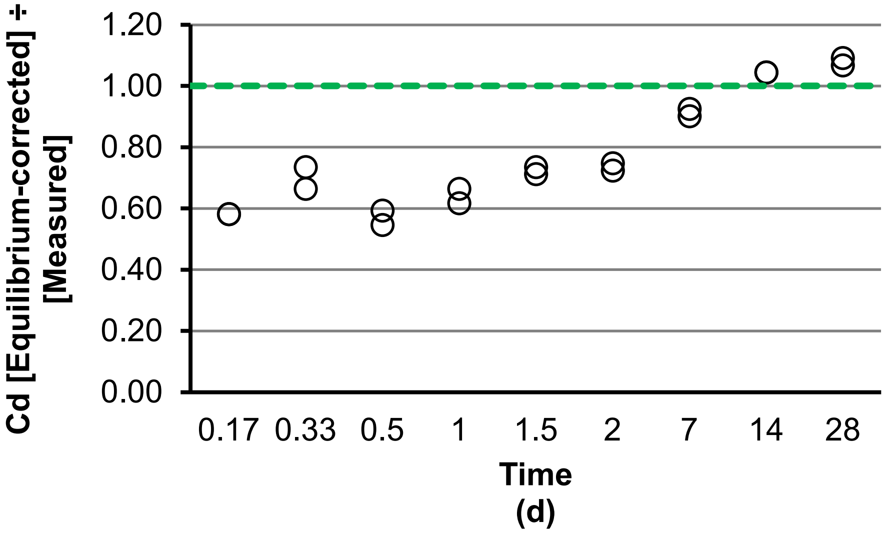


Figure 3-16: Percent to equilibrium for the lithium tracer over the 28-day exposure in water.

(a)



(b)

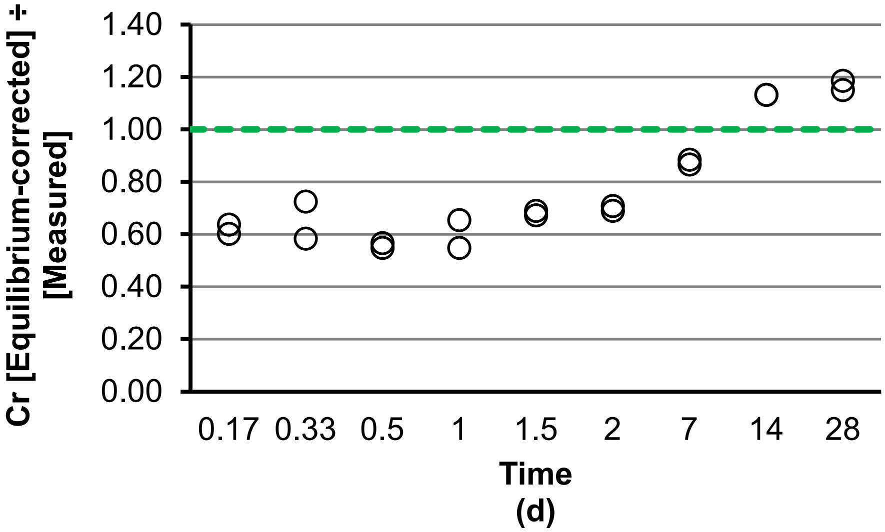
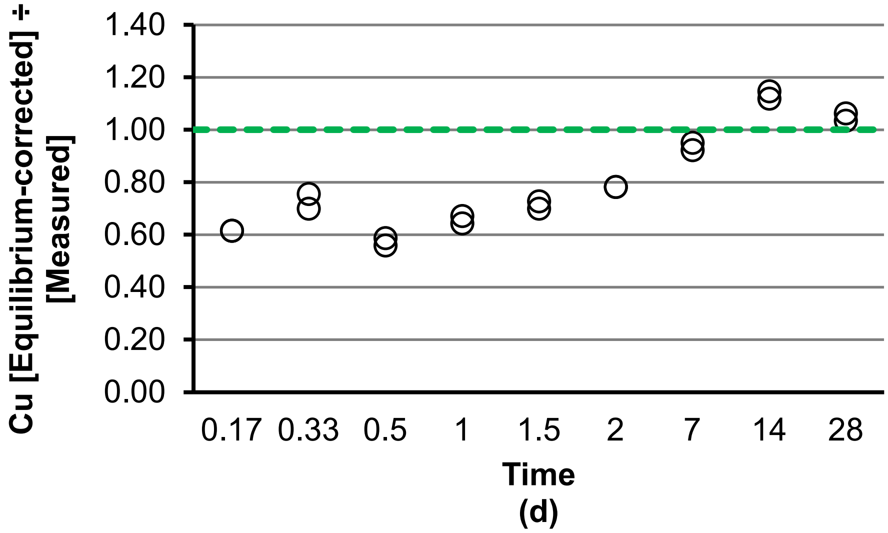
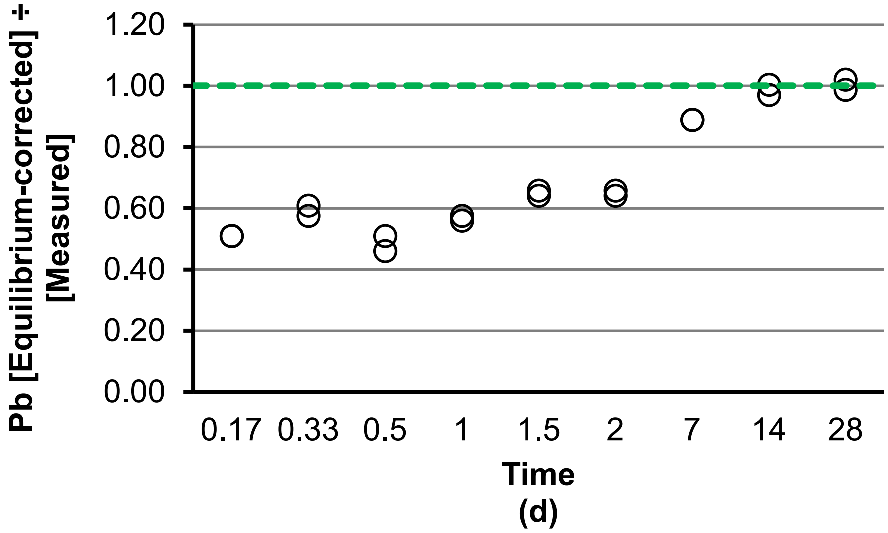


Figure 3-17: Model-predicted equilibrium concentrations for each peeper sample (deployed in metal-spiked water for various time periods) divided by the average measured concentration in the water in which peepers were deployed. The dotted green line indicates perfect agreement (i.e., a value of 1) between the model-predicted equilibrium concentration in the peeper and the average measured concentration of the water.

(c)



(d)



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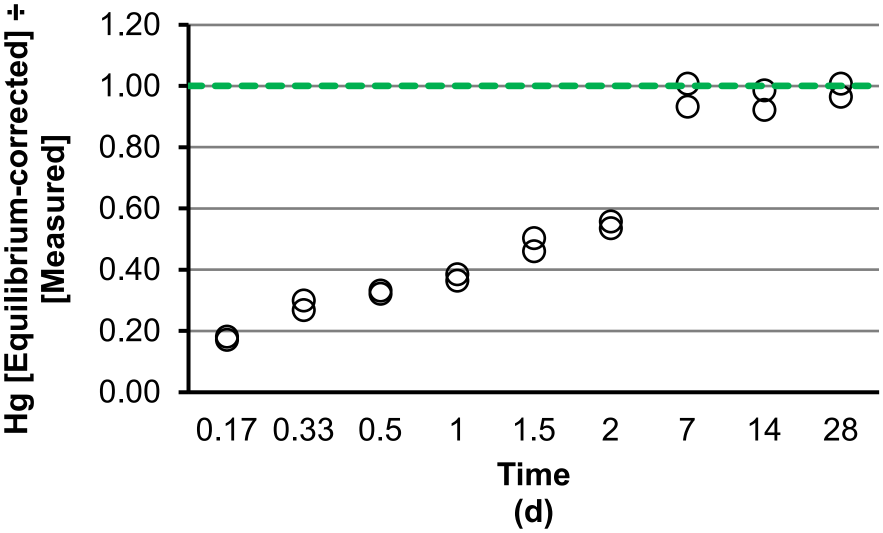
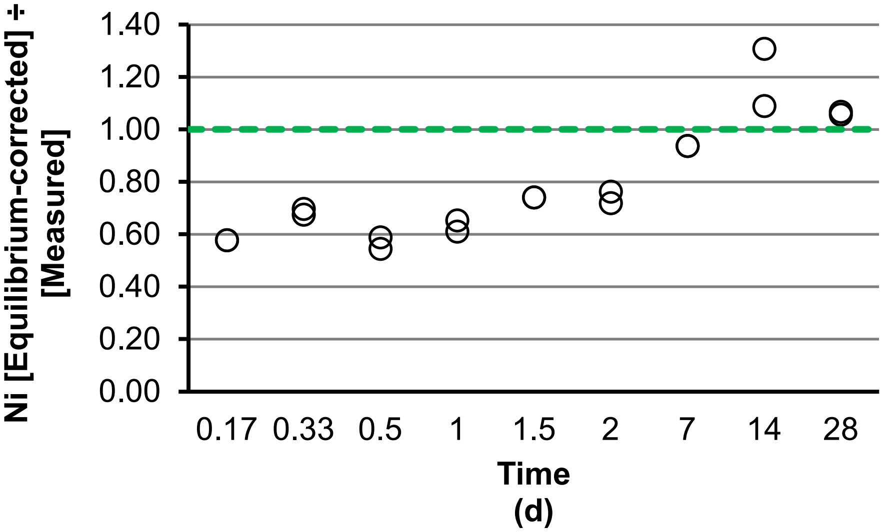
(e)



(f)



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(g)

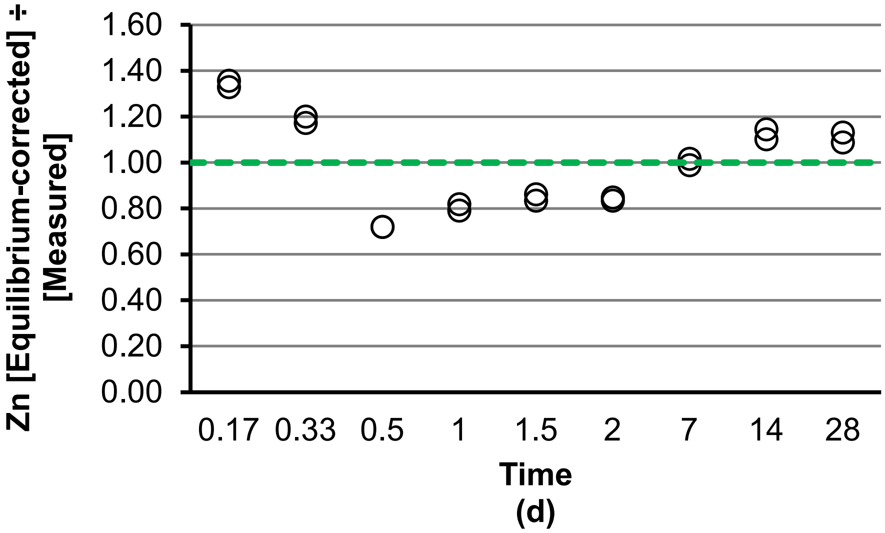
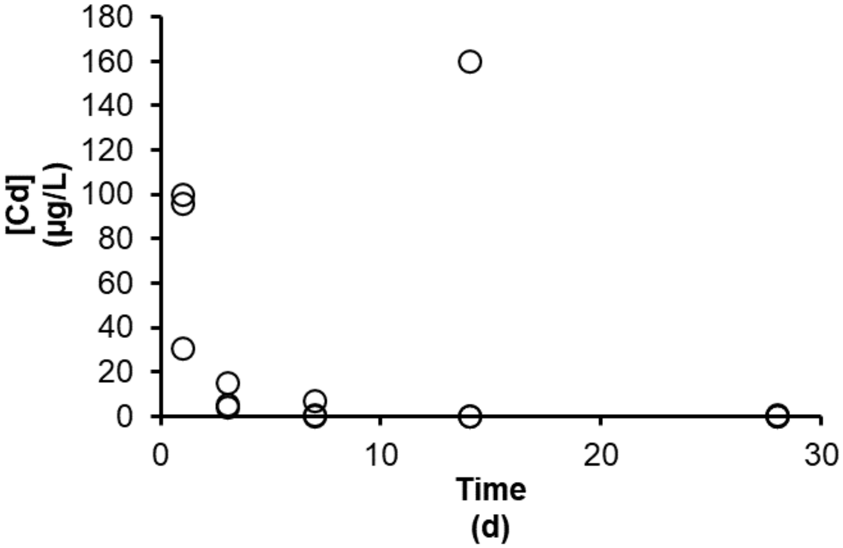


Figure 3-17: Continued.

(a)



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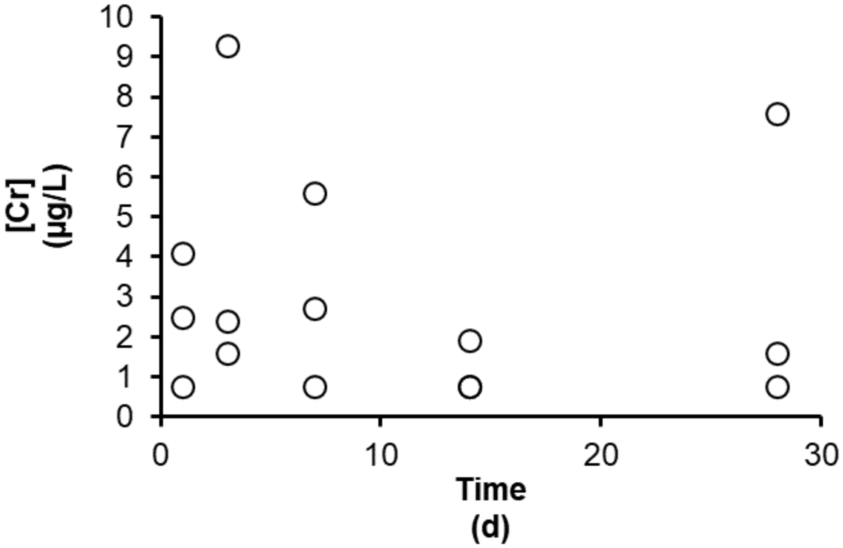
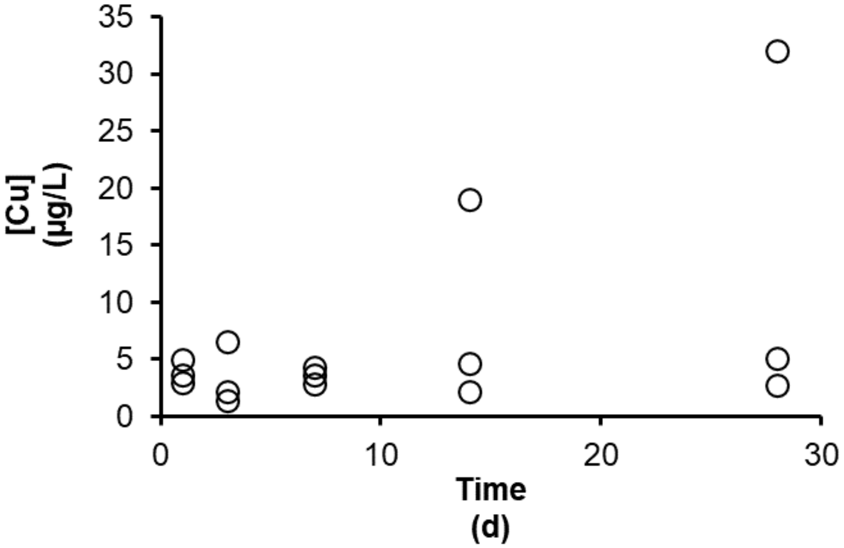
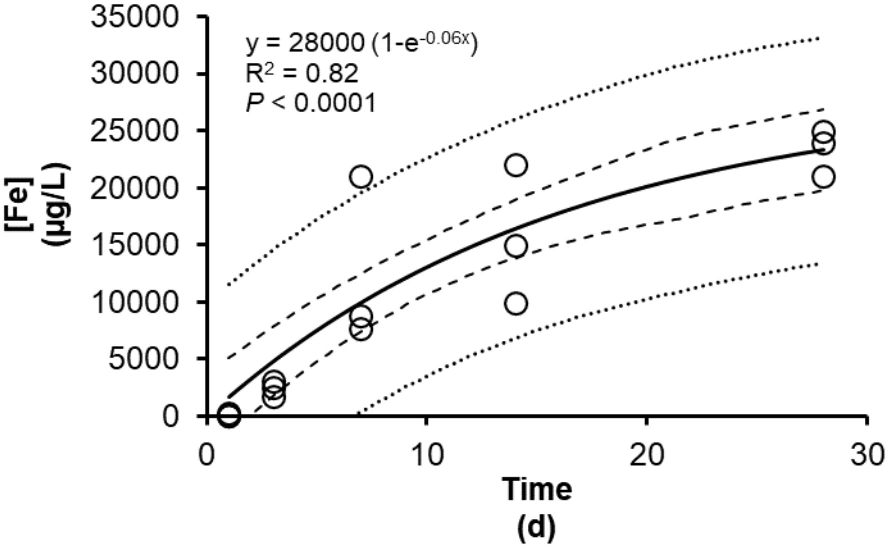


Figure 3-18: Concentrations of target metals, iron, and manganese for peepers deployed in standard metal-spiked sediment (aerated) for various time periods up to 28 days. One-compartment first-order uptake models are shown for iron and manganese, and an elimination model is shown for zinc. Data is not shown for mercury due to the high number of ND results.

(c)



(d)



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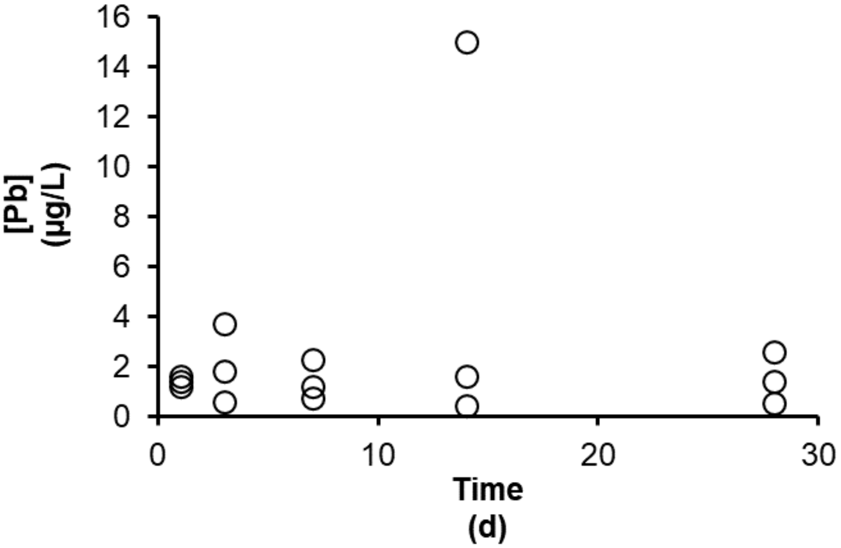
(e)



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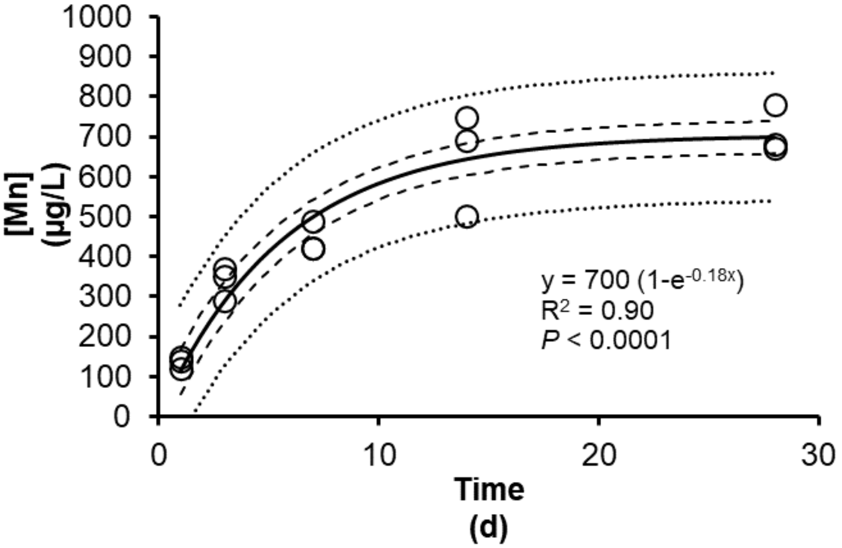

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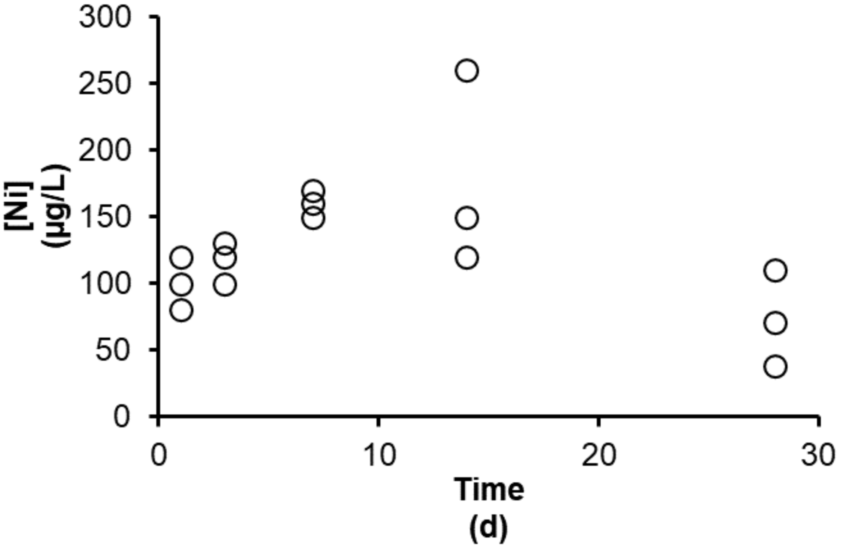
(g)



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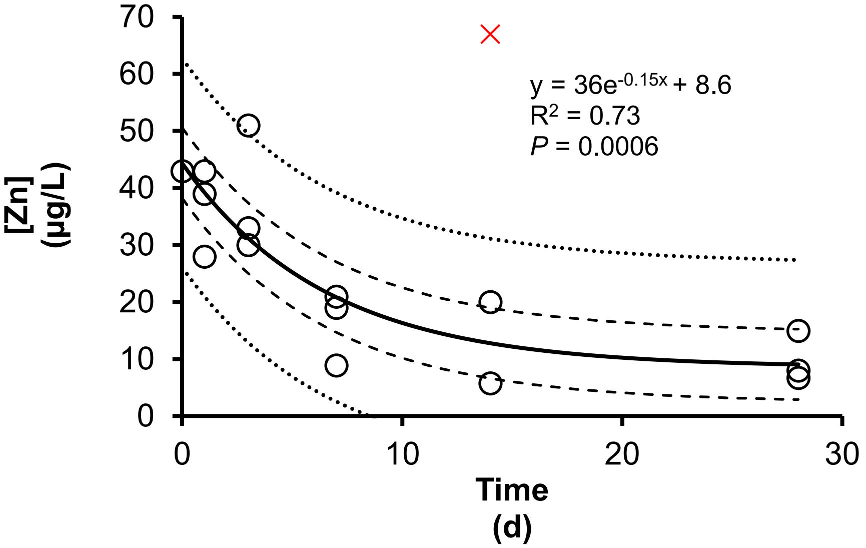

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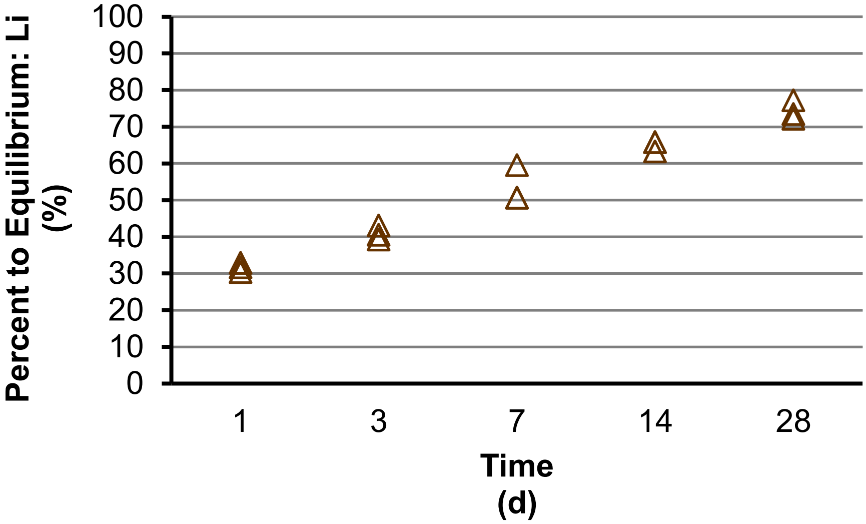
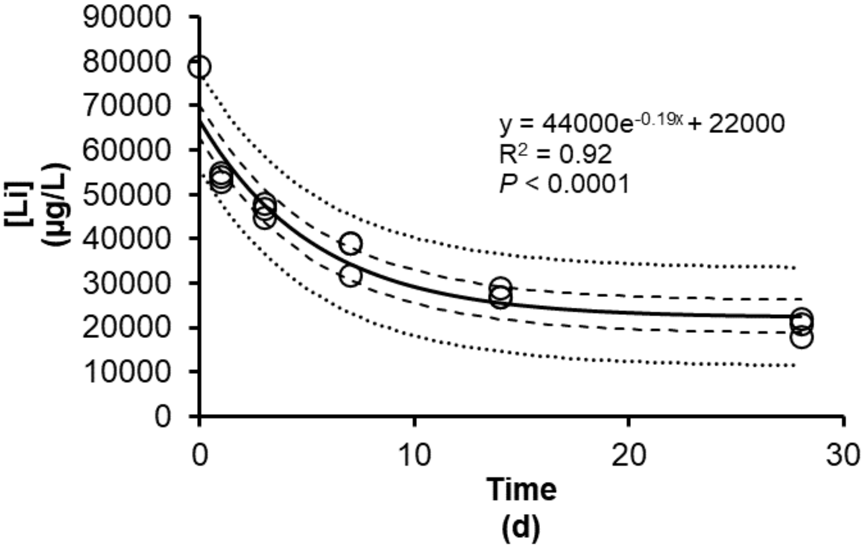


Figure 3-19: Percent to equilibrium for the lithium tracer over the 28-day exposure in the standard spiked sediment.

(a)



(b)

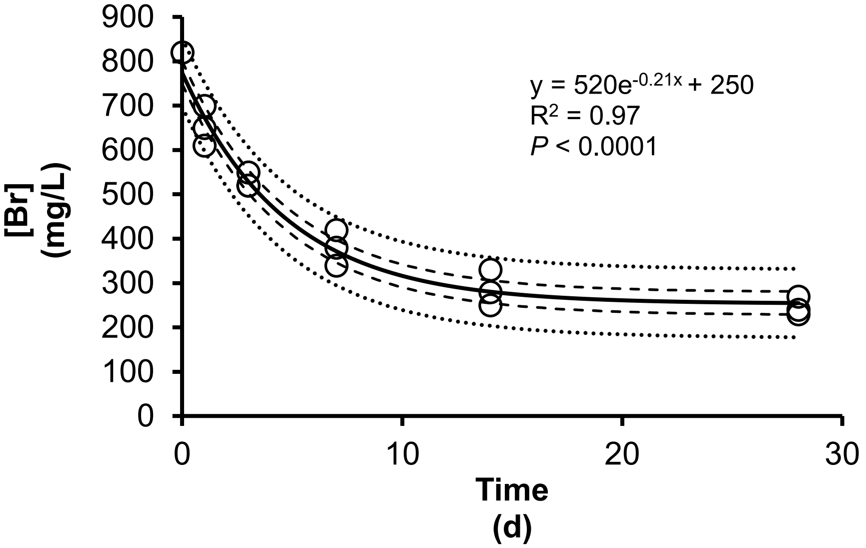
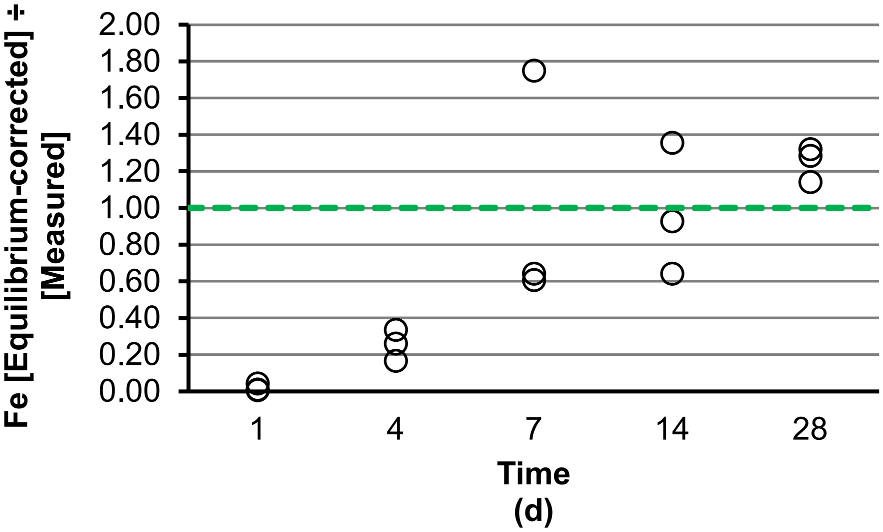


Figure 3-20: One-compartment first-order elimination models for concentrations of lithium and bromide tracers for peepers deployed in standard metal-spiked sediment (aerated) for various time periods up to 28 days.

(a)



(b)

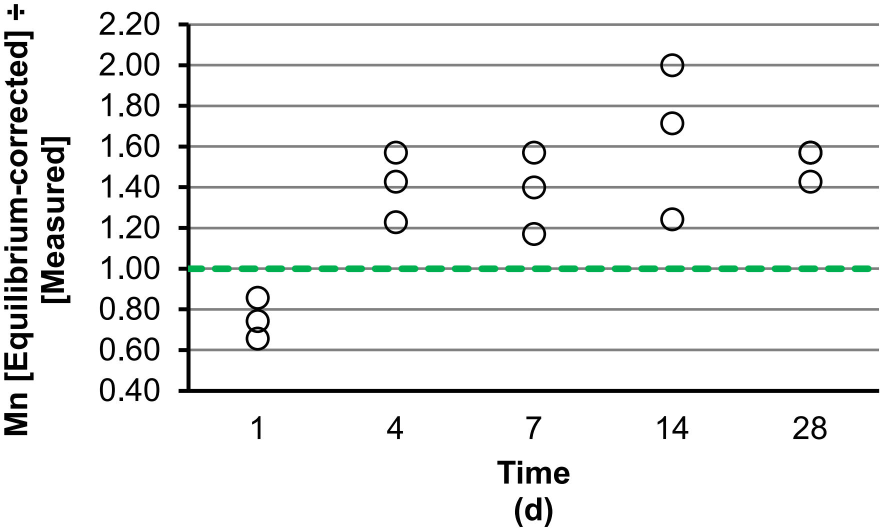
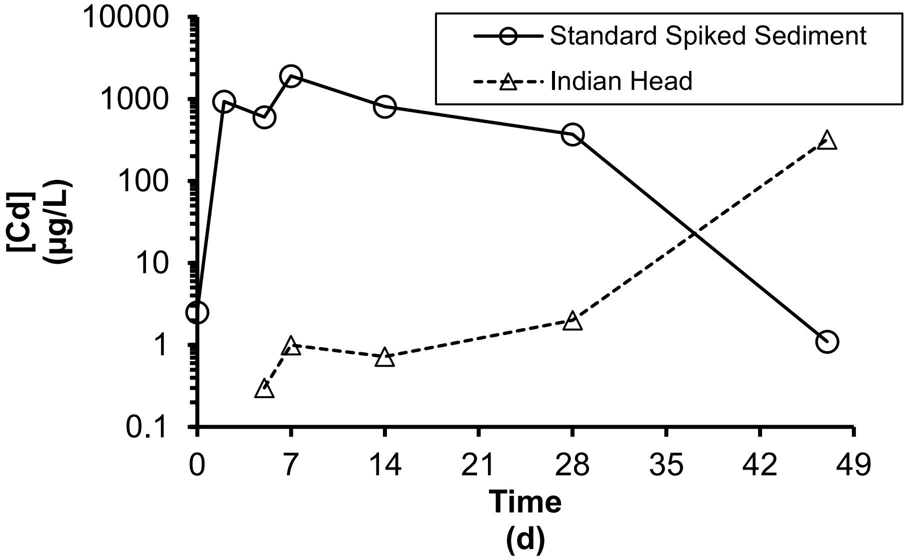


Figure 3-21: Model-predicted equilibrium concentrations of manganese and iron for each peeper sample (deployed in standard spiked sediment for various time periods) divided by the equilibrium concentrations of manganese (700 µg/L) and iron (28000 µg/L) estimated by the one-compartment first-order kinetics models. The dotted green line indicates perfect agreement (i.e., a value of 1) between the model-predicted equilibrium concentration in the peeper and the model-predicted equilibrium concentration.

(a)



(b)

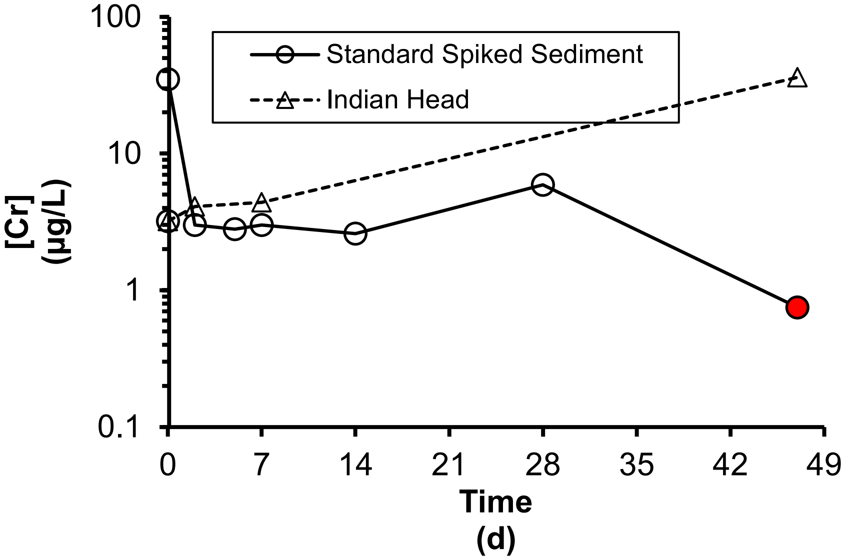
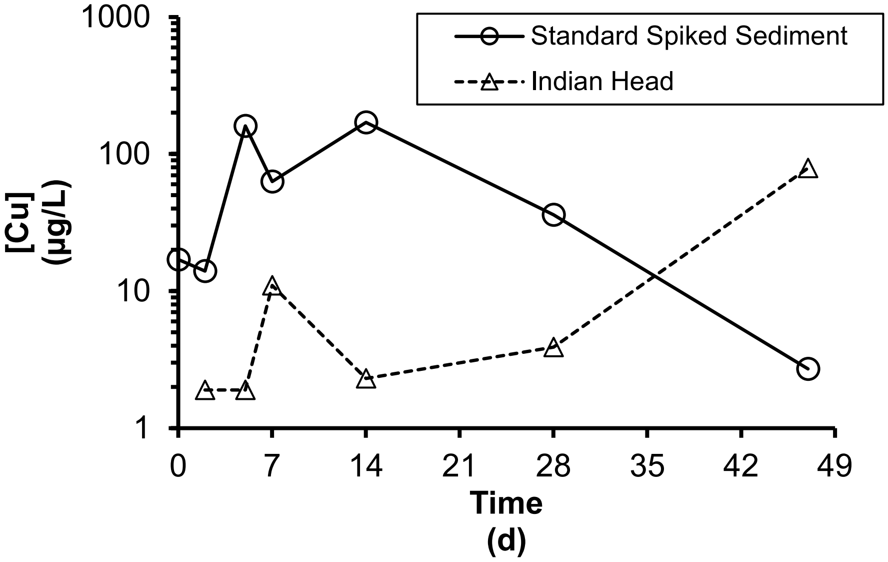
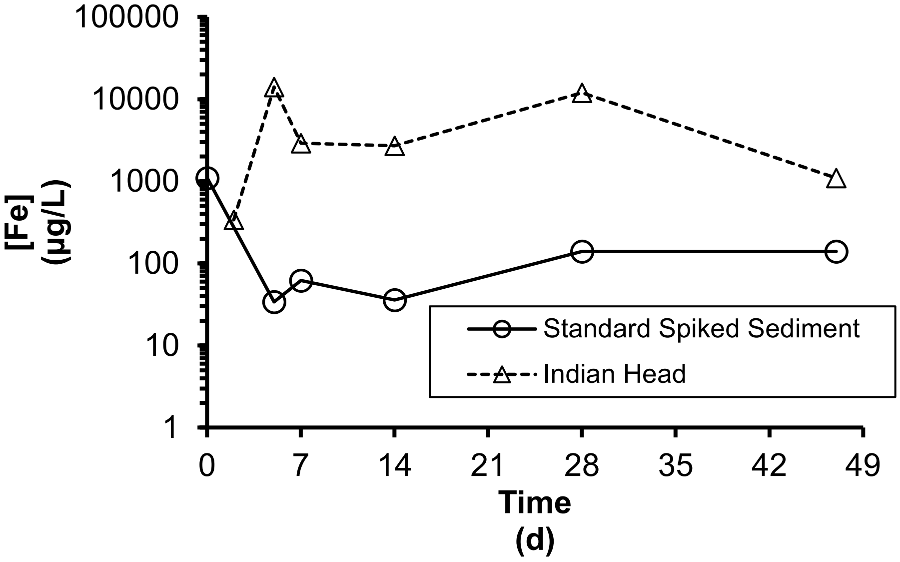


Figure 3-22: Concentrations of target metals, iron, and manganese for peepers deployed in standard metal-spiked sediment and Indian Head sediment (aerated) for various time periods up to 47 days. Data is not shown for mercury due to the high number of ND results.

(c)



(d)



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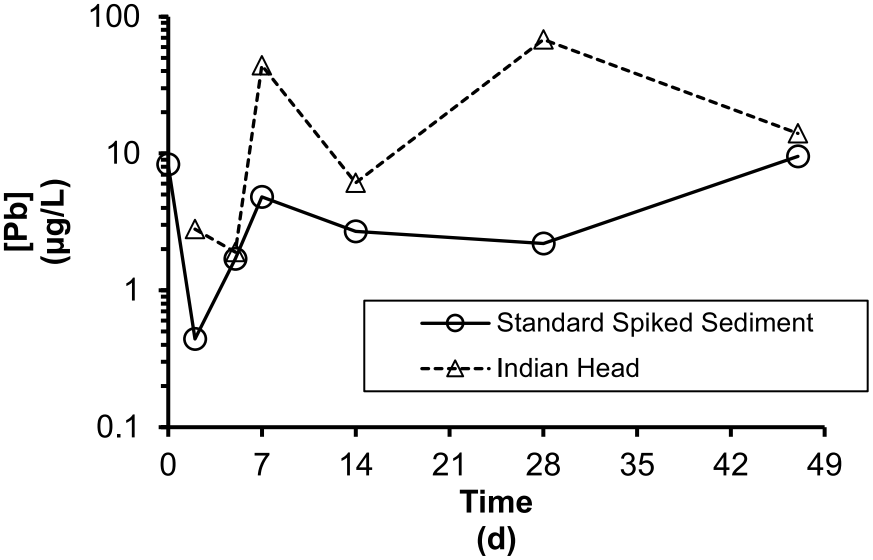
(e)



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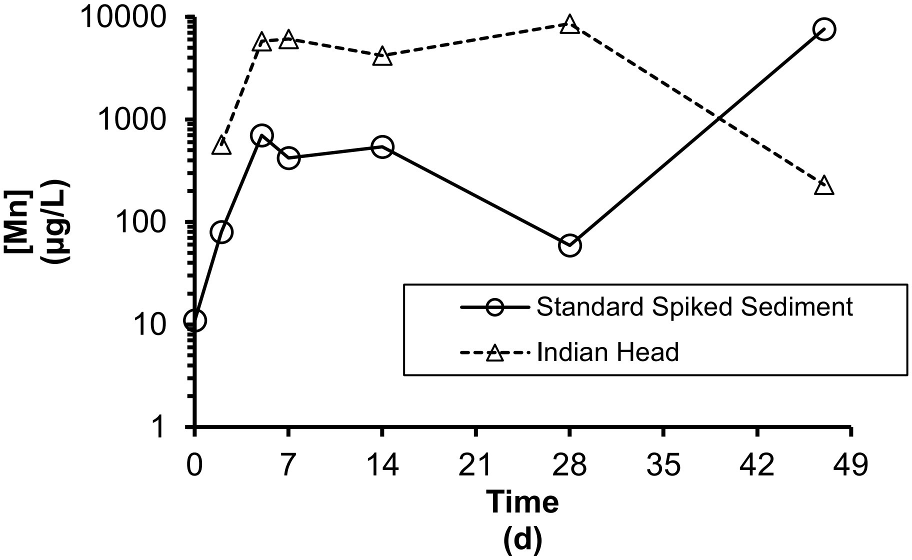
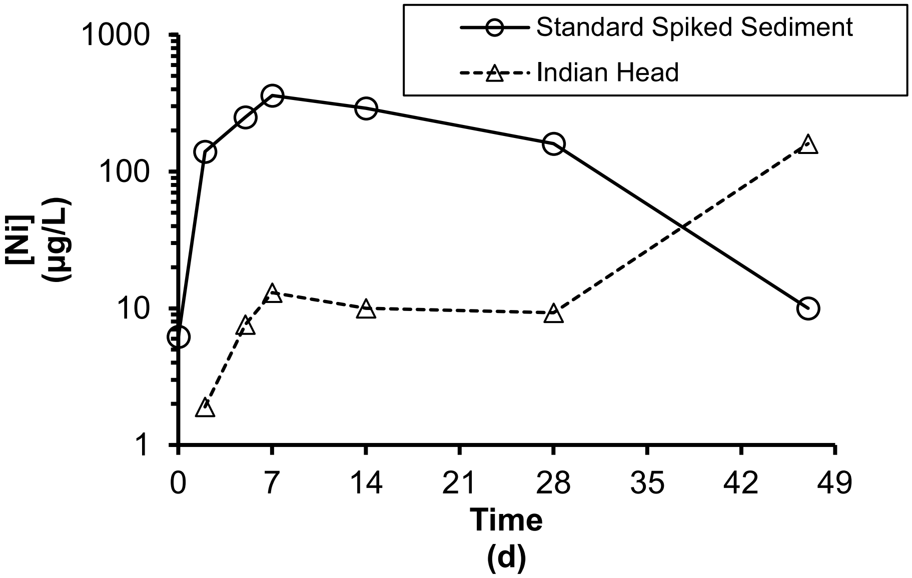


Figure 3-22: Continued.

(g)



(h)

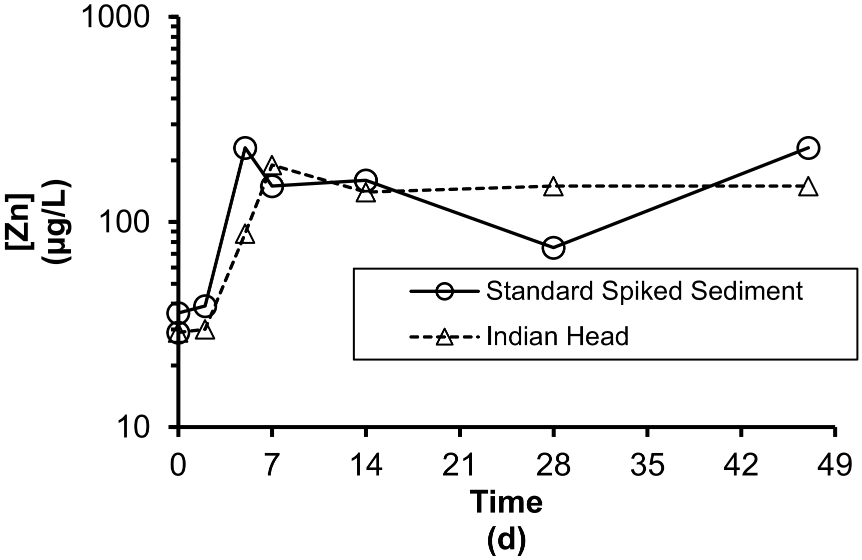
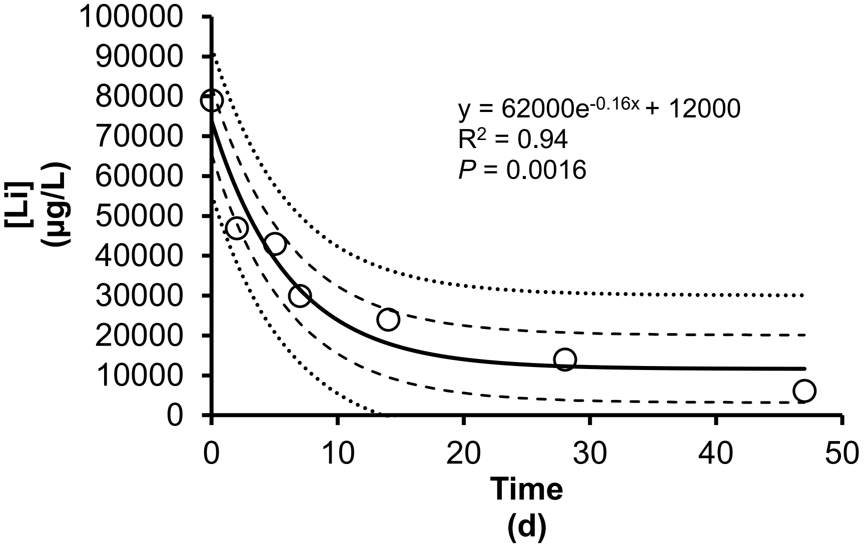


Figure 3-22: Continued.

(a)



(b)

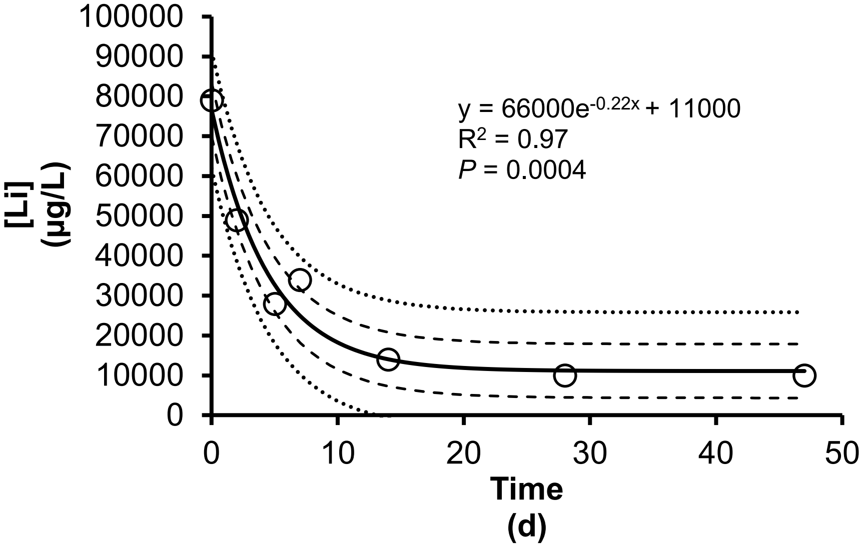


Figure 3-23: One-compartment first-order elimination models for concentrations of lithium for peepers deployed in standard metal-spiked sediment (a) and Indian Head sediment (b) for various time periods up to 47 days. Sediments were aerated.

3.7 Experiment 7: Peeper Water Salinity

3.7.1 Rationale and Methods for Experiment 7

Experiment 7 was conducted to evaluate the effects of initial peeper water salinity water when deploying peepers in marine sediment.

Differences in salinity between fresh/deionized peeper water and external saline water when a peeper is first deployed in a saline sediment or water have been hypothesized to result in density gradients that could affect diffusive processes during peeper sampling (Risacher et al., 2023a). Peeper waters are usually prepared with deionized water rather than saline water, and it is usually not feasible or practical to attempt to match the salinity of the peeper water with that expected in the sediment or water in which it is deployed.

Experiment 7 was conducted to test the impact of initial peeper water salinity on diffusion speeds and overall results for peepers deployed in marine sediment. Half of the peepers were prepared following the standard method with no deoxygenation of the peeper water prior to deployment. Half of the peepers were prepared in the same manner, but with water containing 35 g/L of trace-metal grade sodium chloride (salinity level of sea water used in the mesocosms) instead of deionized water. Six mesocosms were prepared using the standard spiked sediment. Three mesocosms received four peepers prepared with standard deionized water while the other three mesocosms received saline peepers. Peepers were deployed for 14 days in the aerated mesocosms, after which they were processed using the pipette method in air. Samples were analyzed for target metals, manganese, iron, lithium and bromide. Blanks were also prepared using both peeper solutions and analyzed for target metals, manganese, iron, lithium, and bromide.

3.7.2 Results and Discussion for Experiment 7

Raw data for Experiment 3 are shown in Table 3-17, with supporting analytical chemistry reporting in Appendix B. A high proportion of ND results precluded evaluation of the effects of peeper water salinity on mercury results. Outliers were limited to an anomalously low value for iron and anonymously high value for cadmium in a sample in the "deionized water" treatment group.

As shown in Figure 3-24, 14-day deployment results for the peepers indicated no significant differences ($P > 0.05$) between peepers prepared using the standard approach (i.e., filled with deionized water), and peepers prepared with saline water. Individual figures for each metal are shown in Figure 3-25. Although the presence of a salinity difference between the peeper water and the external matrix in which it is deployed was hypothesized to affect equilibration, the average (SD) percentage equilibration for the 14-d deployment indicated the lithium tracers for the deionized and saline peepers were 63% (6%) and 59% (3%) equilibrated, respectively, and not significantly different ($P > 0.05$). As in previous experiments with peepers prepared with deionized water and deployed in the sediment for 14 days, these results are within the 50% to 70% range typically observed.

Overall, the results of Experiment 7 indicate that the initial low salinity of a peeper prepared using deionized water does not affect the overall results for metals or the rate of equilibration when the peeper is deployed into a saline marine sediment. There is no need to attempt to prepare peepers with the same salinity as the matrix to which they will be deployed.

Experiment 7 Lessons Learned and Recommendations

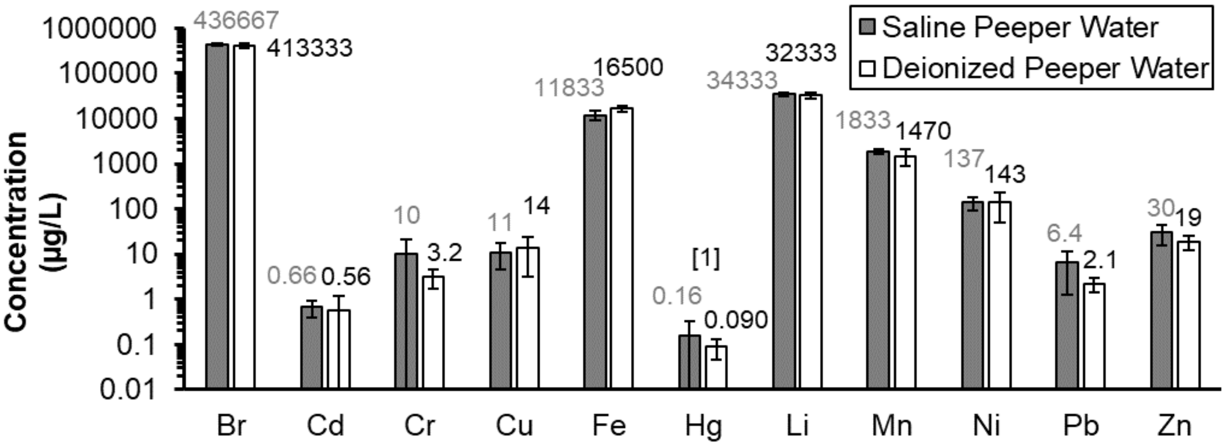
- Peepers to be deployed in marine or estuarine sediment or water can be prepared with deionized water.

Table 3-17: Concentrations of target metals, manganese, iron, and lithium and bromide tracers for peepers. Peepers were deployed in aerated, spiked sediment for 14 days prior to samples being extracted.

Solution	Sample ID	Concentration (µg/L)										[mg/L]
		Cadmium	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Zinc	Lithium	Bromide
Approximate Method Detection Limit		**0.22**	**1.5**	**1.1**	**28**	**0.17**	**1.3**	**0.13**	**0.52**	**2.9**	**42**	**2.7**
Deionized Water	EXP7-SP15-DI-1	710*	2.6	26	460*	1.8	810	ND	250	140*	36000	440
	EXP7-SP15-DI-2	ND	2.1	6.2	18000	1.6	1800	ND	87	14	35000	440
	EXP7-SP15-DI-3	1	4.8	9.3	15000	3	1800	0.14	93	23	26000	360
Saline Water	EXP7-SP15-SA-1	0.35	2.4	7.1	15000	1.8	1700	ND	92	16	37000	420
	EXP7-SP15-SA-2	0.75	5.3	7.4	9500	5.4	1700	ND	140	30	32000	420
	EXP7-SP15-SA-3	0.89	22	18	11000	12	2100	0.34	180	45	34000	470
	EXP7-SP15-SA-BLK	ND	ND	1.7	ND	ND	ND	ND	ND	4.6	83000	790
	EXP7-SP15-DI-BLK	ND	ND	1.9	ND	ND	ND	ND	ND	5	88000	900

Notes:

* - Identified as an outlier



[1]: Unable to statistically compare due to high proportion (≥ 50%) of ND results.

Figure 3-24: Average concentrations of metals and tracers in peepers prepared with deionized water and saline water, as deployed in standard spiked sediment for 14 days.

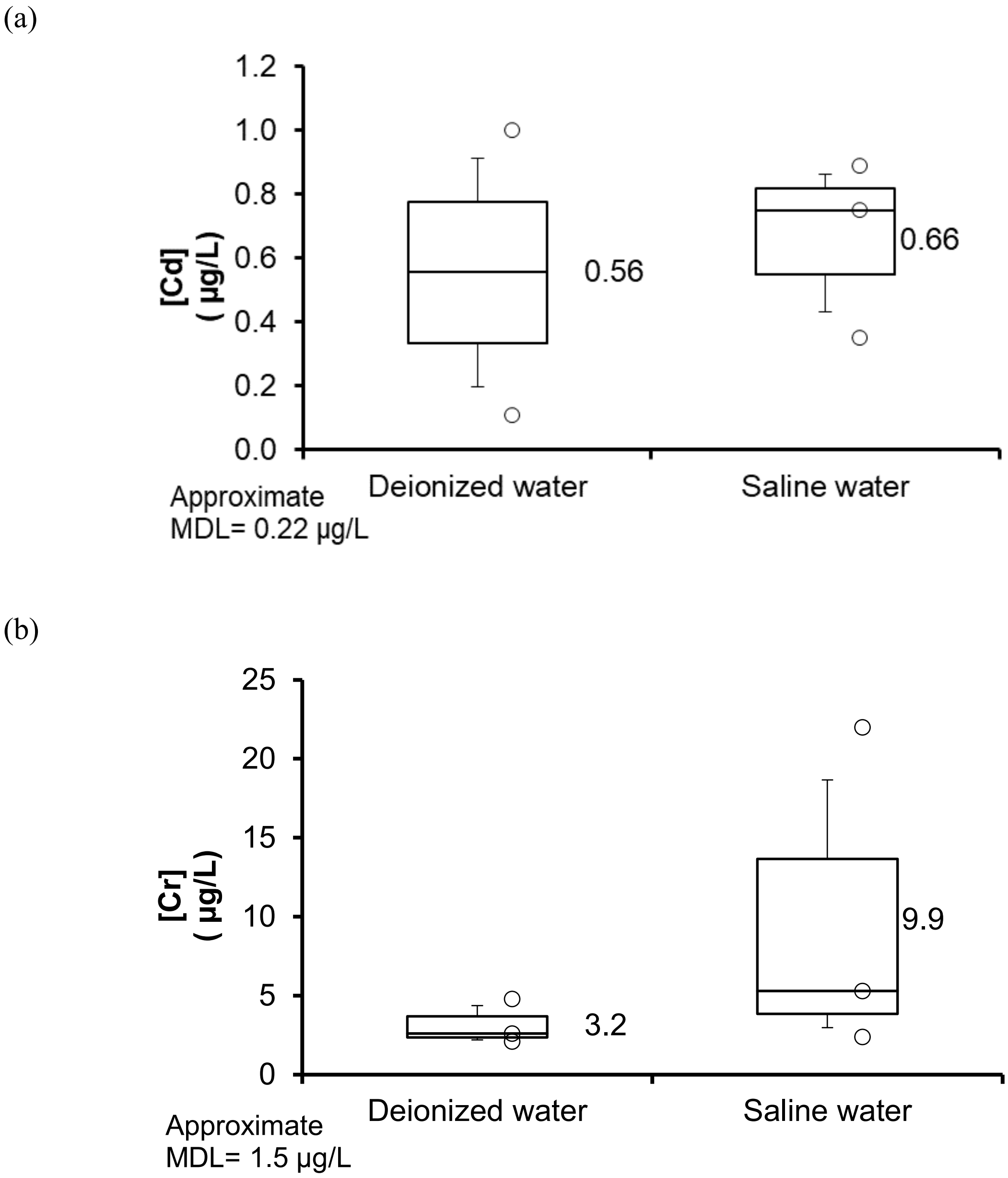
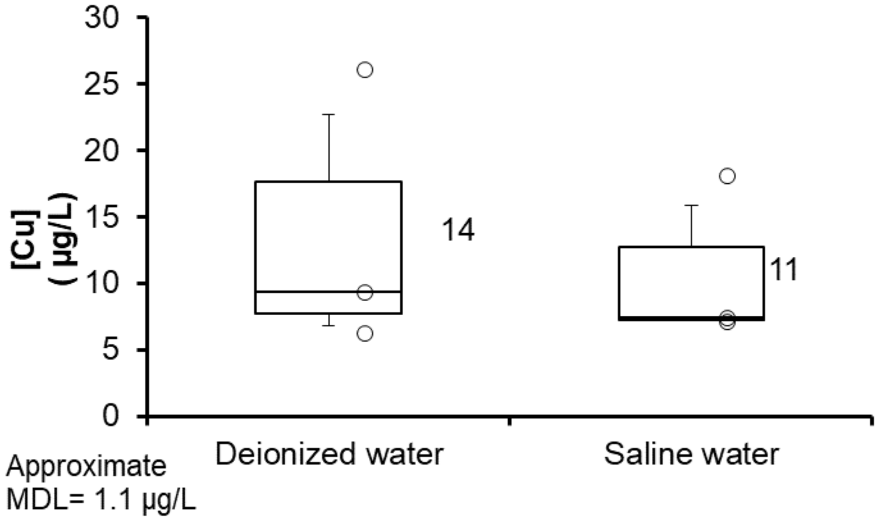
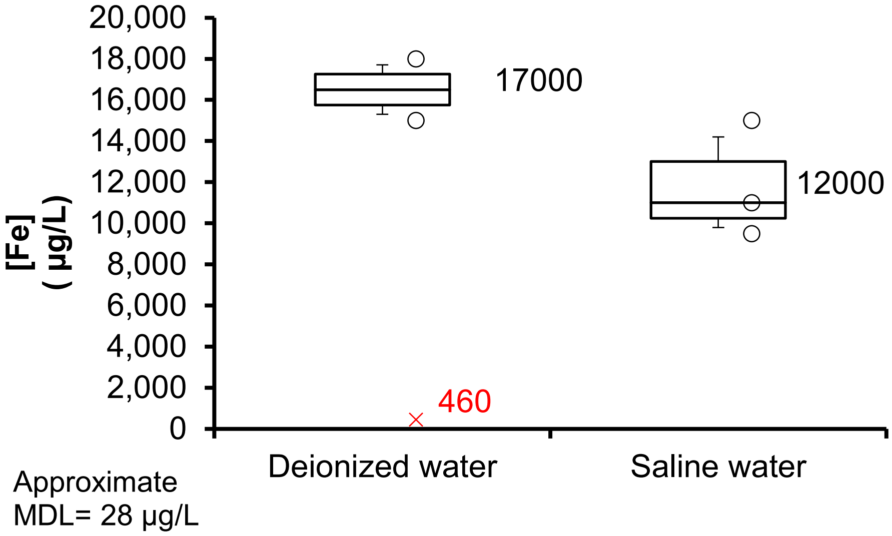


Figure 3-25: Concentrations of metals and tracers in peepers prepared with deionized water and saline water, as deployed in standard spiked sediment for 14 days. Data are not shown for mercury due to the high number of ND results. One outlier for cadmium and zinc in the deionized data are not shown because they would distort the figure scale.

(c)



(d)



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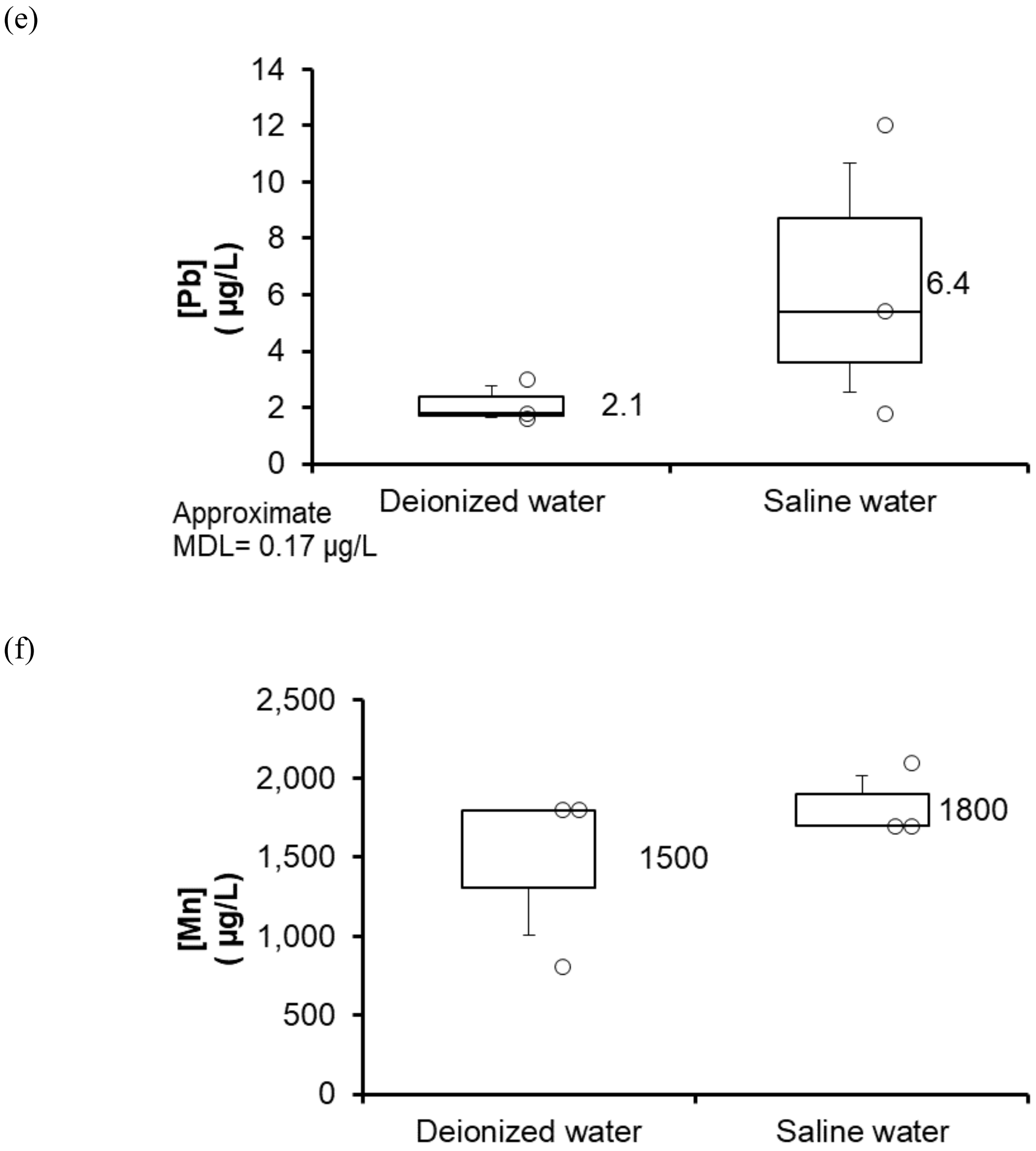

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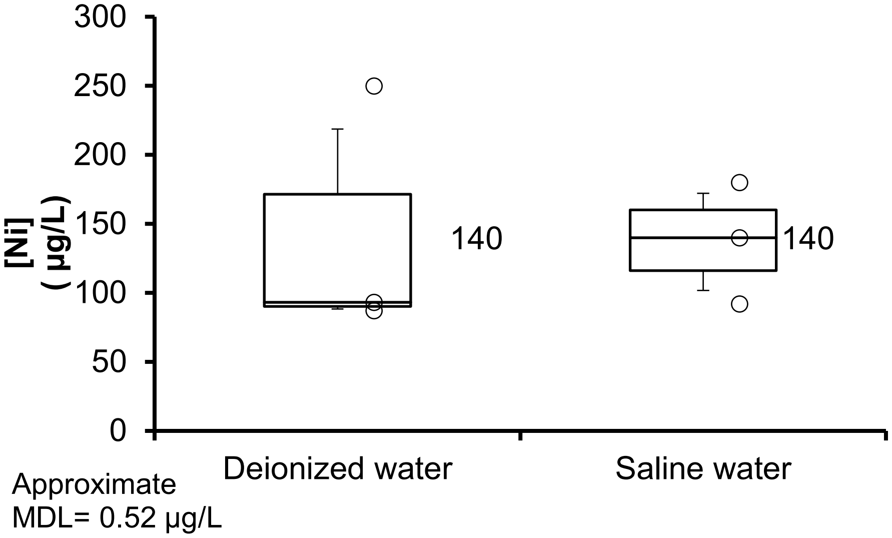
(g)



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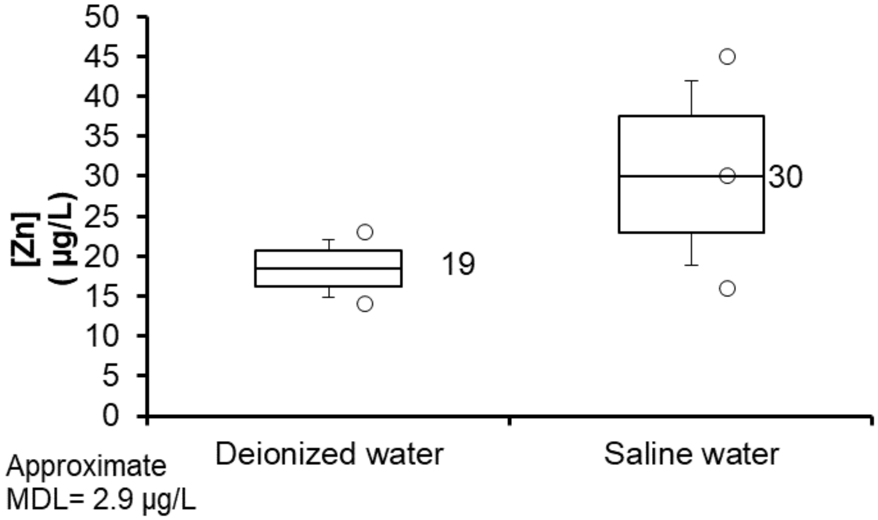

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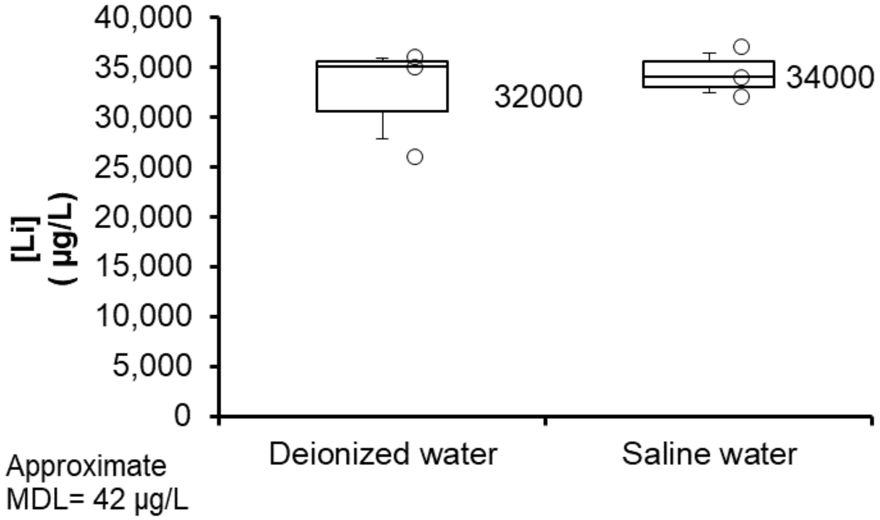
(i)



(j)

Figure 3-25: Continued.

4. CONCLUSIONS

Based on the analysis of 122 peeper samples from seven laboratory experiments conducted over a period of 17 months, a number of key aspects of peeper methodology to measure the availability of divalent target metals (cadmium, chromium, copper, lead, nickel, mercury, and zinc) as well iron and manganese in porewater were evaluated. Table 4-1 provides a summary of the conclusions reached with this data.

Table 4-1: Overview of laboratory results by experiment.

Experiment	Main Conclusions
1: Peeper Design	• A 15-mL peeper design offered the most optimal balance in low cost and rapid sampling times (i.e., 14 days or less) for this experiment.
2: Peeper Deoxygenation	• Peepers do not need to be deoxygenated prior to deployment in sediment. • Lithium (added to the peepers as lithium bromide) makes an optimal tracer analyte.
3: Peeper Sample Processing	• After peeper retrieval from sediment, peeper water is best transferred to sample storage containers using a pipette. • Transfer of the peeper water can be performed in air – there is no need to process peepers in an inert atmosphere.
4: Peeper Storage - Oxygen	• Within approximately 10 to 30 minutes of peeper retrieval from sediment, peepers should be stored in an airtight bag containing oxygen muncher packets.
5: Peeper Storage - Post Deployment	• Within approximately 8 hours of peeper retrieval from sediment, peeper waters should be transferred to sample storage containers.
6: Tracers for Pre-equilibrium Deployments	• The uptake of target metals and elimination of lithium tracers follow one-compartment, first order kinetics, as demonstrated in water. • Additional experiments to evaluate a time series in field sediments would provide the best demonstration of the pre-equilibrium approach. • The use of the lithium tracer enables pre-equilibrium short-term deployments of peepers in sediment and water; some uncertainty remains for sediment, and this can be managed by increasing deployment time.
7: Peeper Water Salinity	• Peepers to be deployed in marine or estuarine sediment or water can be prepared with deionized water.

These conclusions were used to generate final SOPs for peeper methods in the Final Demonstration Best Practices Report (expected in October 2023).

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Appendix A: Peeper Preparation Standard Operating Procedure

Peeper Preparation Method

OVERVIEW

- Peepers are a small chamber containing deionized water capped with a semi-permeable membrane. The water may be spiked with lithium and/or bromide tracer.

PREPARATION

Materials for Preparation:

- A large plastic bin to contain a weak acid bath.
- Materials for Peepers: Vials and caps, approximately 15-mL; e.g., 1/2 oz. Natural Polypropylene (PP) Straight-Sided Thick Wall Round Jar with 43/400 Neck and 43/400 White Polypropylene (PP) Unlined Ribbed Cap (US Plastics, https://www.usplastic.com/
- Nitrile gloves.
- 1.25-inch diameter hole saw drill bit and drill press
- 0.45-µm pore size Polyethersulfone (PES) filters, 47-mm diameter
- Lithium bromide (LiBr)
- 70% Nitric Acid (trace metal grade)
- Laboratory Detergent
- Reverse osmosis (RO) water
- Deionized water: Ultrapure 18.2 MΩ/cm deionized (DI) water
- Chemical waste container
- Mylar zipseal storage bags
- Additional personal protective equipment as needed (eye protection, etc.)

Preparation of Peeper Vials

1. Drill out the center of each cap of the peeper caps with the hole saw (drill press), leaving a 1.25-inch diameter hole in the center of the cap.

Cleaning of Peepers

1. Clean the vials and caps with laboratory-grade detergent and RO water, followed with an RO water rinse, and a final DI water rinse.
2. Place vials and caps (and any other peeper support material) in a large plastic tote.
3. Rinse bin and its contents, with DI water three times.
4. Prepare a 5% trace metal grade nitric acid bath using concentrated nitric acid and DI water, and place in the bin with its contents.
5. Soak contents in the bin for 24 hours.
6. Drain bin and dispose of acid bath solution in the appropriate waste container.
7. Rinse the bin and its contents 5 times with DI water.
8. Repeat steps 5-8 once more, for a second acid wash.
9. Fill the bin with DI water and let soak for 24 hours.
10. After the 24-hour soak, drain the bin.
11. Rinse the bin and its contents 3 times with DI water.

Peeper Water Preparation

1. Calculate the mass of lithium bromide (LiBr) necessary to obtain the desired concentration of LiBr: 1 g/L (deployments in marine water) or 0.1 g/L (deployments in freshwater) of LiBr for the volume of water needed to fill the peepers.
2. Add LiBr to an acid-cleaned bottle or flash and bring to volume with DI water; mix until all solids have dissolved.

Peeper Assembly

1. Gather all necessary components needed for peeper construction (e.g., PES membranes, Mylar bags, caps and vials, LiBr solution)
2. Fill the peepers with LiBr solution such that the solution beads up above the lip of the vial.
3. Gently place the 0.45-μm PES filter on top of the vial opening and tighten the cap over the vial, ensuring no bubbles are present in the solution.
4. Ensure a seal has been made between the vial and the cap via the membrane by visually inspecting the peeper.
5. Check to make sure that there are no rips, tears, or wrinkles in the membrane. Any deformities in the membrane could prevent the peeper performing correctly.
6. Repeat above steps with remaining vials.

7. Final example product:

8. Once peepers have been prepared, place in a mylar zipseal storage bag. Include approximately 5 to 10 mL of the LiBr solution in the mylar bag so the atmosphere in the mylar bag remains moist.
9. In the mylar bag, ensure peepers are lying flat within the bag so the filter membranes are not punctured by the bottom of another peeper.
10. Repeat above until all peeper required for the project have been constructed.
11. Store peepers in their mylar bags, lying flat, under ambient conditions (20-25°C) or in cold conditions (4°C) until shipment.

Appendix B: Analytical Laboratory Reports

Laboratory experiment analytical reports can be found attached to this document.

Appendix C: Field Demonstration Report

Field Deployment Report

Standardizing Sediment Porewater Passive Samplers for Inorganic Constituents of Concern
ESTCP ER20-5261

January 2023

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Acronyms and Abbreviations

ANOVA	Analysis of Variance
Br	Bromide
cc	Cubic Centimeters
CCC	Criterion Continuous Concentration
Cd	Cadmium
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
cm	Centimeter
Cr	Chromium
Cu	Copper
DGT	Diffusive Gradients in Thin-Films
DOC	Dissolved Organic Carbon
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
Fe	Iron
FY	Fiscal Year
HDPE	High Density Polyethylene
Hg	Mercury
km	Kilometer
Li	Lithium
mg	Milligram
mg/L	Milligrams per liter
mL	Milliliter
Mn	Manganese
NBSD	Naval Base San Diego
Ni	Nickel
NIWC	Naval Information Warfare Center
P	P-value associated with statistical test
Pb	Lead
PP	Polypropylene
QA/QC	Quality Assurance / Quality Control
SD	Standard Deviation
SERDP	Strategic Environmental Research and Development Program
SCCWRP	Southern California Coastal Water Research Project
SCUBA	Self-Contained Underwater Breathing Apparatus
SWRCB	State Water Resources Control Board
USA	United States of America
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
Zn	Zinc
µg/L	Micrograms per liter

EXECUTIVE SUMMARY

The overall objective of SERDP Project ER20-5261 (https://serdp-estcp.org/projects/details/db871313-fbc0-4432-b536-40c64af3627f) is to enhance the standardization of, and confidence in, the use of peepers for passive sampling of inorganic constituents such as metals, metalloids and anions in sediment porewater. This document details the results of a field demonstration in which peepers were deployed in surface sediment and surface water at Naval Base San Diego, San Diego, California, in October 2022. Over the course of 2 days, commercially available peepers were deployed at 10 stations, left to equilibrate for approximately 10 days, then retrieved over a course of 2 days, after which they were processed and shipped to a commercial analytical laboratory. Ninety percent of peeper samples were successfully analyzed (peepers at 1 station were not able to be retrieved) for target metal analytes cadmium, chromium, copper, iron, lead, manganese, mercury, and zinc. Lithium and bromide tracers spiked into the peepers indicated that greater than 70% equilibration was reached for all target metals during the 10-day exposure. Both tracers performed similarly. In the future, use of the lithium tracer (rather than bromide) is recommended, as the use of a lithium tracer is most efficient in terms of method simplicity and analytical cost savings. Method detection limits for peepers were sufficiently sensitive to detect concentrations lower than USEPA's saltwater Criterion Continuous Concentration (CCC) for aquatic life. All metals except for mercury (detection limit of approximately 0.1 to 0.4 µg/L) were detected in at least one peeper sample. Differences in concentrations in sediment porewater and surface water were noted for some, but not all, metals. Detailed methods are presented, as well as logistical details and recommendations for planning and executing successful peeper investigations.

1. INTRODUCTION

The overall objective of SERDP Project ER20-5261 (https://serdp-estcp.org/projects/details/db871313-fbc0-4432-b536-40c64af3627f) is to enhance the standardization of and confidence in the use of peepers for passive sampling of inorganic constituents such as metals, metalloids and anions in sediment porewater. This work would support the critical priorities highlighted by the Workshop on Research and Development for Long-Term Management of Contaminated Sediments (SERDP, 2016) as well as the FY2020 Broad Agency Announcement (ESTCP, 2019) which re-iterates interest in facilitating the application/commercialization of passive samplers.

The technical objectives of this project are intended to enhance the commercial application of sediment porewater passive sampler and capture the latest technological advances that have been made in the field of passive sampling, following the successful approaches for passive samplers for organic chemicals pioneered by SERDP and ESTCP research.

The primary objective of the work described in this Field Report was to demonstrate best practices for the field deployment of sediment porewater passive samplers ("peepers") for inorganic contaminants at an active Department of Defense (DoD) sediment site. This field deployment was a culmination of the laboratory work conducted as part of ER20-5261, and served to implement, in the field, the methods developed and optimized in the laboratory experiments. The field deployment focused on quantifying the logistical aspect of a field mobilization and highlight the required effort to successfully ship, deploy, retrieve and process peepers in the field. The intended audience for this information is project managers and consultants that wish to plan and conduct field projects using peepers to measure metals in sediment and/or surface water at a freshwater or marine sediment site.

This remainder of this report describes the work and results of the Field Campaign that was conducted in October 2022 in San Diego, consisting of the following sections:

- **Section 2 Site Description:** Describes the site at which the peepers were deployed.
- **Section 3 Field Methods:** Describes the methods and materials used for the field work, including the peeper deployment, retrieval, processing, analysis, and data procedures.
- **Section 4 Results:** Provides the concentrations of metals in sediment porewater and surface water, as measured by the peepers, and metals in surface water, as measured by the DGTs, as well as other ancillary results associated with the measurements.
- **Section 5 Results:** Provides logistical information associated with the field work, with a focus on recommendations for conducting peeper investigations.
- **Section 6 References:** Provides a list of the references cited.

The following appendices are also provided:

- **Appendix A:** Detailed peeper calculation sheets, which are also provided attached to this PDF as Microsoft Excel^{TM} files.
- **Appendix B:** Detailed Diffusive Gradient in Thin Film (DGT) calculation sheets, which are also provided, which are also provided attached to this PDF as Microsoft Excel^{TM} files.
- **Appendix C:** Field notes and forms used during the field work.
- **Appendix D:** Chain of custody produced for the peeper and DGT samples.
- **Appendix E:** Analytical laboratory reports for the analyses of the peeper water and DGTs.
- **Appendix F:** Step-by-step methods for peeper deployment, retrieval, and processing.

2. SITE DESCRIPTION

The site selected for the demonstration of the inorganic passive samplers was the mouth of Paleta Creek (hereinafter referred to as “Paleta Creek”), located in the Naval Base San Diego (NBSD), San Diego Bay, San Diego, California, USA. Access to the site was facilitated though a collaboration with Mr. Gunther Rosen from US Navy NIWC Pacific (San Diego), who had agreement with NBSD to access the proposed demonstration site. The following section describes the selected site.

2.1. SITE LOCATION AND HISTORY

Paleta Creek is a man-made urban creek located on the eastern shoreline of the Naval Base of San Diego, California, USA (32°40' 21.49"N, 117° 7'1.93"W) (Figure 1). At this location, Paleta Creek joins with San Diego Bay, and the Paleta Creek site location can be considered a cove area of San Diego Bay. San Diego Bay is relatively long and narrow, 25 km length and 1–3 km wide, and tides and currents within the bay can move sediment around, and in and out, of the bay, as can storm events and resuspension from propeller wash (Wang et al., 2000; ESTCP, 2016). The California State Water Resources Control Board has characterized Paleta Creek as a high priority toxic hot spot due to amphipod sediment toxicity findings in the Consolidated Toxic Hotspots Cleanup Plan (SWRCB, 1999), and added Paleta Creek to the Federal list of impaired waters for impaired benthic communities, sediment toxicity, sediment contamination, or a combination of these three (SCCWRP, 2007).

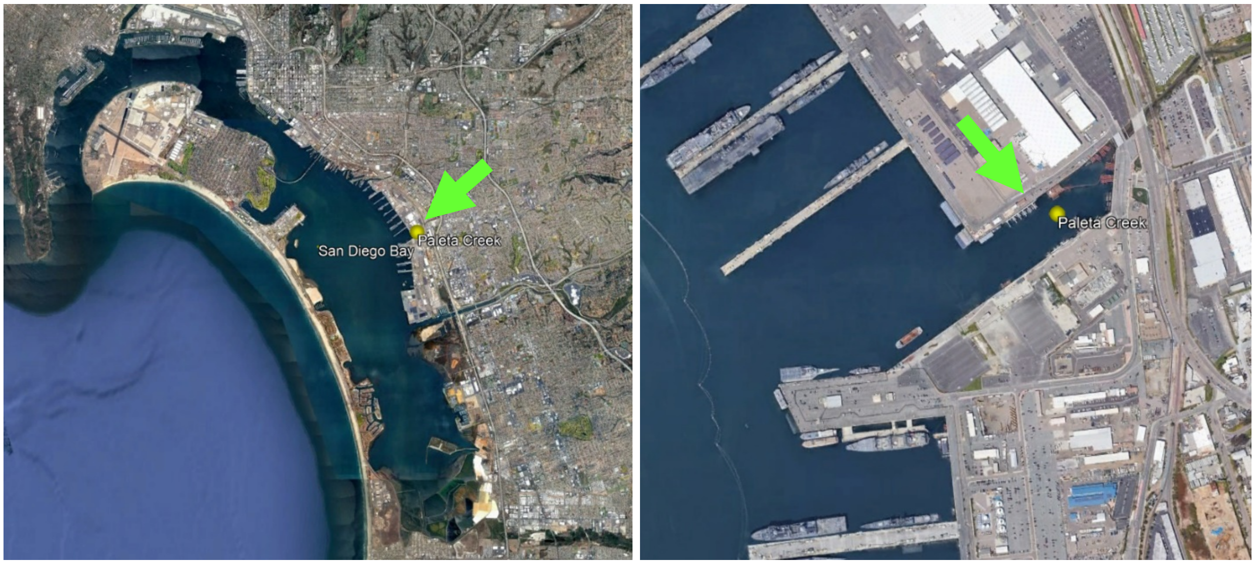


Figure 1: Paleta Creek site location (Naval Base San Diego, San Diego Bay, San Diego, California)

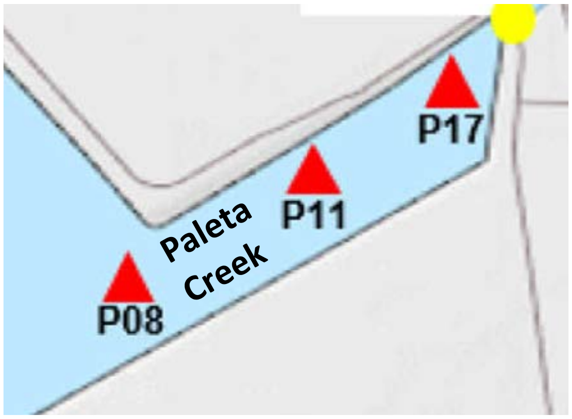
2.2. SITE GEOLOGY/HYDROGEOLOGY

Paleta Creek receives high water flow from winter storms as well as low flow during dry periods for the rest of the year from Seventh Street Channel. It receives stormwater from an urbanized (San Diego) watershed and is tidally influenced by San Diego Bay. Water depths in Paleta Creek are between approximately 15 to 26 feet (USACE, 2020), which is shallow enough to allow the use of the diver-less push-pole deployment system for peepers, even during the highest tides (+4 to +5 feet) that occurred during our field work (October 2022). Creek flow is minimal (unless during storms), so water salinity is consistent with the saline nature of the remainder of San Diego Bay.

2.3. CONTAMINANT DISTRIBUTION

Recent studies (Drygiannaki et al., 2020; Hayman et al., 2019; Rosen et al. 2017) identified Paleta Creek as a site of sediment contamination due to stormwater and observed sediment toxicity resulting in impacts on the benthic community. Other studies have been conducted to characterize sediments at the mouth of Paleta Creek, and metals like copper, lead, and zinc are contaminants of concern (City of San Diego, 2009; SCCWRP, 2007). Spatial and temporal impacts of metals in sediment were investigated near the mouth of Paleta Creek using a 95% prediction limit based on a pool of stations representing baseline conditions in San Diego Bay. Sediment samples from monitored stations at Paleta Creek presented Cd, Cr, Cu, Pb, Ni, and Zn concentrations that exceeded the baseline threshold values and/or the 95% prediction limit. Concentrations of silver (Ag), arsenic (As), and Cr were within a factor of two of concentrations from reference sites, and concentrations of Cu, Hg, Pb, and Zn were approximately three times higher than concentrations at reference sites (SCCWRP, 2011).

A SERDP-funded research effort by Drygiannaki et al. (2020) provides some of the most relevant recent data on metals in surface sediments in Paleta Creek. In general, data indicate the presence of metals in sediment, with detectable levels of metals in porewater (as measured by DGT) that exceed the approximate method detection limits for target metals. Consistent with other studies in this area, Drygiannaki et al. (2020) results indicated that surface sediments at this location were fine grained (60 to 85% fines (clay plus silt)), indicating an ideal sediment substrate for the insertion of peepers.



Metal	Drygiannaki et al. (2020a) Stations P08, P11, and P17 Concentrations in surface sediment (mg/kg)	Concentrations in surface sediment porewater, measured by DGT (µg/L)	Approximate method detection limit in porewater for peepers (this study, (µg/L)
Ni	17 - 23	0.7 - 3.6	0.5
Cu	210 - 260	1.7 - 16	0.6
Zn	290 - 620	6.2 - 68	3
Cd	0.09 - 2.3	non-detect - 0.34	0.2
Hg	0.35 - 1.1	non-detect - 0.18	0.1
Pb	78 - 260	0.18 - 1.3	0.1

Figure 2: Ranges of recent concentrations of metals in sediment and porewater (table, right) collected at three stations (map, left) in Paleta Creek (Drygiannaki et al., 2020a) compared to approximate method detection limits for peepers to be used in the field study

Dredging was conducted in 2020 (USACE, 2020) to remove a portion of sediment along the north-west edge of Paleta Creek (Figure 3). This area was not sampled by Drygiannaki et al. (2020), as shown in Figure 3. This study was not conducted in this dredged area since it is possible that the area may now be relatively uncontaminated and may not yield samples containing elevated or detectable levels of metals in porewater.

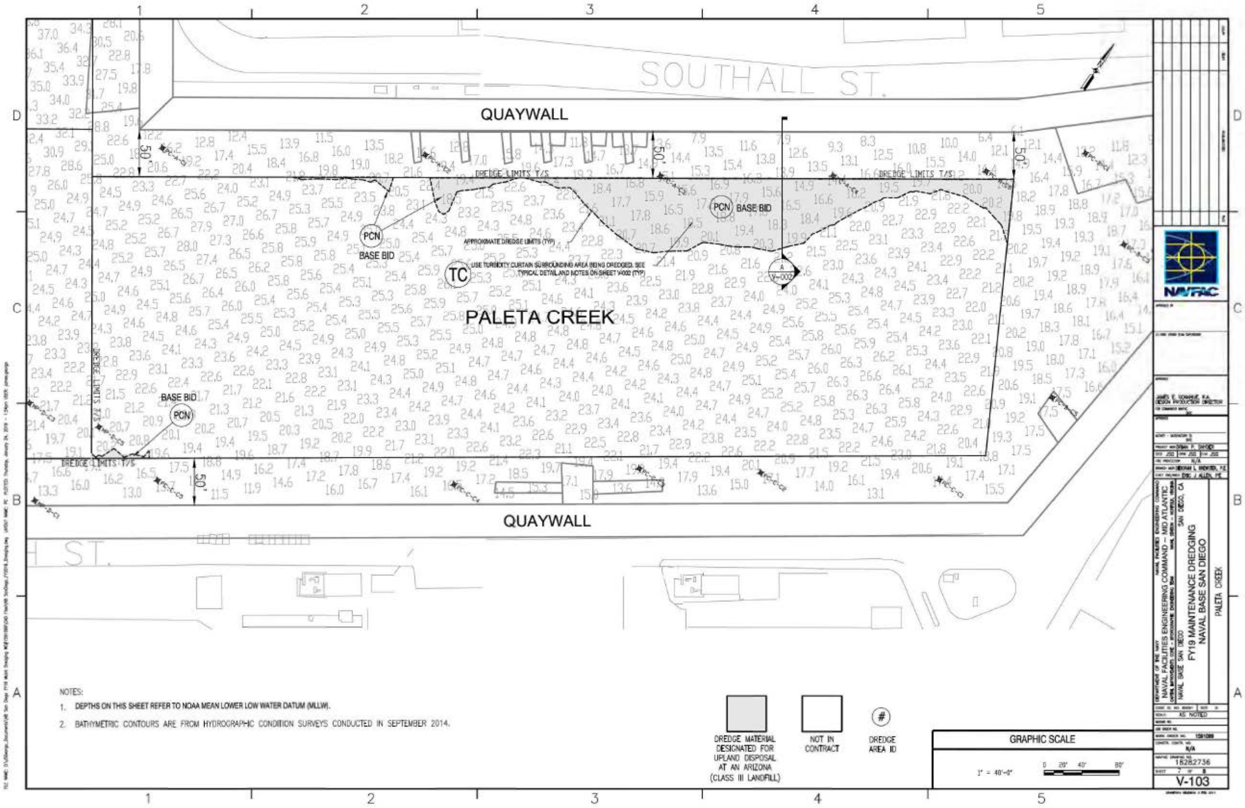


Figure 3: Dredging footprint (shown in grey shading) at Paleta Creek (USACE, 2020)

3. FIELD METHODS

This section provides a description of the field experimental design, sampling methods, and analytical methods that were used in the field demonstration. Peeper passive samplers were deployed at eight sampling locations (Figure 4). Two passive samplers consisting of four peepers samplers each were deployed at each sampling location, one for porewater and one for surface water analysis. Two surface water diffusive gradients in thin films (DGTs) were also deployed at each sampling location (Table 2). Field Notes can be found in Appendix C. A general step-by-step guide for deployment, retrieval, and processing of peeper samplers is provided in Appendix F.

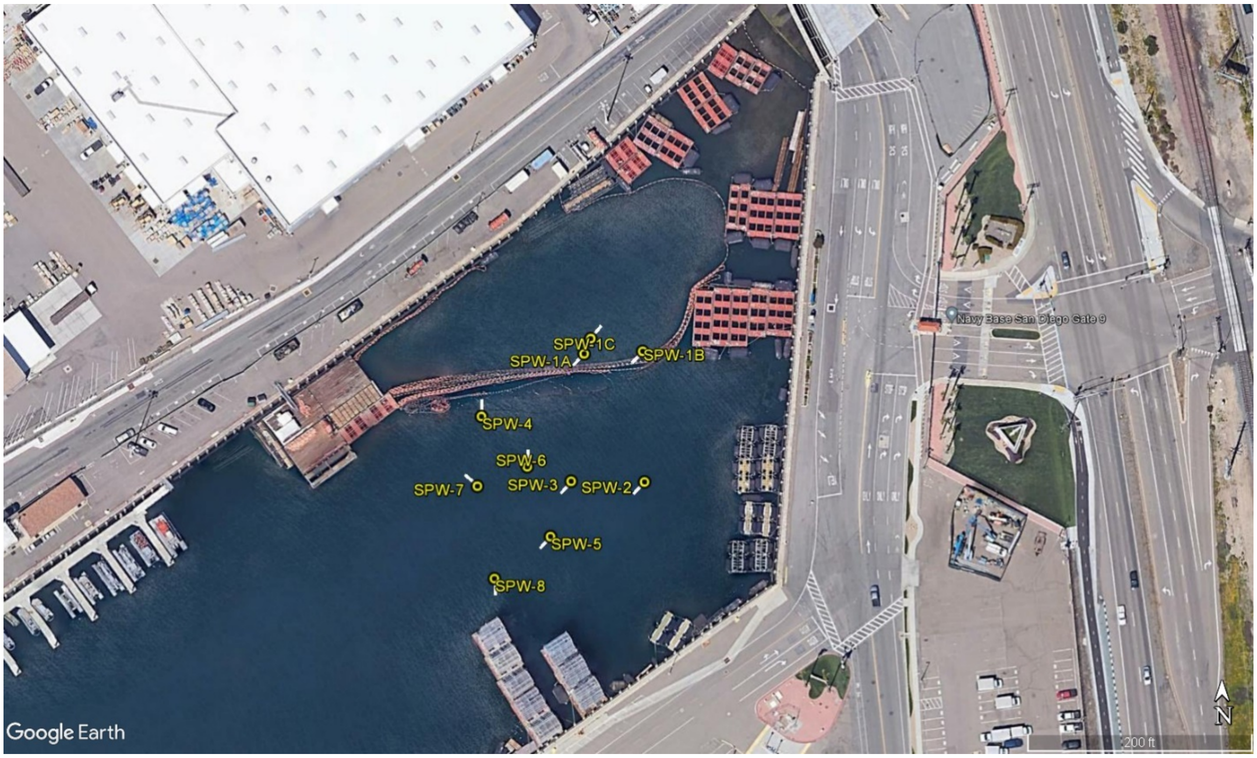


Figure 4: Field Sampling Sediment Stations. The dots are the sampling stations and the lines represent the direction of the deployed anchor line.

3.1. Field Mobilization

The field mobilization effort started four months ahead of the field event by scheduling the final field dates and reserving the services of a vessel and its crew. Field personnel that would be involved were also notified to ensure availability of key staff. In total, six people were selected, each with a defined role (Table 1).

Table 1: Field personnel and responsibilities for this field study

Field Personnel	Responsibilities
Field Coordinator	Coordinate field deployment. Organize material shipping and receiving. Direct staff during field event.
Principal Investigator	Overseeing of field event. Taking detailed notes during field event.
Site Access Contact	Direct contact with site owner for access and onsite scheduling.
Boat Captain	Vessel support.
Deck Hand	Vessel support.
Staff Support	Support for field event.

Material orders for the peepers, peeper frames, and DGT were placed 3 months ahead of the field event to allow for any delays due to potential supply chain issues. Peepers and frames were prepared by SiREM laboratories (https://www.siremlab.com/) and DGT were ordered from DGT Research (https://www.dgtresearch.com/). The diverless push-pole system that was used for this deployment was reserved from SiREM alongside the peeper order. Sampling bottles were ordered from Eurofins Environment Testing America (Eurofins). All materials were shipped to the local Geosyntec office to be picked up by staff ahead of deployment. Peepers and DGTs were both shipped in a cooler, on ice, and were stored in the fridge until the first field deployment day.

3.2. Passive sampler deployment

Peeper passive samplers were deployed from a boat using the push-pole and camera system to ensure proper deployment and placement. Deployment took place from October 3 and 4, 2022. Prior to deployment, the peeper frames (each frame holding 4 peepers) were assembled by attaching plastic wings to support frames using supports and screws. The wings were attached to the frames to prevent the frame from over-penetrating the sediment. Two frames were attached together as to have one embedded in the sediment and one (above the wings) in the surface water. A laminated sample ID card was secured to one side of the frame, using a zip-tie and a sinking anchor line approximately 35 feet in length was attached to the other (Figure 5).

Peepers were removed from the Mylar® peeper bags, visually inspected for bubbles and damage during shipment, and secured into the peeper frame. Damaged peepers were discarded and not used for sampling purposes (Figure 6). Four peepers were inserted into the frame for porewater and four inserted for surface water sampling. One Agarose DGT, for mercury and one Chelex DGT, for other metals (i.e., cadmium, chromium, copper, iron, lead, manganese, nickel, and zinc) were attached to the peeper frame using a loop of monofilament fishing line (Figure 7), with the following exceptions: Two Agarose DGTs for mercury and no Chelex DGTs for metals were deployed at stations SPW-1A, SPW-1B and SPW-1C. Two Chelex DGTs for metals and no agarose DGTs for mercury were deployed at SPW-6. This modification in the sampling approach for DGT served as a “duplicate” to compare the precision of surface water results.

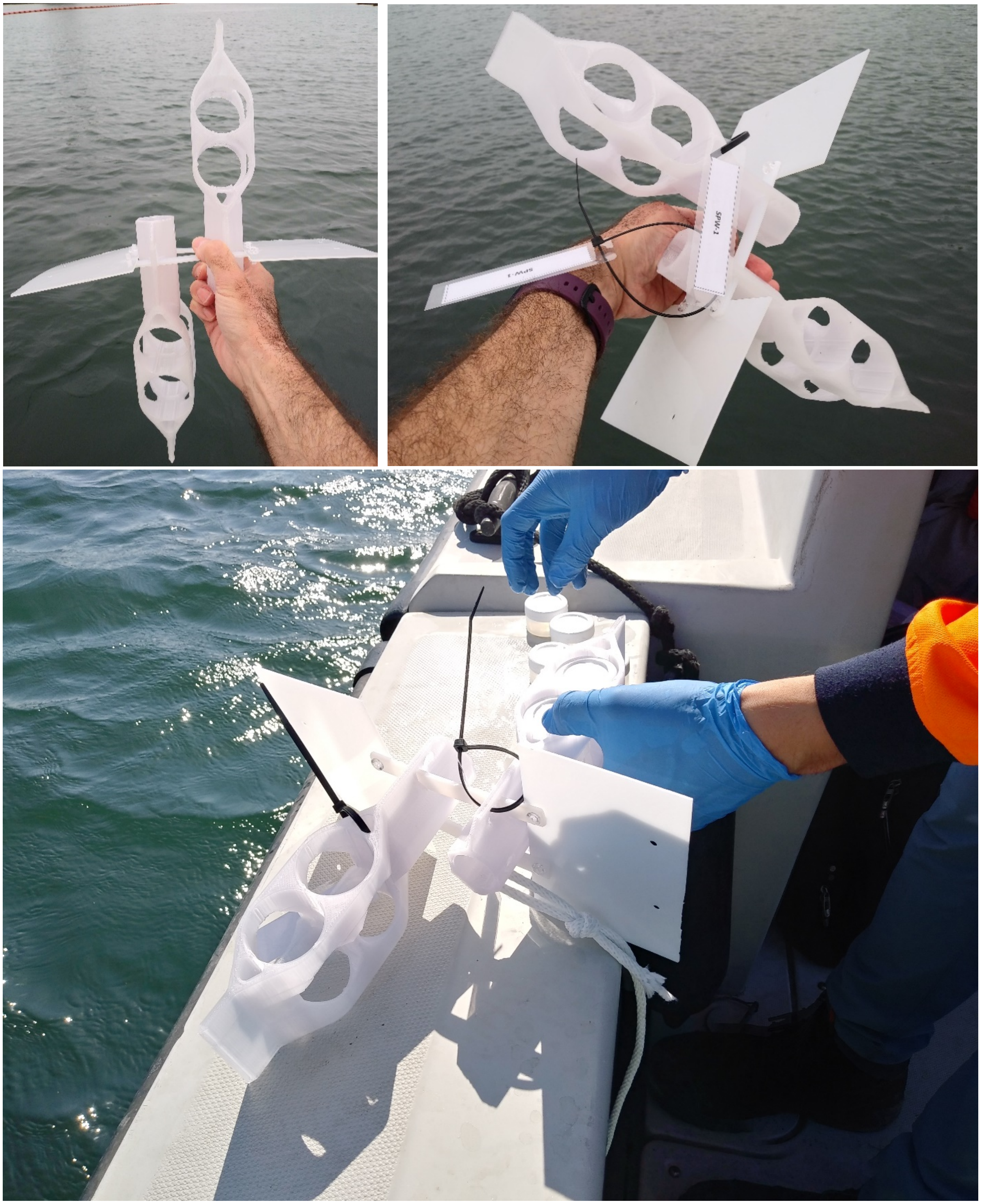


Figure 5: Peeper frame (top) and frame with peepers being inserted (bottom).

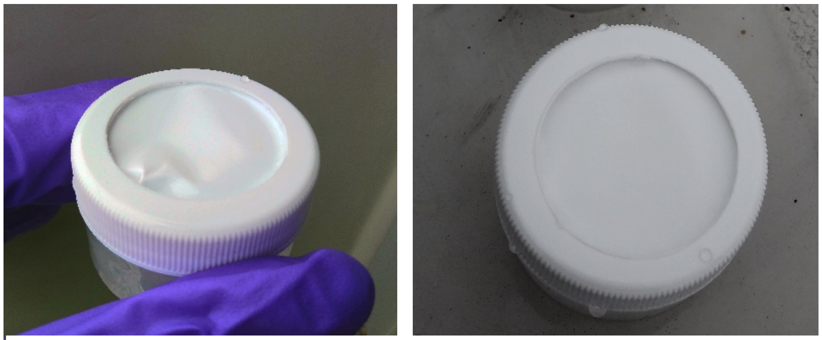


Figure 6: Peeper with membrane damage (left) and peeper with no damage (right).

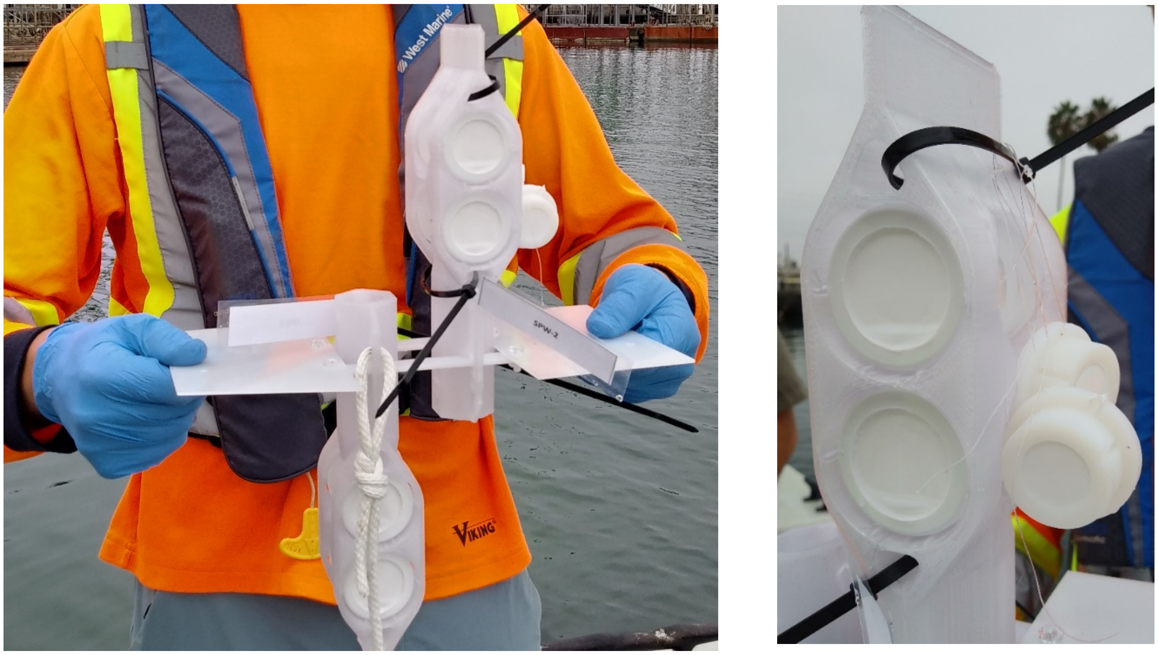


Figure 7: Fully assembled frame (left) with detail showing portion of frame that will be exposed to the surface water (right).

After positioning the vessel at each station, the vessel anchored to secure position. The water depth was confirmed at each sampling location using GPS and sonar. Two aluminum push poles were attached together and the deployment head containing the release mechanism was attached. The camera system (SondeCAM HD) was secured to the bottom of the push poles. The fully assembled and loaded peeper frame was inserted into the deployment head slot on the push-pole deployment device (Figure 8) and a spring-loaded pin was inserted into the pole. The anchor, camera, and spring-loaded pin lines were all held above the water and managed on board the boat to ensure no tangling occurred during deployment. To deploy, the attached peeper frames were slowly lowered into the water and poles were added to the top of the push-pole system until the length was enough to reach the sediment. The peeper frame was then inserted into the sediment until the frame wings were flush with the sediment. This was visually confirmed using the camera system, which was viewed on cell phone wirelessly. After confirmation, the anchor line was tossed into the water, and the line direction was recorded as a cardinal direction. The spring-loaded pin was released, and the push poles were slowly removed from the frame and back onto the boat.

Figure 8: Fully assembled frame (left) with detail showing portion of frame that will be exposed to the surface water (right).

GPS coordinates were collected and recorded immediately upon deployment of the peeper frame. The coordinates for SPW-8 were recorded after the frame had been deployed and the boat position had shifted. Therefore, the coordinates for SPW-8 are considered approximate and may not reflect the actual location of the deployed frame. In total 10 frames were deployed at all the planned locations (Table 2).

Table 2: Sampling locations and associated sample collection

Sampling Station	Passive Sampling Platforms	Coordinates as Deployed	Water depth (feet)	Samplers Deployed
SPW-1A	1	32°40'25.039"N 117° 6'58.693"W	24.4	1 porewater metal (peeper) 1 surface water metal (peeper) 2 surface water mercury (DGT)
SPW-1B	1	32°40'25.060"N 117° 6'58.079"W	24.4	1 porewater metal (peeper) 1 surface water metal (peeper) 2 surface water mercury (DGT)
SPW-1C	1	32°40'25.174"N 117° 6'58.623"W	25.2	1 porewater metal (peeper) 1 surface water metal (peeper) 2 surface water mercury (DGT)
SPW-2	1	32°40'23.907"N 117° 6'58.064"W	25.0	1 porewater metal (peeper) 1 surface water metal (peeper) 1 surface water mercury (DGT) 1 surface water metal (DGT)
SPW-3	1	32°40'23.915"N 117° 6'58.833"W	28.0	1 porewater metal (peeper) 1 surface water metal (peeper) 1 surface water mercury (DGT) 1 surface water metal (DGT)
SPW-4	1	32°40'24.489"N 117° 6'59.771"W	25.1	1 porewater metal (peeper) 1 surface water metal (peeper) 1 surface water mercury (DGT) 1 surface water metal (DGT)
SPW-5	1	32°40'23.427"N 117° 6'59.051"W	28.0	1 porewater metal (peeper) 1 surface water metal (peeper) 1 surface water mercury (DGT) 1 surface water metal (DGT)
SPW-6	1	32°40'24.044"N 117° 6'59.293"W	25.8	1 porewater metal (peeper) 1 surface water metal (peeper) 2 surface water metal (DGT)
SPW-7	1	32°40'23.874"N 117° 6'59.816"W	26.3	1 porewater metal (peeper) 1 surface water metal (peeper) 1 surface water mercury (DGT) 1 surface water metal (DGT)
SPW-8[1]	1	32°40'23.058"N 117° 6'59.640"W	27.9	1 porewater metal (peeper) 1 surface water metal (peeper) 1 surface water mercury (DGT) 1 surface water metal (DGT)
FB	-	-	-	1 Trip Blank (peeper)
			Total Samples Deployed	**21 Peeper, 19 DGT**

[1] Peeper array and samples were deployed, but not retrieved from SPW-8. Samples were not collected or processed from this location.

3.3. Passive sampler retrieval

Prior to retrieval, the peeper passive samplers and DGTs were allowed to equilibrate for ten days after deployment. Retrieval took place on October 13-14, 2022. Retrieval of the passive samplers was initially attempted using a grappling hook attached to a retrieval rope (Figure 9). Using this method for ~ 1 day, only one of the peeper frames was able to be retrieved. This low recovery rate was due to a combination of debris found in Paleta Creek (old oil booms, ladders) and the short length of the anchor lines. Anchor lines were cut at 36 feet long. Since the water depth was between 25 to 28 feet at the stations, this resulted in only 6 to 10 feet of line extending laterally on the seabed. This small amount of lateral length was not sufficiently long to be efficiently targeted using the grappling hook. After multiple unsuccessful attempts using the grappling hook, a diver was employed to retrieve the sampler frames. The diver conducted a circle search around a dropped buoy deployed at the GPS coordinates to locate and retrieve the passive samplers (Figure 10).

Figure 9: Grappling hook and retrieval rope.

Figure 10: Diver retrieval and marker buoy.

Upon retrieval of the samplers from the diver, the peepers were immediately removed from the frame and placed flat in a Mylar® bag with 3-4 500-cc oxygen absorbing packets (Figure 11). Three of the 80 peepers exhibited broken membranes, and these were discarded (Figure 12); the damage may have occurred due to mishandling during retrieval (finger pokes were noted on the membrane). The outside of the storage bag was labeled with the sample nomenclature and stored in a cooler with wet ice until processing. DGTs were also removed from the frames, placed flat inside a labeled Mylar® bag and stored on wet ice until shipped.

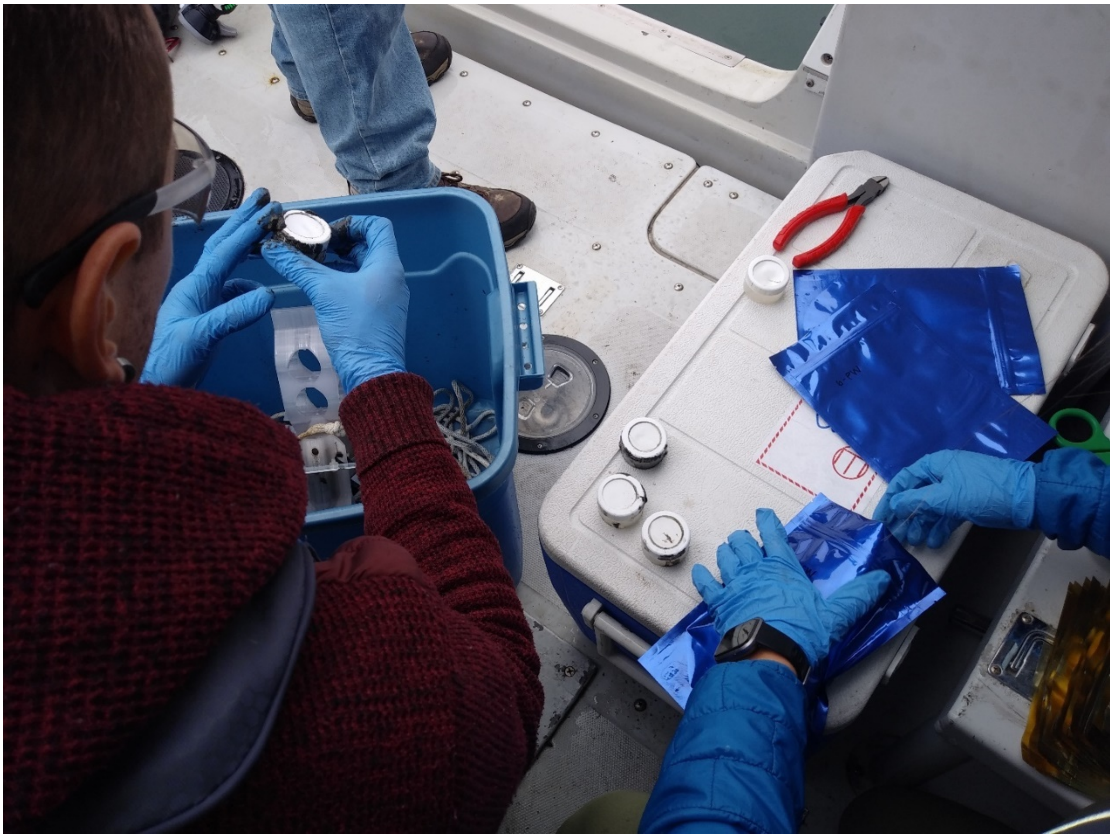


Figure 11: Peeper and DGT storing after retrieval.

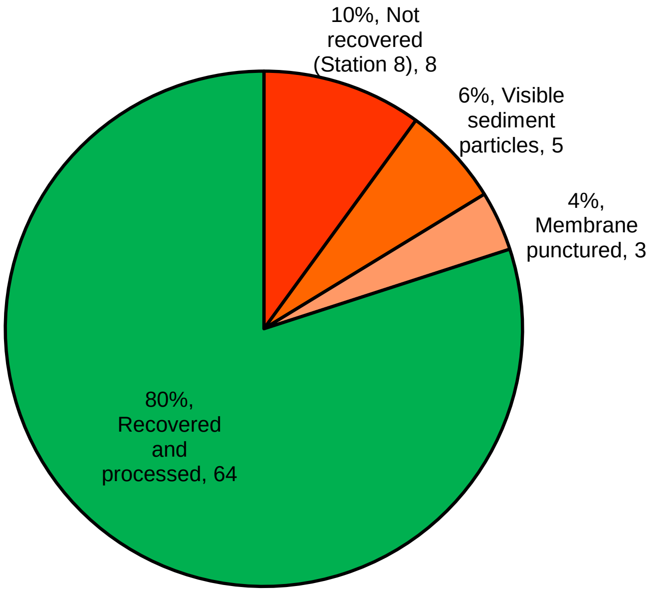


Figure 12: Recovery summary of the 80 peepers that were deployed in surface water and sediment at the 10 stations.

3.4. Passive sampler processing

At the end of each field day, the passive samplers were processed at a secure location onshore. Each peeper was removed from the storage bag and the membrane was washed with distilled water dispensed from a spray bottle (Figure 13). Each peeper was inspected for contamination by sediments (Figure 14). If particles were seen inside the peeper (5 of the 80 peepers, Figure 12), the peeper was not processed, as this can affect the metal concentration results (i.e., particle bound metals inside the peeper would cause an overestimation of the freely dissolved concentration of metals). Particles inside peepers were likely a result of inadvertently pressing upon the membranes by the diver and field crew. Peepers were also inspected for any biofilm or other biological growth on the membrane that could have impacted the performance of the device. No biofilm or any biological growth was noted on the membranes, the sampler or the frames. In total, 80% of the peepers (64 of 80) were recovered for processing (Figure 12). As peeper samples for the metals analysis can be comprised of 1, 2, or 3 peepers, however, 90% of the peeper samplers were able to be submitted for analysis. Only the sediment peeper sample and surface water peeper sample from station 8 was unable to be analyzed, as the peepers from this station were not able to be recovered. Thus, overall, the sampling effort achieved a 90% success rate.

Figure 13: Washing peepers to remove sediments from the membrane.

Figure 14: Contaminated peeper with particles (left) vs peeper without any contamination (right).

To process and sample the peeper water, a 25-mL serological pipette was inserted into the bottom of the peeper by puncturing the membrane, and the water inside the peeper was drawn up (Figure 15). The water from one peeper (~20 mL) was dispensed into a sample container for bromide analysis (100-mL polypropylene bottle, supplied by the analytical laboratory). The remaining three peepers (~60 mL) were dispensed into the sample container for metal analysis (100-mL HDPE bottle containing 2.5 mL 1:4 concentrated nitric acid:water, supplied by the analytical laboratory)[1]. The following exceptions are noted:

- One of the peepers retrieved from SPW-1A for surface water was punctured and not useable for sampling purposes while another peeper was contaminated by sediment particles Therefore, only one peepers was used for metals analysis, instead of three.

- One of the peepers retrieved from SPW-1A for sediment porewater was contaminated by sediment particles. Therefore, only 2 peepers were used for metals analysis, instead of three.

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[1] It is recommended that a small volume from each peeper (e.g., 5 mL) should be used for the bromide analysis, rather than the entire 20-mL originating from a single peeper (as reflected in the recommended standard operating procedures attached to this document). For this experiment, using 20 mL from a single peeper did not affect the results; however, in sediments that are very heterogenous in texture in the top 5 to 10 cm, differences in diffusion among the four peepers could be significant.

- One of the peepers retrieved from SPW-3 for sediment porewater was punctured and not useable for sampling purposes. One of the peepers was contaminated by sediment particles. Therefore, only one peeper was used for metals analysis, instead of three.

- Two of the peepers retrieved from SPW-4, one for surface water, and one for porewater were contaminated with sediments. Therefore, only two peepers were used for metals analysis for surface water and porewater at this location.

- One of the peepers retrieved from SPW-6 for surface water was punctured and not useable for sampling purposes. Therefore, only two peepers were used for metals analysis, instead of three.

In cases in which only one peeper (i.e., 20 mL) was available for analysis, this resulted in an approximate increase in detection limit by a factor of 2 to 3. As long as 40 to 60 mL were available, detection limit was not affected.

One field blank was prepared using four unexposed peepers which was brought to the field during deployment and retrieval. All sample bottles were capped and labeled with their sample IDs.

No further processing was required for the DGTs.

Figure 15: Peeper processing.

3.5. Sample storage and shipment

Sample bottles and Mylar® bags containing the DGTs were stored on wet ice immediately after processing, until sample shipment. Samples were shipped on ice via Fedex, under Chain of Custody procedures (Appendix D), to Eurofins Environment Testing America of Seattle and Pittsburgh.

3.6. Sample Analysis

Peeper samples were analyzed for metals and bromide by Eurofins Pittsburgh, Pennsylvania laboratory using the analytical specifications outlined in Table 3. All method detection limits were below the USEPA's saltwater Criterion Continuous Concentration (CCC) for aquatic life (https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table#table). The analytical report is available in Appendix E.

Table 3: Analytical specifications for inorganic analytes in peeper water

Analyte	Analytical Method	Sample Type	Container	Preser-vative	Holding Time (days)	Average Method Detection Limit (µg/L)	USEPA Saltwater Criterion Continuous Concentration (µg/L)
Cadmium (Cd)	EPA Method 6020B	60 mL of peeper water from three peepers	100-mL HDPE bottle	Nitric Acid	180	0.22	7.9
Chromium (Cr)	EPA Method 6020B		100-mL HDPE bottle	Nitric Acid	180	1.5	NA
Copper (Cu)	EPA Method 6020B		100-mL HDPE bottle	Nitric Acid	180	1.1	3.1
Iron (Fe)	EPA Method 6020B		100-mL HDPE bottle	Nitric Acid	180	28	NA
Lead (Pb)	EPA Method 6020B		100-mL HDPE bottle	Nitric Acid	180	0.17	8.1
Total Mercury (Hg)	EPA Method 7470A		100-mL HDPE bottle	Nitric Acid	180	0.13	0.94
Manganese (Mn)	EPA Method 6020B		100-mL HDPE bottle	Nitric Acid	180	1.3	NA

Nickel (Ni)	EPA Method 7470B		100-mL HDPE bottle	Nitric Acid	180	0.52	8.2
Zinc (Zn)	EPA Method 6020B		100-mL HDPE bottle	Nitric Acid	180	2.9	81
Lithium (Li)	EPA Method 6020B		100-mL HDPE bottle	Nitric Acid	180	0.83	NA
Bromide (Br)	EPA Method 9056A	20 mL of peeper water from one peeper	100-mL HDPE bottle	None	180	2,700	NA

Note: NA: Not Available

DGTs were analyzed for metals and mercury by Eurofins Tacoma, Washington laboratory using the analytical specifications outlined in Table 4. Results are reported as the total µg of analyte detected from the gel portion of the DGT. The analytical report is available in Appendix E.

Table 4: Analytical specifications for inorganic analytes in DGT.

Analyte	Analytical Method	Sample Type	Container	Preserv-ative	Holding Time (d)	Method Detection Limit (µg/sample)
Cadmium (Cd)	EPA Method 1638	DGT resin obtained from one general metals DGT	Plastic zipseal bag containing DGT	None	180	0.00075
Chromium (Cr)	EPA Method 1638		Plastic zipseal bag containing DGT	None	180	0.0053
Copper (Cu)	EPA Method 1638		Plastic zipseal bag containing DGT	None	180	0.01
Iron (Fe)	EPA Method 1638		Plastic zipseal bag containing DGT	None	180	0.075
Lead (Pb)	EPA Method 1638		Plastic zipseal bag containing DGT	None	180	0.00068
Manganese (Mn)	EPA Method 1638		Plastic zipseal bag containing DGT	None	180	0.0045

Nickel (Ni)	EPA Method 1638		Plastic zipseal bag containing DGT	None	180	0.0058
Zinc (Zn)	EPA Method 1638		Plastic zipseal bag containing DGT	None	180	0.021
Total Mercury (Hg)	EPA Method 1631B	DGT resin obtained from one mercury-specific DGT	Plastic zipseal bag containing DGT	None	180	0.00001

3.7. Peeper Equilibrium Calculations

For all peepers deployed in the sediments and in the surface water, the bromide and lithium tracer data was used to estimate the equilibrium freely-dissolved concentration of the target metals using the modeling techniques of Thomas and Arthur (2010). Thomas and Arthur (2010) studied the use of the bromide reverse tracer to estimate percent equilibrium in lab experiments and a field application. They concluded that bromide can be used to estimate concentrations in porewater using measurements obtained before equilibrium is reached. The study included a mathematical model for estimating concentrations of ions in external media ($C_{e,i}$) based on measured concentrations in the peeper chamber ($C_{p,i}$), the elimination rate of the target analyte (K_i) and the deployment time (t):

$$C_{e,i} = \frac{C_{p,i}}{1 - e^{-K_i t}}$$

Where K_i is the elimination rate of the target analyte, calculated using the ratio of the free-water diffusion coefficient of the tracer (D_t) and the target analyte (D_i) (Thomas and Arthur, 2010):

$$K_i = K_t \left(\frac{D_i}{D_t}\right)$$

D values for the 7 target analytes and 2 tracers are provided in Table 5.

Table 5: Free-water diffusion coefficient (D) for inorganics.

Analyte	**D ($\times 10^{-5}$ cm^2/s)**	**Reference**
Cadmium (Cd)	0.63	Buffle et al. (2007)
Chromium (Cr)	0.52	
Copper (Cu)	0.62	
Iron (Fe)	0.63	

Lead (Pb)	0.83	
Manganese (Mn)	0.62	
Mercury (Hg)	0.74	
Nickel (Ni)	0.62	
Zinc (Zn)	0.61	
Lithium (Li)	0.90	
Bromide (Br)	1.8	

The elimination rate of the tracer (K_t) is calculated using the following equation:

$$K_t = \frac{-ln\,(1 - \frac{Tr_{p,t} - Tr_{p,0}}{Tr_{e,t} - Tr_{p,0}})}{t}$$

Where:

- $Tr_{p,0}$ is the measured concentrations of the tracer in the peeper prior to deployment (mg/L or µg/L),
- $Tr_{p,t}$ is the measured concentrations of the tracer in the peeper at time of retrieval (mg/L or µg/L),
- $Tr_{e,t}$ is the concentrations of the tracer in the external media (mg/L or µg/L) which for seawater is 65 mg/L for bromide and 100 µg/L for lithium, and
- t is the deployment time (days)
- K_t is the elimination rate of the tracer

Additional laboratory experiments conducted by our team indicated that for marine sediment, lithium can be used in conjunction with bromide as a tracer to provide more robust equilibrium calculations.

These calculations were conducted on every porewater and surface water sample obtain from each station. This resulted in a corrected "at equilibrium" metal concentrations that was used to assess the peepers and was compared to the DGT. Details of the calculations and Excel file attachments can be found in Appendix A.

3.8. DGT Porewater Concentration Calculations

The data obtained from the analysis of metals in the gels obtained from the DGTs used in the surface water were processed to be converted to a concentration due to their non-equilibrium mechanism (i.e. binding layer adsorbs continuously for the deployment length) using the approach detailed by Zhang and Davison (1995). The calculation of the aqueous concentration of any metal species using DGT data is as follows:

$$C_{DGT} = \frac{M\Delta_g}{D^{mdl}A_p t}$$

Where:

- C_{DGT} (ng/L for Hg, µg/L for other metals) is the concentration of metal in water measured by the DGT.
- M (ng for Hg, µg for other metals) is the mass of analyte in the gel from the binding layer of the DGT. It is obtained from the laboratory analysis (Appendix E).
- Δg (cm) is the total thickness of the materials (diffusive gel and membrane) in the diffusion layer (0.094 cm, as indicated by the DGT manufacturer).
- D^{mdl} (cm^2/s) is the diffusion coefficient of the metal in the diffusion layer for the assumed deployment temperature (15°C, table of values provided by the DGT manufacturer, see Appendix B).
- A_p (cm^2) is the physical area of the exposed filter membrane (3.14 cm^2, as provided by the manufacturer).
- t (s) is the deployment time (as determined from the field notes, Appendix C).

The mass, M, of analyte in the binding layer, of volume V^{bl} (mL), is calculated from the measured concentration of analyte c_e in the acid eluent of the volume V_e (mL) of DGT gel, remembering to consider any subsequent dilution.

$$M = \frac{c_e(V^{bl} + V_e)}{f_e}$$

Each DGT deployed in the surface water at each station was processed using these formulas to obtain a dissolved metal concentration that can be compared to the concentration obtained using peepers deployed in surface water. Details of the DGT calculation can be found in Appendix B.

4. RESULTS

4.1. Sediment Porewater Concentration Results Measured with Peepers

Bromide and lithium results for the sediment porewater peepers are presented in Table 6 for each station. Deployment time varied between 9 to 11 days. The percentage of the equilibrium reached was calculated using the equations presented in section 3.7 and the initial peeper concentrations (980 mg/L Br, 86,000 µg/L Li) measured in the trip blank peeper, the concentrations of bromide and lithium measured in each peeper, and assumed concentration of bromide and lithium in seawater (65 mg/L Br, 100 µg/L Li). Results from peeper bromide and lithium concentrations both indicated that 80% to 100% equilibrium for bromide and lithium had been reached in the peepers deployed in sediment. However, because the target metals diffuse more slowly than tracers (Table 5), the percentage of equilibration estimated for the target metals was less than this 80% to 100% range. For example, the least amount of equilibration was observed for chromium in sediment peepers. Based on calculations using the lithium tracer, the average (SD) percentage equilibration reached by chromium in sediment was 74% (16%) among the 10 sediment peepers. Assuming this corresponds to a site-specific K_i value of 0.12 (day^{-1}), approximately 20 days would be needed to achieve approximately 90% equilibration in sediment. However, 3 to 5 days of deployment time would be sufficient to allow an approximate 30% to 50% equilibration for chromium in sediment (this time period would allow a higher percentage of equilibration for other target metals); this deployment time could be used (with tracers) to estimate the equilibrium concentration of chromium.

Overall, these results indicate that the deployment duration was sufficient to reach equilibrium during the ~10-day deployment period, and little to no correction are needed to account for partial equilibrium between porewater and peepers. Pre-equilibrium corrections were applied to all measured concentrations of metal analytes using the equations provided above. It is acknowledged that peepers that indicate nearly 100% of the equilibrium for lithium or bromide cannot provide exact cues as to when near 100% of equilibrium will be reached for target metals, because the target metals analytes measured in this study diffuse more slowly than lithium and bromide. Conceptually, this could prevent accurate pre-equilibrium correction. For example, among the metal analytes measured in this experiment, chromium is the slowest to reach equilibrium (lowest D value, Table 5). Given the equilibrium equations, if results indicated lithium has reached 96% of equilibrium, chromium would be expected to be only at 82% of equilibration. For this example, the concentration of chromium measured in the peeper water would be corrected by a factor of 1.2 (i.e., 1 ÷ 82%) to estimate the concentration of chromium at equilibrium. This pre-equilibration correction is relatively minor such that if no multiplication of chromium results were applied, the uncorrected (pre-equilibrated result) would be a factor of 1.2 or less than the true equilibrated concentration of chromium. This error rate is at most 20%, and would be lower for other metals diffusing at faster speeds. A ± 20% uncertainty or error rate is a reasonable level of uncertainty for measurements of metals in water (USEPA, 2014). Thus, overall, for samples that indicate a high degree of equilibration for lithium (e.g., approximately 95% or more), the amount of uncertainty in predicting the equilibration of the other analytes lies in a reasonable ± 20% range typical of analytical measurement uncertainty. In cases in which lithium has equilibrated 95% or more, the use of pre-equilibrium correction is not likely to indicate meaningfully different results from the uncorrected results for the metals measured in this study. Overall, despite the fact that lithium and bromide diffuse faster than the slowest analytes in this study (chromium), the difference is minor such that, even when tracers are fairly well equilibrated, equilibrium estimated for the metals are likely to be within ± 20% of true equilibrated values, which is a reasonable level of uncertainty. Extending the deployment time would decrease this error rate even further.

Table 6: Peeper Porewater Equilibrium Results

Sample	Deployment Duration (d)	Bromide	Lithium	Br Equilibrium	Li Equilibrium
		mg/L	µg/L	%	%
1A-PW	11.10	220	16000	83	81
1B-PW	11.06	120	510	94	100
1C-PW	10.92	230	19000	82	78
2-PW	9.14	120	5100	94	94
3-PW	10.96	230	18000	82	79
4-PW	10.16	130	170	93	100
5-PW	10.27	170	15000	89	83
6-PW	10.08	220	17000	83	80
7-PW	10.23	140	9600	92	89

Equilibrium porewater concentrations were calculated from the measured peeper concentrations, as described in section 3.7. Two different tracers were used (bromide and lithium) and thus two different final porewater concentration were calculated for bromide (Table 7) and lithium (Table 8). Concentrations of cadmium, copper, lead, total mercury, and nickel that are highlighted yellow were in exceedance of USEPA's saltwater CCC (Table 1). Copper frequently exceeded the CCC value; this does not indicate that copper is resulting in aquatic toxicity, only that the CCC screening level is exceeded. Despite equilibrium being reached at many stations, the approach was used on all samples to confirm the accuracy of the method. Note that detection limits were also corrected to provide the "at equilibrium" minimum detection limit.

Table 7: Bromide Corrected Porewater Results

Station	Bromide corrected values (µg/L)								
	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Ni	Zn
1A-PW	< 0.59	< 4.8	**7.1**	**480**	**1.6**	**55**	< 0.25	< 1.4	**29**
1B-PW	< 0.35	< 2.7	**7.8**	**7100**	**0.54**	**370**	< 0.19	**1.6**	**33**
1C-PW	< 0.49	< 3.9	**5.9**	**510**	< 0.31	**81**	< 0.26	< 1.2	**13**
2-PW	< 0.35	< 2.7	**5.8**	**2300**	< 0.24	**120**	< 0.19	< 0.84	**5.1**
3-PW	< 0.8	< 6.7	< 4.3	**340**	< 0.52	**41**	< 0.66	**2.5**	**25**
4-PW	< 0.37	< 2.8	**10**	< 47	**0.29**	**8.8**	< 0.5	**1.9**	**27**
5-PW	< 0.42	< 3.3	**3.5**	**2800**	< 0.27	**210**	< 0.22	< 1	**5.8**
6-PW	< 0.48	< 3.8	< 2.4	**6800**	< 0.31	**330**	< 0.25	< 1.1	< 6.5
7-PW	< 0.38	< 2.9	< 1.9	**2100**	< 0.25	**170**	< 0.2	**1.3**	**11**
USEPA Saltwater CCC	*7.9*	*NA*	*3.1*	*NA*	*8.1*	*NA*	*0.94*	*8.2*	*81*

Table 8: Lithium Corrected Porewater Results

Station	**Lithium corrected values (µg/L)**								
	Cd	**Cr**	**Cu**	**Fe**	**Pb**	**Mn**	**Hg**	**Ni**	**Zn**
1A-PW	< 0.39	< 3	**4.7**	**320**	**1.1**	**36**	< 0.17	< 0.95	**19**
1B-PW	< 0.23	< 1.6	**4.9**	**4500**	**0.39**	**240**	< 0.13	**1**	**21**
1C-PW	< 0.34	< 2.6	**4**	**350**	< 0.23	**56**	< 0.18	< 0.8	**8.7**
2-PW	< 0.25	< 1.9	**4.2**	**1600**	< 0.18	**90**	< 0.14	< 0.61	**3.6**
3-PW	< 0.54	< 4.4	< 2.9	**220**	< 0.37	**27**	< 0.46	**1.7**	**17**
4-PW	< 0.22	< 1.5	**6.2**	< 28	**0.2**	**5.2**	< 0.33	**1.1**	**16**
5-PW	< 0.31	< 2.4	**2.6**	**2100**	< 0.21	**160**	< 0.17	< 0.74	**4.3**
6-PW	< 0.32	< 2.5	< 1.6	**4600**	< 0.22	**220**	< 0.18	< 0.77	< 4.3
7-PW	< 0.28	< 2.1	< 1.4	**1500**	< 0.2	**130**	< 0.16	**0.99**	**8**
USEPA Saltwater CCC	*7.9*	*NA*	*3.1*	*NA*	*8.1*	*NA*	*0.94*	*8.2*	*81*

The range of porewater concentration results between lithium and bromide correction are overlapping showing that both tracers are equally appropriate. Copper in the porewater was measured between < 1.4 to 10 µg/L, iron between < 28 to 6800 µg/L, lead between < 0.18 and 1.6 µg/L, manganese between 5.2 and 370 µg/L, nickel between < 0.61 and 2.5, and zinc between < 4.3 and 33. Cadmium, chromium and mercury were not detected in any of the porewater samples.

4.2. Surface Water Concentrations Measured with Peepers

Equilibrium results of the surface water peepers are presented in Table 9 for each station. Deployment time varied between 9 to 11 days. The percentage of the equilibrium reached was calculated using the equations presented in section 3.7 and uses the initial peeper concentrations (980 mg/L Br, 86,000 µg/L Li) and the seawater concentration (65 mg/L Br, 100 µg/L Li). Results from peeper bromide and lithium concentrations both indicated that 92% to 100% equilibrium had been reached. As in sediment, the least amount of equilibration was observed for chromium in surface water peepers. Based on calculations using the lithium tracer, the average (SD) percentage equilibration reached by chromium in water was 98% (0.15%) among the 10 surface water peepers. Assuming this corresponds to a site-specific K_i value of 0.39 (day^{-1}), approximately 6 days would be needed to achieve approximately 90% equilibration in surface water. However, 1 to 2 days of deployment time would be sufficient to allow an approximate 30% to 50% equilibration for chromium in surface water (this time period would allow a higher percentage of equilibration for other target metals); this deployment time could be used (with tracers) to estimate the equilibrium concentration of chromium. These results indicate that the deployment duration was sufficient to reach equilibrium during the ~10-day deployment period, and little to no correction are needed to account for partial equilibrium between surface water and peepers. As for the treatment of peepers deployed in sediment porewater, corrections based on lithium and bromide tracer measurements were applied to all measured concentrations. Because the percentage of equilibration for lithium was approximately 99.9% and 92% or greater for bromide for all samples, little correction was needed.

Table 9: Peeper Surface Water Equilibrium Results

Sample	Deployment Time (d)	Br	Li	Br Equilibrium	Li Equilibrium
		mg/L	µg/L	%	%
1A-SW	11.10	120	150	94	100
1B-SW	11.06	120	180	94	100
1C-SW	10.92	120	180	94	100
2-SW	9.14	110	180	95	100
3-SW	10.96	140	170	92	100
4-SW	10.16	130	170	93	100
5-SW	10.27	130	170	93	100
6-SW	10.08	130	180	93	100
7-SW	10.23	130	190	93	100

Equilibrium porewater concentrations were calculated from the measured peeper concentration as described in section 3.7. Two different tracers were used (bromide and lithium) and thus two different final porewater concentration were calculated for bromide (Table 10) and lithium (Table 11). Concentrations of cadmium, copper, lead, total mercury, and nickel that are highlighted yellow were in exceedance of USEPA's CCC (Table 3). Copper frequently exceeded the CCC value and nickel exceeded its CCC at one station (1A-SW); this does not indicate that copper or nickel are resulting in aquatic toxicity, only that the CCC screening level is exceeded. Despite equilibrium being reached at many stations, the approach was used on all samples to confirm the accuracy of the method. Note that detection limits were also corrected to provide the "at equilibrium" minimum detection limit.

Table 10: Bromide Corrected Surface Water Results

Station	Bromide corrected values (µg/L)								
	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Ni	Zn
1A-SW	< 0.58	**36**	**21**	**180**	**0.5**	**19**	< 0.48	**47**	**38**
1B-SW	< 0.35	< 2.7	**16**	< 45	**0.62**	**8.4**	< 0.19	**1.6**	**54**
1C-SW	**0.58**	< 2.7	**12**	< 45	< 0.24	**11**	< 0.19	**1.3**	**25**
2-SW	< 0.34	< 2.6	**10**	< 43	**0.24**	**9.8**	< 0.18	**1.1**	**17**
3-SW	< 0.38	< 2.9	**11**	< 48	< 0.25	**11**	< 0.2	**1.4**	**18**
4-SW	< 0.4	< 3.2	**8.9**	**110**	< 0.26	**15**	< 0.2	**1.7**	**15**
5-SW	< 0.37	< 2.8	**9.4**	< 47	**0.33**	**13**	< 0.2	**1.6**	**20**
6-SW	< 0.37	< 2.8	**8.1**	< 47	**0.37**	**12**	< 0.5	**1.3**	**17**
7-SW	< 0.37	< 2.8	**9.3**	**48**	**0.37**	**13**	< 0.2	**1.6**	**22**
USEPA Saltwater CCC	*7.9*	*NA*	*3.1*	*NA*	*8.1*	*NA*	*0.94*	*8.2*	*81*

Table 11: Lithium Corrected Surface Water Results

Station	Lithium corrected values (µg/L)								
	Cd	**Cr**	**Cu**	**Fe**	**Pb**	**Mn**	**Hg**	**Ni**	**Zn**
1A-SW	< 0.36	**20**	**13**	**110**	**0.36**	**12**	< 0.33	**29**	**23**
1B-SW	< 0.22	< 1.5	**10**	< 28	**0.45**	**5.2**	< 0.13	**1**	**33**
1C-SW	**0.36**	< 1.5	**7.5**	< 28	< 0.17	**6.7**	< 0.13	**0.8**	**15**
2-SW	< 0.22	< 1.5	**6.7**	< 28	**0.18**	**6.4**	< 0.13	**0.72**	**11**
3-SW	< 0.22	< 1.5	**6.2**	< 28	< 0.17	**6.5**	< 0.13	**0.8**	**10**
4-SW	< 0.24	< 1.7	**5.3**	**63**	< 0.18	**9**	< 0.13	**1**	**9**
5-SW	< 0.22	< 1.5	**5.6**	< 28	**0.23**	**7.8**	< 0.13	**0.98**	**12**
6-SW	< 0.22	< 1.5	**4.8**	< 28	**0.26**	**7**	< 0.33	**0.78**	**10**
7-SW	< 0.22	< 1.5	**5.5**	**29**	**0.26**	**7.6**	< 0.13	**0.97**	**13**
USEPA Saltwater CCC	*7.9*	*NA*	*3.1*	*NA*	*8.1*	*NA*	*0.94*	*8.2*	*81*

The range of peeper surface water concentration results between lithium and bromide correction are overlapping showing that both tracers are equally appropriate. Cadmium in the surface water was measured between < 0.22 to 0.58 µg/L, chromium between < 1.5 and 36 µg/L, copper between 4.8 and 21 µg/L, iron between < 28 to 180 µg/L, lead between < 0.17 and 0.62 µg/L, manganese between 5.2 and 19 µg/L, nickel between 0.72 and 47, and zinc between 9 and 54 µg/L. Mercury was not detected in any of the surface water samples.

4.3. Comparison of Peeper Results Estimated with Lithium Tracers Versus Bromide Tracers

Concentrations of metals in peepers, as calculated with the bromide (Table 7 and Table 8) and lithium (Table 10 and Table 11) were similar. This lack of difference was not unexpected given that the tracers indicated that the sediment and water peepers were near equilibrium (87% on average for all peepers). As shown in Figure 16, the percentage of equilibration was generally higher in the surface water peepers compared to the sediment peepers, which, is to be expected given that water flows around the peepers that were deployed in surface water which will agitate the boundary layer at the outside surface of the peeper membrane, facilitating a faster diffusive transfer. For the sediments, the amount of equilibration achieved by the lithium tracer was not statistically different than that achieved with the bromide tracer (average of 88% versus 87%), while for surface water the amount of equilibration achieved by the lithium tracer (average of 99.9%) was statistically significantly higher than that achieved with the bromide tracer (average of 93%).

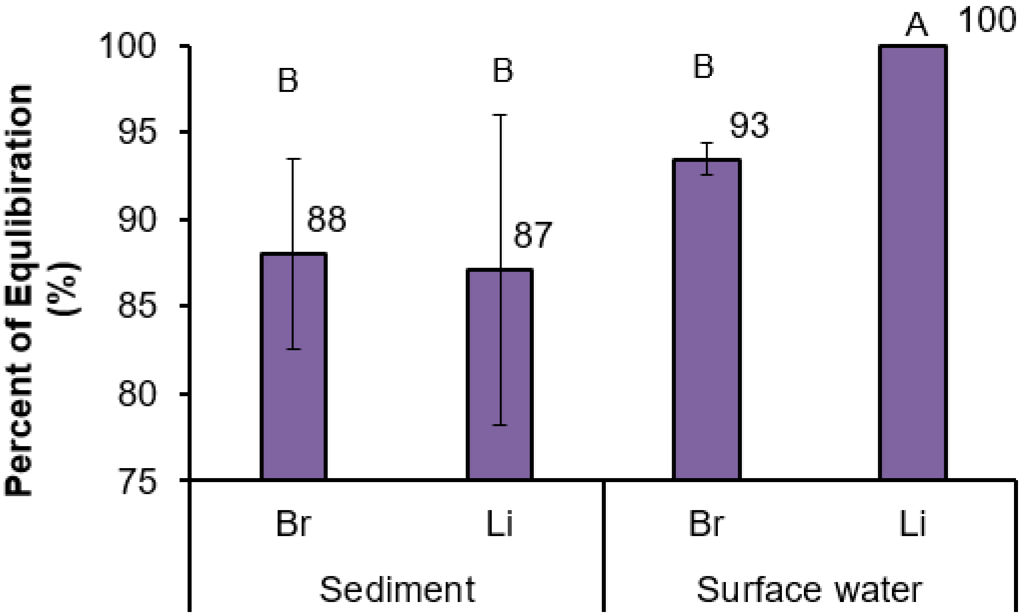

Figure 16: Percentage of equilibration achieved by the bromide and lithium tracers for peepers deployed in sediment and surface water.

Note: Columns are average (SD) values; numerical labels are averages; columns with the same letter are not statistically different (ANOVA with Tukey's Honestly Significant Difference).

Data were further evaluated by comparing the concentrations of copper, manganese, and zinc in sediment porewater and surface water as estimated by the bromide tracer to those estimated using the lithium tracer (Figure 17). These three metals were evaluated because they were the metals with the highest percentages of detected results in both sediment and water. Results indicated that in all cases, the concentrations for copper, zinc, and manganese estimated using the bromide tracer were an average of 37%, 24% and 31% higher, respectively, than the concentrations indicated using the lithium tracer. Specifically:

- The average (SD) concentration of copper estimated using the bromide tracer (8.3 (5.0) µg/L) was statistically different from that estimated using the lithium tracer (5.2 (3.0) µg/L)), based on a paired t-test ($P < 0.0001$).
- The average (SD) concentration of zinc estimated using the bromide tracer (17.3 (10.1) µg/L) was statistically different from that estimated using the lithium tracer (13.1 (7.6) ug/L)), based on a paired t-test ($P = 0.0001$).
- The average (SD) concentration of manganese estimated using the bromide tracer (83.2 (114.1) µg/L) was not statistically different from that estimated using the lithium tracer (57 (78) ug/L)), based on a paired t-test ($P < 0.0001$).

Overall, the 24-37% difference between the approaches is within an acceptable level of uncertainty for the measurement approaches such that either the concentrations estimated using the lithium tracer or the concentrations estimated using the bromide tracer would be assumed to be accurate measurements. However, it is important to note that diffusion coefficient for bromide (1.8×10^{-5} cm^2/s, Table 5) is much higher compared to lithium (0.9×10^{-5} cm^2/s, Table 5) and thus bromide is expected to diffuse faster than lithium in sediments and in surface water. Since the opposite is observed for surface water while no difference is observed for sediments, we can hypothesize that either the diffusion of lithium is faster that theorical values or that the diffusion of bromide is slower that theorical values. However, based on the diffusion coefficients, bromide should have reached equilibrium earlier in the given deployment time, thus using bromide correction may slightly overestimate porewater and surface water concentrations for this study. Indeed, corrections using lithium provided concentrations of copper, manganese and zinc that were only within a factor of 1.06 to 1.2 from the measured concentrations, which is expected based on the samplers having reached equilibrium. For this reasons, the lithium tracer results will be used for the remainder of the discussion in this study.

It is important to note that both lithium and bromide tracer indicate 80% or more of the equilibrium has been reach in both porewater and surface water peepers. Corrections are still applied in this study to provide the methods to other studies that may retrieve peepers before equilibrium is established.

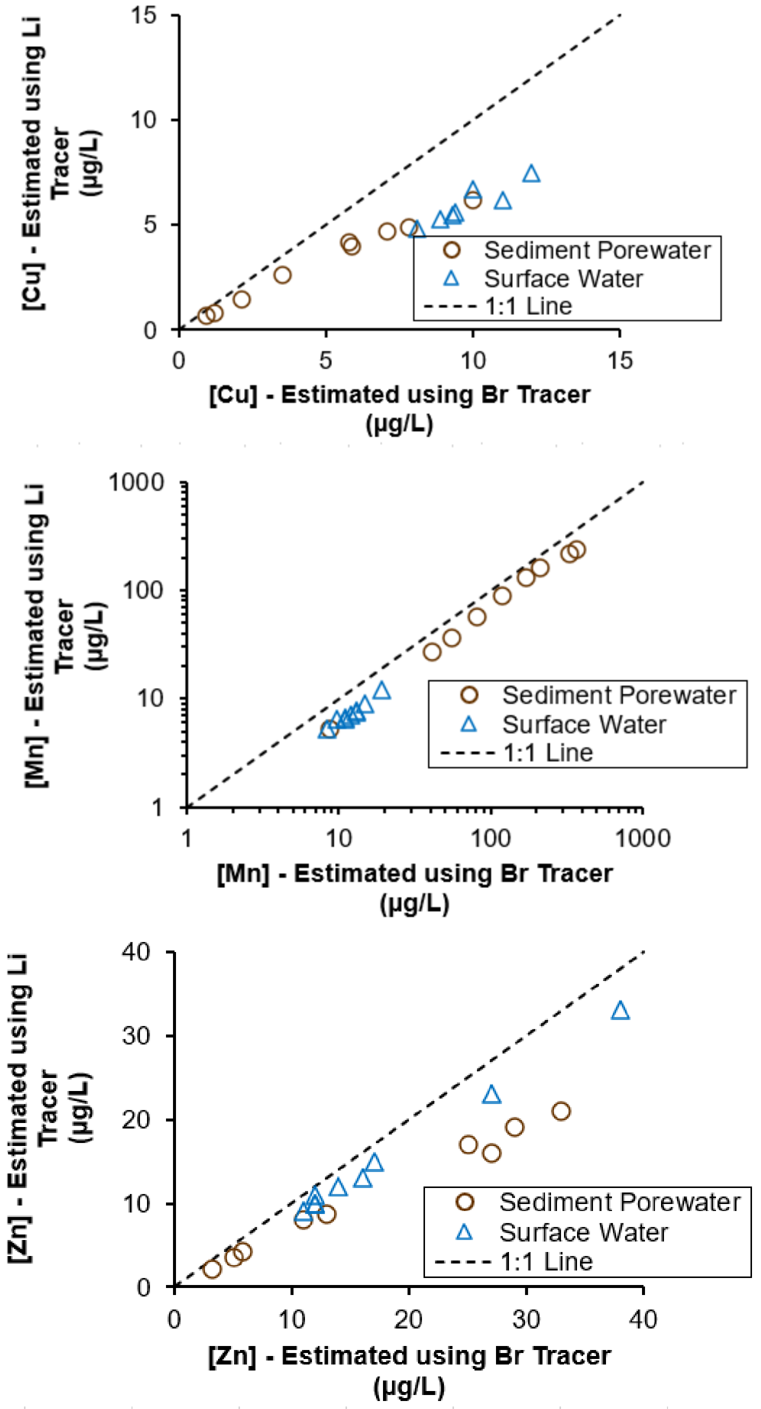

Figure 17: Concentrations of copper, manganese, and zinc, as estimated using the lithium tracer (y-axis) compared to concentrations as estimated using the bromide tracer (x-axis) for peepers deployed in sediment and surface water.

4.4. Comparison of Sediment Porewater and Surface Water Peeper Results

Concentrations of copper, manganese, and zinc in peepers deployed in sediment were compared to concentrations in surface water (calculated using the lithium tracer, Figure 18). There was a lack of a clear correlation between concentrations of metals in sediment porewater and the corresponding concentration in surface water at each station. Differences in concentrations between sediment porewater and surface water were noted for copper and manganese, but not zinc:

- The average (SD) concentrations of copper in sediment porewater (3.3 (2.0) ug/L) were statistically lower (by a factor of ~2) than that of surface water (7.2 (2.7) ug/L), based on paired t-test (P = 0.0014).
- The average (SD) concentrations of manganese in sediment porewater (107 (86) ug/L) were statistically higher (by a factor of 14) than that of surface water (7.6 (2.0) ug/L), based on paired t-test (P = 0.0087).
- The average (SD) concentrations of zinc were not statistically different between sediment porewater (11.1 (7.2) ug/L) and surface water (15 (7.9) ug/L), based on paired t-test (P = 0.1061).

Overall, the differences between sediment porewater and surface water for copper and zinc were minor (factor of 2 or less difference), indicating some degree of potential equilibration between surface sediment and surface water. In contrast, concentrations of manganese in sediment porewater were much higher (factor of 14) than surface water. This is expected given that the sediment was likely anoxic or partly anoxic, which would facilitate the presence of freely available manganese compared to the more oxygenated surface water, where manganese availability would be limited.

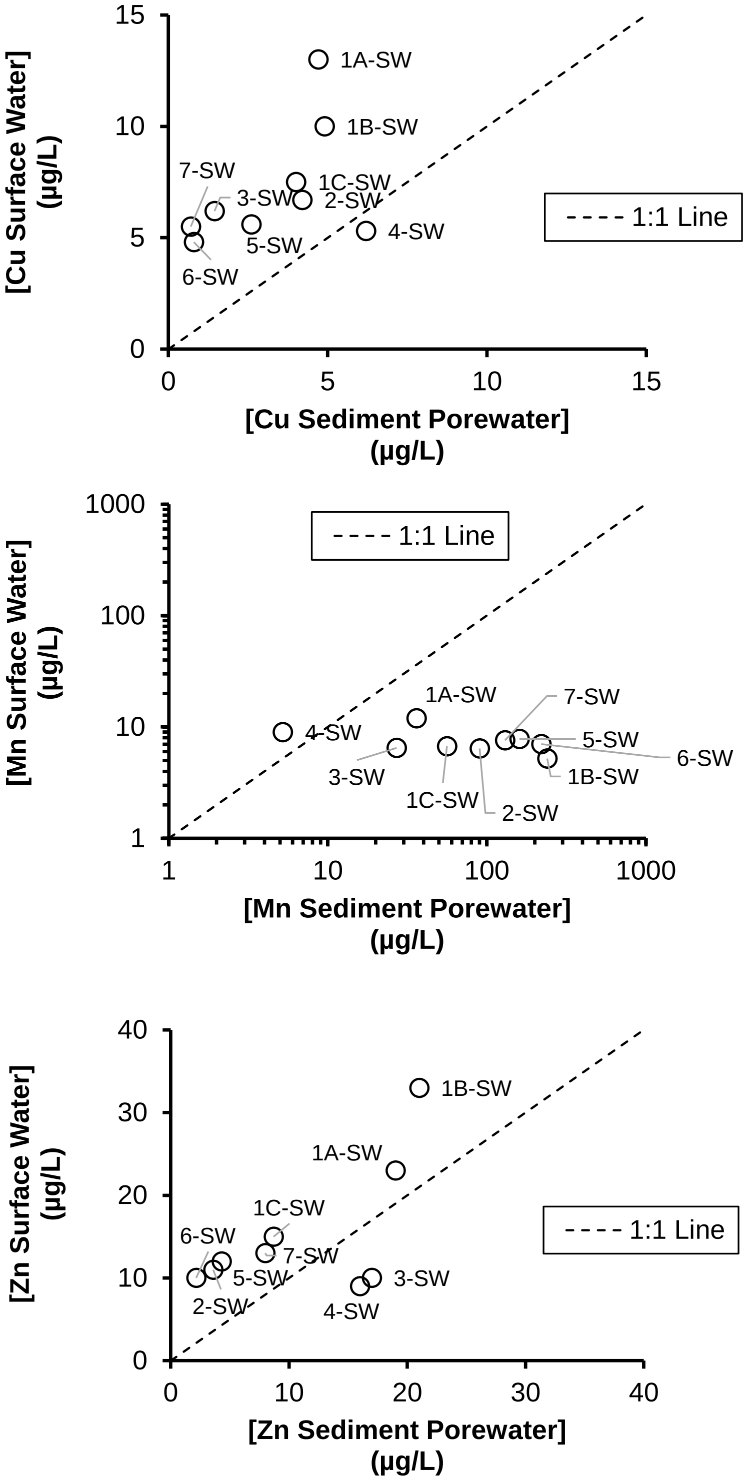

Figure 18: Concentrations of copper, manganese, and zinc, as estimated using the lithium tracer (y-axis) compared to concentrations as estimated using the bromide tracer (x-axis) for peepers deployed in sediment and surface water.

Note: Labels indicate stations.

4.5. Surface Water Concentrations Measured with DGTs

Concentrations of metals as measured by the DGTs is presented in Table 12. No concentrations of cadmium, copper, lead, total mercury, or nickel (measured by DGTs) were in exceedance of USEPA's saltwater CCC (Table 3).

Table 12: DGT Surface Water Results

Station	Hg	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
	ng/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
1A-SW*	< 0.520	-	-	-	-	-	-	-	-
	< 0.520	-	-	-	-	-	-	-	-
1B-SW*	**1.409**	-	-	-	-	-	-	-	-
	< 0.522	-	-	-	-	-	-	-	-
1C-SW*	< 0.529	-	-	-	-	-	-	-	-
	< 0.529	-	-	-	-	-	-	-	-
2-SW	< 0.632	**0.024**	< 0.053	**1.054**	**1.74**	**0.088**	**1.99**	**0.37**	**4.91**
3-SW	< 0.527	**0.030**	< 0.044	**0.743**	< 0.52	**0.068**	**2.38**	**0.38**	**5.06**
4-SW	< 0.569	**0.032**	< 0.048	**0.875**	**1.04**	**0.079**	**2.18**	**0.39**	**5.84**
5-SW	< 0.562	**0.030**	< 0.047	**0.865**	**2.50**	**0.078**	**2.07**	**0.30**	**4.44**
6-SW*	-	**0.031**	< 0.048	**0.808**	< 0.56	**0.068**	**2.51**	**0.36**	**5.13**
	-	**0.029**	< 0.048	**0.808**	< 0.56	**0.068**	**1.88**	**0.34**	**4.82**
7-SW	< 0.564	**0.030**	< 0.047	**1.013**	< 0.55	**0.090**	**1.47**	**0.34**	**5.57**

- : Not analyzed

*: Represents stations at which duplicate DGTs for mercury (1A-SW, 1B-SW, and 1C-SW) or other metals (6-SW) were deployed.

DGTs indicated lower method detection limits than peepers, but detection limits for peepers were generally an order of magnitude lower than USEPA's saltwater CCC for aquatic life (Table 3), making them sufficient for most investigations of metals that consider potential risks to aquatic life. Cadmium in the surface water was measured between 0.024 to 0.032 µg/L, chromium between < 0.044 and < 0.053 µg/L, copper between 0.743 and 1.054 µg/L, iron between < 0.52 to 2.50 µg/L, lead between 0.068 and 0.090 µg/L, manganese between 1.47 and 2.51 µg/L, nickel between 0.030 and 0.38, and zinc between 4.44 and 5.57 µg/L. Mercury was only detected in one of the surface water samples at 1.409 ng/L.

It is notable that the surface water peepers identified copper as consistently exceeding the saltwater CCC, but the DGTs did not identify copper as an issue. Copper is a known contaminant of concern at Naval Base San Diego (Drygiannaki et al., 2020; Hayman et al., 2019; Rosen et al. 2017).

The DGT data in Table 12 indicated lower concentrations of metals in the surface water compared to peepers (Table 10 and Table 11). For example, as shown in Figure 19, concentrations at the stations at which both peepers and DGTs were used to measure copper, manganese, and zinc in surface water (stations 2 through 7) were statistically different, with average values differing by a factor of 2 to 6 between DGTs and peepers:

- The average (SD) concentration of copper in peepers (estimated using the lithium tracer, 5.7 (0.67) µg/L, was statistically higher (by a factor of 6) than that indicated by DGTs (0.89 (0.12) µg/L) based on paired t-test ($P < 0.0001$).
- The average (SD) concentration of manganese in peepers (estimated using the lithium tracer, 7.4 (0.97) µg/L, was statistically higher (by a factor of 4) than that indicated by DGTs (2.1 (0.31) µg/L) based on paired t-test ($P < 0.0001$).
- The average (SD) concentration of zinc in peepers (estimated using the lithium tracer, 11 (1.5) µg/L, was statistically higher (by a factor of 2) than that indicated by DGTs (5.1 (0.50) µg/L) based on paired t-test ($P = 0.0004$).

The lower concentrations obtained from DGT in comparison to peeper data may be in part due to differences in the mechanisms by which metals are sampled by the devices. Strivens et al. (2019) hypothesized that Dissolved Organic Carbon (DOC) bound copper may not freely diffuse and bind to the chelex binding layer of DGT, thus recording lower dissolved metals concentrations in DOC rich environment compared to other methods. In comparison, peeper membranes may not prevent DOC-metal complexes from diffusing inwards allowing the measurement of DOC-metal complexes. Additional study may be needed to refine the differences in DGT and peeper measurements, although the fact that these very different measurement techniques were within an approximately factor of 5 agreement is notable. Given this relative level of agreement, differences between DGT and peeper measurements may be within typical levels of variation and measurement error, but more research would be beneficial to evaluate the comparison.

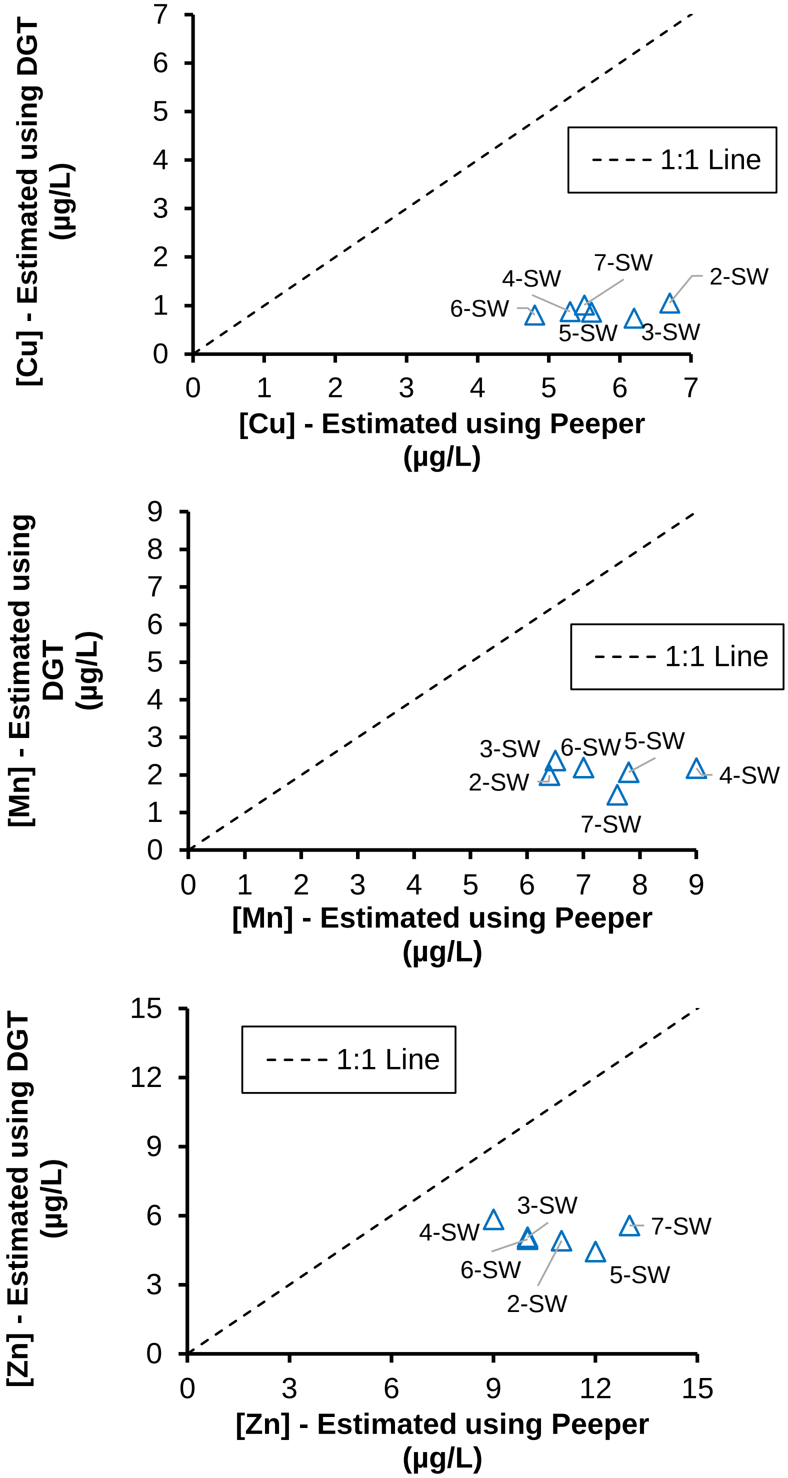

Figure 19: Concentrations of copper, manganese, and zinc, as estimated using peepers and the lithium tracer (x-axis) compared to concentrations as estimated using DGTs (x-axis) for peepers and DGTs deployed in surface water.

Note: Labels indicate stations.

Concentrations of metals in sediment porewater obtained from peepers were also compared to concentrations obtained in a previous SERDP-funded research effort by Drygiannaki et al. (2020) (Table 13). Ranges of concentrations of cadmium, copper, lead, total mercury, and nickel that are highlighted yellow included ranges that were in exceedance of USEPA's saltwater CCC (Table 3). Both studies were in agreement that copper exceeded the CCC value in sediment porewater. The Drygiannaki et al. (2020) study used DGT to measure availability of metals in the porewater at three locations in Paleta creek (Figure 2) that were in the vicinity of the locations sampled in this study (Figure 4).

Table 13: Comparison of Sediment Porewater Metal Concentration in Paleta Creek

Metal	Concentration Range Measured in DGT (µg/L) (Drygiannaki et al., 2020)	Concentration Range Measured in Peepers (µg/L) (this study)
Ni	0.7 – 3.6	< 0.6 – 1.7
Cu	1.7 – 16	< 1.3 – 7.4
Zn	6.2 – 68	< 4.2 – 23
Cd	ND – 0.34	< 0.22 – < 0.54
Hg	ND – 0.18	< 0.17 – < 0.46
Pb	0.18 – 1.3	< 0.17 – 1.1

Overall, the concentration ranges for metals in sediment porewater measured in this study overlaps with the range measured by Drygiannaki et al. (2020), indicating that the peeper method provides similar results as DGT in sediment. Additional comparisons between peepers and DGTs may be needed to resolve the differences observed between peepers and DGTs deployed in surface water.

5. ANALYSIS OF PEEPER FIELD SAMPLING LOGISTICS AND RECOMMENDATIONS FOR CONDUCTING PEEPER INVESTIGATIONS

The purpose of this section is to review the logistical details associated with the field efforts and provide recommendations for future peeper field investigations. This information is provided to aid in the planning and execution of future efforts. Details are organized according to the basic steps involved in the peeper field investigation:

1. Planning
2. Preparation and Shipment of Peepers
3. Mobilization for Deployment
4. Deployment Period
5. Mobilization for Retrieval
6. Retrieval
7. Processing and Shipment

Step 1: Planning. Planning the field work was typical of that at an aquatic sediment site, and was initiated 3 to 4 months ahead of the planned deployment date. Key activities included identifying optimal dates, ordering the peepers, arranging the vessel support, and working with local site personnel regarding access to the site.

- Key recommendations for planning:
    - Plan field work well in advance, ideally several months ahead of the planned deployment date, if possible.
    - Assume a less than 100% success rate for peeper sampling, as peepers may be lost or samples compromised; it is recommended to deploy at least 1.25X to 1.5X the number of stations required for the investigation.

Step 2: Preparation and Shipment of Peepers. Peeper preparation was conducted at SiREM approximately 2 weeks in advance of the field deployment. It is recommended to coordinate the peeper preparation well in advance to allow adequate time for preparation and shipping of peepers to the field.

In this experiment, peepers were prepared using bromide and lithium tracers. For the peepers deployed in sediment, the amount of equilibration indicated by bromide and lithium did not greatly differ. The bromide data and lithium data from each deployed peepers were then used independently to calculate the concentrations of metals at equilibrium. Among the metals that were frequently detected in both sediment and water (copper, manganese, and zinc), average results estimated using the lithium tracer data were within approximately 24-37% of the results indicated using the bromide tracer. This difference has been observed in laboratory experiments as well (conducted by this team – available in a subsequent report), even when peepers were deployed for time periods that only allowed partial (i.e., 20%, 50%, etc.) equilibration. Given the minimal difference between results estimated with bromide tracer versus the lithium tracer, the fact that bromide concentrations in seawater are likely much higher than concentrations lithium (resulting in some uncertainty regarding tracer elimination rates for bromide), and that fact that the analysis of bromide requires a separate sample preservation and analysis, the use of lithium as a single tracer may be advantageous for future work. This would save analytical costs (i.e., not having a separate analysis for bromide), simplify the processing step, and allow more peeper water sample to be devoted to the analysis of the target metal analytes, which will improve analytical precision.

- Key recommendations for peeper preparation and shipment:
    - Begin peeper preparation (ideally) at least 2-3 weeks in advance.
    - Peepers can be prepared with either bromide or lithium tracers (or both), although it is recommended to use lithium only.
    - Order at least 5-10% more peepers than required for deployment; this will provide a buffer against damage to peeper that may occur during shipping and handling and will not greatly increase investigation costs.
    - Arrange shipping of peepers to a secure location where peepers can be stored at room temperature (or refrigerated) at least one week in advance of the field deployment.
    - Immediately upon arrival of peepers and frames, verify the number of peepers and support frames that were shipped.
    - Immediately upon arrival of peepers and frames, have a field staff construct at least one peeper frame so that it is clear to staff the manner in which the frames are assembled and that all pieces required for the frame construction are available and line up properly.

Step 3: Mobilization for Deployment. Mobilization for retrieval was typical of field work at an aquatic sediment site. Approximately 2 hours during the first morning of the first field day (deployment) was spent organizing the deployment equipment, preparing the frames for deployment, launching the vessel, and coordinating the field staff. Although some portion of this work may have been able to have been accomplished prior to the start time, projects should plan on at least 1 to 2 hours at the beginning of field events to conduct this mobilization and organization activity. This allows extra time for troubleshooting if any issues arise and gives times to safely travel to and from the deployment locations.

- Key recommendations for deployment mobilization:
    - Plan for a “slow start” on the first day of field work.

Step 4: Deployment. Overall, 1.5 days were spent to deploy peeper frames at 10 stations, all which included 1 peeper frame with 4 surface water peepers, 4 porewater peepers, and 2 surface water DGTs. This time includes the approximate 30- to 45-minute transit time to and from the vessel launch area to the Site.

At the site, positioning of the vessel at each station required 5 to 37 minutes (average of 13 minutes per station, Table 14), although this was dependent on the wind conditions, which affected the ability to anchor securely at certain stations. It is important to note that boating to the locations and anchoring could take up to 40-60 minutes depending on the weather and site conditions, which can extensively add to the field effort. Deployment locations at the field site were within 10 to 50 feet of the planned locations.

Once on station, peepers and DGTs were assembled into a single peeper frame device deployed using a driverless push-pole system. The assembly of the frames, insertion of peepers and DGTs into the frames, and attachment of the frame to the push pole required approximately 5 minutes per frame (data not shown); this primarily accomplished by 1 field staff. After the peepers were attached to the push pole, the pole and peepers were inserted into the water. This process required at least two field staff to handle the push pole and attach the additional lengths of pole required (i.e., approximately 30 feet of pole), while a third field staff viewed the video camera feed to note when the peeper frame approached the sediment, monitor the insertion, and confirm detachment of the push pole from the peeper frame. From the time the peeper frame entered the water, the first station (1A) required approximately 26 minutes to install the peeper frame (Table 14). This was largely a factor of field staff optimizing and becoming familiar with the equipment and process. The next two deployments (1B and 1C) required only 5 and 3 minutes, respectively. Not counting station 1A, the peeper frame insertion process required an average of 5 minutes per peeper frame. This gain in efficiency can be attributed to field personnel familiarization with the material and efficiencies found during deployment. Example of these efficiencies include pre-assembly of material during anchoring and attribution of defined roles to field crew members.

Table 14: Preparation and Deployment Time

Sampling station	Vessel Positioning Time (minutes)	Push Pole Deployment Time (minutes)
1A	16	26
1B	0 (same location as 1A)	5
1C	0 (same location as 1A)	3
2	14	5
3	37	8
4	9	6
5	9	4
6	5	3
7	7	6
8	13	8

The optimal rate of efficiency for the deployment was realized on the second day of deployment. During the 3 hours spent on site (not counting transit time from the vessel launch to the site), 6 peeper frames were deployed at 6 different locations, an approximate 2 stations per hour rate of deployment. This rate would afford typical projects being able to deploy approximately 10 to 20 peeper frames in a single field day using this push pole method.

Deployment of peepers using divers is likely to be closer to the 10 peeper frames per day rate rather than 20 peeper frames per day rate. In this case, only 1 field staff would be needed to construct and arrange peepers and frames, although many more field staff would be needed for diving (i.e., 1 to 2 divers, 1 to 2 dive support staff, etc.). With that approach, stations are usually marked with a buoy, then the diver is provided the peeper frame on the vessel. The diver then descends to the station, manually inserts the peeper frame, and returns to the surface. Multiple stations can be coordinated on a single dive depending on site conditions.

- Key recommendations for deployment:
    - Deployment of peepers requires 2 to 3 field staff if using push pole system, or 1 field staff plus divers and associated diver support personnel if divers are used for deployment.
    - Deployment of peeper frames can likely achieve rates of 10 to 20 stations per day; this rate is highly depending on field staff, site conditions, arrangement of stations, transit times, deployment approaches, and other factors.
    - Once at a site, it is recommended to conduct a practice run using a sacrificial peeper frame so that push pole operators or divers (and field staff) can familiarize themselves with the process.

Step 5: Deployment Period. The final day of retrieval was on October 4, 2022. During the period of October 5 to October 12 (8 days), no active field work occurred. This period allowed the peepers to be exposed to the site sediment or surface water for approximately 10 days. Since retrieval was completed in 2 days' time (October 13-14, 2022), the entire field work program was completed in two working weeks.

As discussed in the results, the tracer data indicated that peepers used in this investigation were 70% to 100% equilibrated for all target metals over a period of 10 days. Data suggested that approximately 3 weeks would be needed for all target metals to approach 90% of equilibrium in sediment (6 days for surface water). However, 30% to 50% levels of equilibration could be achieved for the slowest diffusing metal (chromium) in as little as 3 to 5 days in sediment and 1 to 3 days in surface water. Reducing the deployment periods to less than one week (using the lithium tracer to correct for equilibrium) could enable more efficient field programs, especially when overnight travel for field staff is a logistical component. Additional field deployment kinetic studies may be useful in refining the ability to reduce the deployment period.

Alternately, the peeper design used in this experiment has been successfully deployed in sediment for periods of 28 days. Increasing the deployment period provides more assurance that equilibrium is attained for all analytes, but the risk of sampler loss increases with time. Additionally, for very long deployments in surface water, biofilms that impede diffusion may affect the peeper membrane. This issue has not been observed for typical long-term deployments (e.g., 28 days) with this type of peeper, however.

- Key recommendations for deployment periods:

  - Deployment periods for peepers in sediment and surface water may be able to be reduced to less than one week, depending on the peeper design being used.
  - Deployment periods of 2, 3, or 4 weeks are also acceptable, as full equilibration or all metals is expected at approximately 3 weeks (in sediment); although risk of sampler loss increases with deployment time.

Step 6: Mobilization for Retrieval. Mobilization for retrieval was typical of field work at an aquatic sediment site. Mobilization for retrieval on the first day was efficient (approximately 45 minutes), but a change in the retrieval approach (see below), required approximately 3 hours for mobilization.

- Key recommendations for retrieval mobilization:
  - Plan for a “slow start” on the first day of field work.

Step 7: Retrieval. Day 1 of retrieval was largely unsuccessful. Retrieval methods featured throwing a grappling hook from the vessel and dragging bottom in an attempt to snag anchor lines attached to the peeper frames. Because the anchor lines were only 36 feet in length and the water depth was > 20 feet, only 5 to 10 feet of anchor line extended laterally on the sediment surface. This was not a sufficient target to snag using the grappling hook. This was compounded by the heavy debris at the location, as noted per the diver that noted that peepers at stations 1A and 1B were under debris (a sunken boom). Only one peeper frame (station 2) was recovered using the grappling hook method, and the peeper samples from this station were processed at the end of the field day.

Day 2 of retrieval featured the use of a scuba diver to retrieve the peeper frames. On average, the diver required approximately 20 minutes per station to enter the water, search for the peeper frame, and return the frame to the vessel. Additional time was needed to mark the approximate locations of the sites with marker buoys and transit between stations.

Table 15: Retrieval Times for Day 2

Sampling station	Diver Retrieval Time (minutes)
1A	40*
1B	
1C	5
2	Retrieved on Day 1
3	15
4	10
5	30
6	30
7	30
8	-

* Station 1A and 1 B were recovered together within 40 minutes.

\- Station 8 was not retrieved.

Once the peeper frame was aboard the vessel, 2 field staff quickly removed the peepers and DGTs from the frame and recorded information on the retrieval forms. One “dirty hands” and one “clean hands” staff are recommended for this process. Packaging the peepers into storage bags required approximately 5 minutes or less (data not presented), and was conducted while the vessel was moving to the next station. Processing of the peeper (rather than packaging for storage) could be conducted at this stage of the field work, as discussed below.

Eight peeper frames were retrieved and packaged over a 5-hour period on day 2 using the diver. Assuming having access to a second diver and saving 1 to 2 hours of time in the field day to process peepers onshore, it may be possible to retrieve peepers from approximately 10 stations per day. Retrieval rates using the driverless grappling hook method (when a proper length of anchor line is used) are likely to be higher (i.e., 10 to 20 stations per day).

- Key recommendations for retrieval:
    - Retrieval of peepers is most optimal with 2 field staff; additional staff may be needed if processing occurs on the vessel.
    - Time on the water should be limited to allow 1 to 2 hours onshore work at the end of the field day for processing the retrieved peepers.
    - Retrieval of peeper frames can likely achieve rates of 10 stations per day when divers are used, or higher rates (10 to 20 stations per day) when diverless techniques are optimally employed; these rates is highly depending on field staff, site conditions, arrangement of stations, transit times, deployment approaches, and other factors.
    - If an anchor line is used to mark peeper stations, ensure it extends at least 30 feet from the peeper frame insertion point, as this will allow a longer target for snagging with a grappling hook or locating underwater via a diver.

Step 8: Processing and Shipment. In this field event, peepers were processed onshore at the end of the retrieval day. Processing time for the majority of the peepers (16 peeper samples on day 2), from the time at which the vessel arrived onshore to the time the processing equipment and samples were packed for shipment required approximately 2 hours, a rate of approximately 8 minutes per peeper sample. Two field staff are recommended for processing.

Processing of the peeper samples could be conducted on the vessel immediately after obtaining the peepers. This approach would delay the retrieval process unless 1 to 2 additional field staff are available to dedicate their focus to processing steps (while 2 other field staff focused on retrieval of the frames and coordination with the vessel captain and staff). This approach also requires sufficient space to process the samples, and this may interfere with space needed for retrieval activities. Processing also requires fairly sheltered conditions so that samples are not contaminated with precipitation. Precise pipetting and handling of peepers and sample bottles also requires a stable and ergonomic platform. The often unsheltered, uncontrolled, unstable, and cramped conditions on a vessel (wind, precipitation, vessel movement, etc.) may not be ideal for processing peeper samples.

- <u>Key recommendations for processing and shipment:</u>
  - In most cases, peeper samples should be processed at the end of the field day onshore (laboratory research is ongoing to confirm the timing of this recommendation).
  - Peeper processing is possible onboard the vessel immediately after the peepers are retrieved from the sediment or water, although this can be more complicated than onshore processing.
  - If peeper processing is conducted onshore, it is recommended to save at least 1 to 2 hours of time at the end of each field day to process 10 to 20 peeper samples.
  - Preserved peeper samplers should be preserved cold (ice replenished daily) and shipped to the analytical chemistry laboratory, where they should be analyzed before expiration of USEPA method hold times.

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Appendix A: Peeper Calculation Sheets

Table A1. Calculation of Cfree values using the lithium tracer, San Diego peeper samples.

Equilibrium Correction of Porewater Concentration using Lithium Tracer

Sample ID	Sample Deployment Date	Sample Collection Date	Chemical Name	Chemical Abreviation	Report Result Text	Measured Concentration in Peeper	MDL in Peeper	Report Result Unit	Lab Qualifiers	Initial Li Concentration (µg/L)	Deployment Time (days)	Assumed Li Concentration External to Peeper (µg/L)	Sample-Specific Elimination Rate for Li (K_{Li}) (day^{-1})	Diffusion Coefficient for Analytes (Di) (* 10^{-5} cm^2/s)	Di ÷ D_{Li}	Sample-specific Elimination Rate for Analytes (K_i) (day-1)	Percent Equilibrium Reached (%)	Equilibrium Corrected Concentration (µg/L)	Equilibrium Corrected MDL (µg/L)	Equilibrium Corrected Result (µg/L) 2-sig figs
1A-PW	10-3-22 12:30	10-14-22 14:58	Lithium	Li	16000	16000	26	µg/L		86000	11.10	100	0.152	0.90	1.00	0.152	81	--	--	**--**
1A-PW			Cadmium	Cd	ND	0	0.27	µg/L			11.10			0.63	0.70	0.107	69	0.00	0.39	**< 0.39**
1A-PW			Chromium	Cr	ND	0	1.9	µg/L			11.10			0.52	0.58	0.088	62	0.00	3.05	**< 3**
1A-PW			Copper	Cu	3.2	3.2	1.4	µg/L			11.10			0.62	0.69	0.105	69	4.65	2.04	**4.7**
1A-PW			Iron	Fe	220	220	35	µg/L			11.10			0.63	0.70	0.107	69	317.23	50.47	**320**
1A-PW			Lead	Pb	0.88	0.88	0.21	µg/L	J		11.10			0.83	0.92	0.140	79	1.11	0.27	**1.1**
1A-PW			Manganese	Mn	25	25	1.7	µg/L			11.10			0.62	0.69	0.105	69	36.35	2.47	**36**
1A-PW			Mercury	Hg	ND	0	0.13	µg/L			11.10			0.74	0.82	0.125	75	0.00	0.17	**< 0.17**
1A-PW			Nickel	Ni	ND	0	0.65	µg/L			11.10			0.62	0.69	0.105	69	0.00	0.95	**< 0.95**
1A-PW			Zinc	Zn	13	13	3.6	µg/L			11.10			0.61	0.68	0.103	68	19.07	5.28	**19**
1A-SW	10-3-22 12:30	10-14-22 14:58	Lithium	Li	150	150	1.4	µg/L		86000	11.10	100	0.671	0.90	1.00	0.671	100	--	--	**--**
1A-SW			Cadmium	Cd	ND	0	0.36	µg/L			11.10			0.63	0.70	0.470	99	0.00	0.36	**< 0.36**
1A-SW			Chromium	Cr	20	20	2.6	µg/L			11.10			0.52	0.58	0.388	99	20.27	2.64	**20**
1A-SW			Copper	Cu	13	13	1.9	µg/L			11.10			0.62	0.69	0.463	99	13.08	1.91	**13**
1A-SW			Iron	Fe	110	110	46	µg/L			11.10			0.63	0.70	0.470	99	110.60	46.25	**110**
1A-SW			Lead	Pb	0.36	0.36	0.28	µg/L	J		11.10			0.83	0.92	0.620	100	0.36	0.28	**0.36**
1A-SW			Manganese	Mn	12	12	2.2	µg/L			11.10			0.62	0.69	0.463	99	12.07	2.21	**12**
1A-SW			Mercury	Hg	ND	0	0.33	µg/L			11.10			0.74	0.82	0.552	100	0.00	0.33	**< 0.33**
1A-SW			Nickel	Ni	29	29	0.86	µg/L			11.10			0.62	0.69	0.463	99	29.17	0.87	**29**
1A-SW			Zinc	Zn	23	23	4.8	µg/L			11.10			0.61	0.68	0.455	99	23.15	4.83	**23**
1B-PW	10-3-22 13:25	10-14-22 14:56	Lithium	Li	510	510	0.83	µg/L		86000	11.06	100	0.483	0.90	1.00	0.483	100	--	--	**--**
1B-PW			Cadmium	Cd	ND	0	0.22	µg/L			11.06			0.63	0.70	0.339	98	0.00	0.23	**< 0.23**
1B-PW			Chromium	Cr	ND	0	1.5	µg/L			11.06			0.52	0.58	0.280	95	0.00	1.57	**< 1.6**
1B-PW			Copper	Cu	4.8	4.8	1.1	µg/L			11.06			0.62	0.69	0.333	97	4.92	1.13	**4.9**
1B-PW			Iron	Fe	4400	4400	28	µg/L			11.06			0.63	0.70	0.339	98	4506.30	28.68	**4500**
1B-PW			Lead	Pb	0.39	0.39	0.17	µg/L	J		11.06			0.83	0.92	0.446	99	0.39	0.17	**0.39**
1B-PW			Manganese	Mn	230	230	1.3	µg/L			11.06			0.62	0.69	0.333	97	235.91	1.33	**240**
1B-PW			Mercury	Hg	ND	0	0.13	µg/L			11.06			0.74	0.82	0.398	99	0.00	0.13	**< 0.13**
1B-PW			Nickel	Ni	1	1	0.52	µg/L			11.06			0.62	0.69	0.333	97	1.03	0.53	**1**
1B-PW			Zinc	Zn	20	20	2.9	µg/L			11.06			0.61	0.68	0.328	97	20.55	2.98	**21**
1B-SW	10-3-22 13:25	10-14-22 14:56	Lithium	Li	180	180	0.83	µg/L		86000	11.06	100	0.631	0.90	1.00	0.631	100	--	--	**--**
1B-SW			Cadmium	Cd	ND	0	0.22	µg/L			11.06			0.63	0.70	0.442	99	0.00	0.22	**< 0.22**
1B-SW			Chromium	Cr	ND	0	1.5	µg/L			11.06			0.52	0.58	0.365	98	0.00	1.53	**< 1.5**
1B-SW			Copper	Cu	10	10	1.1	µg/L			11.06			0.62	0.69	0.435	99	10.08	1.11	**10**
1B-SW			Iron	Fe	ND	0	28	µg/L			11.06			0.63	0.70	0.442	99	0.00	28.21	**< 28**
1B-SW			Lead	Pb	0.45	0.45	0.17	µg/L	J		11.06			0.83	0.92	0.583	100	0.45	0.17	**0.45**
1B-SW			Manganese	Mn	5.2	5.2	1.3	µg/L			11.06			0.62	0.69	0.435	99	5.24	1.31	**5.2**
1B-SW			Mercury	Hg	ND	0	0.13	µg/L			11.06			0.74	0.82	0.519	100	0.00	0.13	**< 0.13**
1B-SW			Nickel	Ni	1	1	0.52	µg/L			11.06			0.62	0.69	0.435	99	1.01	0.52	**1**
1B-SW			Zinc	Zn	33	33	2.9	µg/L			11.06			0.61	0.68	0.428	99	33.29	2.93	**33**
1C-PW	10-3-22 13:50	10-14-22 11:51	Lithium	Li	19000	19000	42	µg/L		86000	10.92	100	0.139	0.90	1.00	0.139	78	--	--	**--**
1C-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.92			0.63	0.70	0.097	65	0.00	0.34	**< 0.34**
1C-PW			Chromium	Cr	ND	0	1.5	µg/L			10.92			0.52	0.58	0.080	58	0.00	2.57	**< 2.6**
1C-PW			Copper	Cu	2.6	2.6	1.1	µg/L			10.92			0.62	0.69	0.096	65	4.01	1.70	**4**
1C-PW			Iron	Fe	230	230	28	µg/L			10.92			0.63	0.70	0.097	65	351.67	42.81	**350**
1C-PW			Lead	Pb	ND	0	0.17	µg/L			10.92			0.83	0.92	0.128	75	0.00	0.23	**< 0.23**
1C-PW			Manganese	Mn	36	36	1.3	µg/L			10.92			0.62	0.69	0.096	65	55.54	2.01	**56**
1C-PW			Mercury	Hg	ND	0	0.13	µg/L			10.92			0.74	0.82	0.114	71	0.00	0.18	**< 0.18**
1C-PW			Nickel	Ni	ND	0	0.52	µg/L			10.92			0.62	0.69	0.096	65	0.00	0.80	**< 0.8**
1C-PW			Zinc	Zn	5.6	5.6	2.9	µg/L			10.92			0.61	0.68	0.094	64	8.72	4.52	**8.7**
1C-SW	10-3-22 13:50	10-14-22 11:51	Lithium	Li	180	180	0.83	µg/L		86000	10.92	100	0.639	0.90	1.00	0.639	100	--	--	**--**
1C-SW			Cadmium	Cd	0.36	0.36	0.22	µg/L	J		10.92			0.63	0.70	0.448	99	0.36	0.22	**0.36**
1C-SW			Chromium	Cr	ND	0	1.5	µg/L			10.92			0.52	0.58	0.370	98	0.00	1.53	**< 1.5**
1C-SW			Copper	Cu	7.4	7.4	1.1	µg/L			10.92			0.62	0.69	0.441	99	7.46	1.11	**7.5**
1C-SW			Iron	Fe	ND	0	28	µg/L			10.92			0.63	0.70	0.448	99	0.00	28.21	**< 28**
1C-SW			Lead	Pb	0.17	0.17	0.17	µg/L	J		10.92			0.83	0.92	0.590	100	0.17	0.17	**< 0.17**
1C-SW			Manganese	Mn	6.6	6.6	1.3	µg/L			10.92			0.62	0.69	0.441	99	6.65	1.31	**6.7**
1C-SW			Mercury	Hg	ND	0	0.13	µg/L			10.92			0.74	0.82	0.526	100	0.00	0.13	**< 0.13**
1C-SW			Nickel	Ni	0.79	0.79	0.52	µg/L	J		10.92			0.62	0.69	0.441	99	0.80	0.52	**0.8**
1C-SW			Zinc	Zn	15	15	2.9	µg/L			10.92			0.61	0.68	0.434	99	15.13	2.93	**15**
2-PW	10-4-22 8:50	10-13-22 12:07	Lithium	Li	5100	5100	8.3	µg/L		86000	9.14	100	0.311	0.90	1.00	0.311	94	--	--	**--**
2-PW			Cadmium	Cd	ND	0	0.22	µg/L			9.14			0.63	0.70	0.218	86	0.00	0.25	**< 0.25**
2-PW			Chromium	Cr	ND	0	1.5	µg/L			9.14			0.52	0.58	0.180	81	0.00	1.86	**< 1.9**
2-PW			Copper	Cu	3.6	3.6	1.1	µg/L			9.14			0.62	0.69	0.215	86	4.19	1.28	**4.2**
2-PW			Iron	Fe	1400	1400	28	µg/L			9.14			0.63	0.70	0.218	86	1620.75	32.42	**1600**
2-PW			Lead	Pb	ND	0	0.17	µg/L			9.14			0.83	0.92	0.287	93	0.00	0.18	**< 0.18**
2-PW			Manganese	Mn	77	77	1.3	µg/L			9.14			0.62	0.69	0.215	86	89.60	1.51	**90**
2-PW			Mercury	Hg	ND	0	0.13	µg/L			9.14			0.74	0.82	0.256	90	0.00	0.14	**< 0.14**
2-PW			Nickel	Ni	ND	0	0.52	µg/L			9.14			0.62	0.69	0.215	86	0.00	0.61	**< 0.61**
2-PW			Zinc	Zn	3.1	3.1	2.9	µg/L	J		9.14			0.61	0.68	0.211	85	3.63	3.39	**3.6**

Table A1. Calculation of Cfree values using the lithium tracer, San Diego peeper samples.

Equilibrium Correction of Porewater Concentration using Lithium Tracer

Sample ID	Sample Deployment Date	Sample Collection Date	Chemical Name	Chemical Abreviation	Report Result Text	Measured Concentration in Peeper	MDL in Peeper	Report Result Unit	Lab Qualifiers	Initial Li Concentration (µg/L)	Deployment Time (days)	Assumed Li Concentration External to Peeper (µg/L)	Sample-Specific Elimination Rate for Li (K_{Li}) (day^{-1})	Diffusion Coefficient for Analytes (Di) (* 10^{-5} cm^2/s)	Di ÷ D_{Li}	Sample-specific Elimination Rate for Analytes (K_i) (day-1)	Percent Equilibrium Reached (%)	Equilibrium Corrected Concentration (µg/L)	Equilibrium Corrected MDL (µg/L)	Equilibrium Corrected Result (µg/L) 2-sig figs
2-SW	10-4-22 8:50	10-13-22 12:06	Lithium	Li	180	180	0.83	µg/L		86000	9.14	100	0.764	0.90	1.00	0.764	100	--	--	**--**
2-SW			Cadmium	Cd	ND	0	0.22	µg/L			9.14			0.63	0.70	0.536	99	0.00	0.22	**< 0.22**
2-SW			Chromium	Cr	ND	0	1.5	µg/L			9.14			0.52	0.58	0.442	98	0.00	1.53	**< 1.5**
2-SW			Copper	Cu	6.6	6.6	1.1	µg/L			9.14			0.62	0.69	0.527	99	6.65	1.11	**6.7**
2-SW			Iron	Fe	ND	0	28	µg/L			9.14			0.63	0.70	0.536	99	0.00	28.21	**< 28**
2-SW			Lead	Pb	0.18	0.18	0.17	µg/L	J		9.14			0.83	0.92	0.706	100	0.18	0.17	**0.18**
2-SW			Manganese	Mn	6.3	6.3	1.3	µg/L			9.14			0.62	0.69	0.527	99	6.35	1.31	**6.4**
2-SW			Mercury	Hg	ND	0	0.13	µg/L			9.14			0.74	0.82	0.629	100	0.00	0.13	**< 0.13**
2-SW			Nickel	Ni	0.71	0.71	0.52	µg/L	J		9.14			0.62	0.69	0.527	99	0.72	0.52	**0.72**
2-SW			Zinc	Zn	11	11	2.9	µg/L			9.14			0.61	0.68	0.519	99	11.10	2.93	**11**
3-PW	10-3-22 15:00	10-14-22 14:02	Lithium	Li	18000	18000	28	µg/L		86000	10.96	100	0.143	0.90	1.00	0.143	79	--	--	**--**
3-PW			Cadmium	Cd	ND	0	0.36	µg/L			10.96			0.63	0.70	0.100	67	0.00	0.54	**< 0.54**
3-PW			Chromium	Cr	ND	0	2.6	µg/L			10.96			0.52	0.58	0.083	60	0.00	4.36	**< 4.4**
3-PW			Copper	Cu	ND	0	1.9	µg/L			10.96			0.62	0.69	0.099	66	0.00	2.87	**< 2.9**
3-PW			Iron	Fe	150	150	46	µg/L			10.96			0.63	0.70	0.100	67	224.90	68.97	**220**
3-PW			Lead	Pb	ND	0	0.28	µg/L			10.96			0.83	0.92	0.132	77	0.00	0.37	**< 0.37**
3-PW			Manganese	Mn	18	18	2.2	µg/L			10.96			0.62	0.69	0.099	66	27.23	3.33	**27**
3-PW			Mercury	Hg	ND	0	0.33	µg/L			10.96			0.74	0.82	0.118	73	0.00	0.46	**< 0.46**
3-PW			Nickel	Ni	1.1	1.1	0.86	µg/L	J		10.96			0.62	0.69	0.099	66	1.66	1.30	**1.7**
3-PW			Zinc	Zn	11	11	4.8	µg/L			10.96			0.61	0.68	0.097	66	16.79	7.33	**17**
3-SW	10-3-22 15:00	10-14-22 14:02	Lithium	Li	170	170	0.83	µg/L		86000	10.96	100	0.649	0.90	1.00	0.649	100	--	--	**--**
3-SW			Cadmium	Cd	ND	0	0.22	µg/L			10.96			0.63	0.70	0.455	99	0.00	0.22	**< 0.22**
3-SW			Chromium	Cr	ND	0	1.5	µg/L			10.96			0.52	0.58	0.376	98	0.00	1.52	**< 1.5**
3-SW			Copper	Cu	6.2	6.2	1.1	µg/L			10.96			0.62	0.69	0.448	99	6.25	1.11	**6.2**
3-SW			Iron	Fe	ND	0	28	µg/L			10.96			0.63	0.70	0.455	99	0.00	28.19	**< 28**
3-SW			Lead	Pb	ND	0	0.17	µg/L			10.96			0.83	0.92	0.599	100	0.00	0.17	**< 0.17**
3-SW			Manganese	Mn	6.5	6.5	1.3	µg/L			10.96			0.62	0.69	0.448	99	6.55	1.31	**6.5**
3-SW			Mercury	Hg	ND	0	0.13	µg/L			10.96			0.74	0.82	0.534	100	0.00	0.13	**< 0.13**
3-SW			Nickel	Ni	0.79	0.79	0.52	µg/L	J		10.96			0.62	0.69	0.448	99	0.80	0.52	**0.8**
3-SW			Zinc	Zn	10	10	2.9	µg/L			10.96			0.61	0.68	0.441	99	10.08	2.92	**10**
4-PW	10-4-22 10:34	10-14-22 14:20	Lithium	Li	170	170	0.83	µg/L		86000	10.16	100	0.700	0.90	1.00	0.700	100	--	--	**--**
4-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.16			0.63	0.70	0.491	99	0.00	0.22	**< 0.22**
4-PW			Chromium	Cr	ND	0	1.5	µg/L			10.16			0.52	0.58	0.405	98	0.00	1.52	**< 1.5**
4-PW			Copper	Cu	6.2	6.2	1.1	µg/L			10.16			0.62	0.69	0.483	99	6.25	1.11	**6.2**
4-PW			Iron	Fe	ND	0	28	µg/L			10.16			0.63	0.70	0.491	99	0.00	28.19	**< 28**
4-PW			Lead	Pb	0.2	0.2	0.17	µg/L	J		10.16			0.83	0.92	0.647	100	0.20	0.17	**0.2**
4-PW			Manganese	Mn	5.2	5.2	1.3	µg/L			10.16			0.62	0.69	0.483	99	5.24	1.31	**5.2**
4-PW			Mercury	Hg	ND	0	0.33	µg/L			10.16			0.74	0.82	0.577	100	0.00	0.33	**< 0.33**
4-PW			Nickel	Ni	1.1	1.1	0.52	µg/L			10.16			0.62	0.69	0.483	99	1.11	0.52	**1.1**
4-PW			Zinc	Zn	16	16	2.9	µg/L			10.16			0.61	0.68	0.475	99	16.13	2.92	**16**
4-SW	10-4-22 10:34	10-14-22 14:20	Lithium	Li	170	170	0.9	µg/L		86000	10.16	100	0.700	0.90	1.00	0.700	100	--	--	**--**
4-SW			Cadmium	Cd	ND	0	0.24	µg/L			10.16			0.63	0.70	0.491	99	0.00	0.24	**< 0.24**
4-SW			Chromium	Cr	ND	0	1.7	µg/L			10.16			0.52	0.58	0.405	98	0.00	1.73	**< 1.7**
4-SW			Copper	Cu	5.3	5.3	1.2	µg/L			10.16			0.62	0.69	0.483	99	5.34	1.21	**5.3**
4-SW			Iron	Fe	63	63	30	µg/L			10.16			0.63	0.70	0.491	99	63.43	30.21	**63**
4-SW			Lead	Pb	ND	0	0.18	µg/L			10.16			0.83	0.92	0.647	100	0.00	0.18	**< 0.18**
4-SW			Manganese	Mn	8.9	8.9	1.5	µg/L			10.16			0.62	0.69	0.483	99	8.97	1.51	**9**
4-SW			Mercury	Hg	ND	0	0.13	µg/L			10.16			0.74	0.82	0.577	100	0.00	0.13	**< 0.13**
4-SW			Nickel	Ni	1	1	0.56	µg/L	J		10.16			0.62	0.69	0.483	99	1.01	0.56	**1**
4-SW			Zinc	Zn	8.9	8.9	3.1	µg/L			10.16			0.61	0.68	0.475	99	8.97	3.13	**9**
5-PW	10-4-22 9:17	10-14-22 15:52	Lithium	Li	15000	15000	42	µg/L		86000	10.27	100	0.171	0.90	1.00	0.171	83	--	--	**--**
5-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.27			0.63	0.70	0.120	71	0.00	0.31	**< 0.31**
5-PW			Chromium	Cr	ND	0	1.5	µg/L			10.27			0.52	0.58	0.099	64	0.00	2.35	**< 2.4**
5-PW			Copper	Cu	1.8	1.8	1.1	µg/L	J		10.27			0.62	0.69	0.118	70	2.57	1.57	**2.6**
5-PW			Iron	Fe	1500	1500	28	µg/L			10.27			0.63	0.70	0.120	71	2121.18	39.60	**2100**
5-PW			Lead	Pb	ND	0	0.17	µg/L			10.27			0.83	0.92	0.157	80	0.00	0.21	**< 0.21**
5-PW			Manganese	Mn	110	110	1.3	µg/L			10.27			0.62	0.69	0.118	70	156.83	1.85	**160**
5-PW			Mercury	Hg	ND	0	0.13	µg/L			10.27			0.74	0.82	0.140	76	0.00	0.17	**< 0.17**
5-PW			Nickel	Ni	ND	0	0.52	µg/L			10.27			0.62	0.69	0.118	70	0.00	0.74	**< 0.74**
5-PW			Zinc	Zn	3	3	2.9	µg/L	J		10.27			0.61	0.68	0.116	70	4.31	4.17	**4.3**
5-SW	10-4-22 9:17	10-14-22 15:52	Lithium	Li	170	170	0.83	µg/L		86000	10.27	100	0.692	0.90	1.00	0.692	100	--	--	**--**
5-SW			Cadmium	Cd	ND	0	0.22	µg/L			10.27			0.63	0.70	0.485	99	0.00	0.22	**< 0.22**
5-SW			Chromium	Cr	ND	0	1.5	µg/L			10.27			0.52	0.58	0.401	98	0.00	1.52	**< 1.5**
5-SW			Copper	Cu	5.6	5.6	1.1	µg/L			10.27			0.62	0.69	0.478	99	5.64	1.11	**5.6**
5-SW			Iron	Fe	ND	0	28	µg/L			10.27			0.63	0.70	0.485	99	0.00	28.19	**< 28**
5-SW			Lead	Pb	0.23	0.23	0.17	µg/L	J		10.27			0.83	0.92	0.639	100	0.23	0.17	**0.23**
5-SW			Manganese	Mn	7.7	7.7	1.3	µg/L			10.27			0.62	0.69	0.478	99	7.76	1.31	**7.8**
5-SW			Mercury	Hg	ND	0	0.13	µg/L			10.27			0.74	0.82	0.570	100	0.00	0.13	**< 0.13**
5-SW			Nickel	Ni	0.97	0.97	0.52	µg/L	J		10.27			0.62	0.69	0.478	99	0.98	0.52	**0.98**
5-SW			Zinc	Zn	12	12	2.9	µg/L			10.27			0.61	0.68	0.470	99	12.10	2.92	**12**

Table A1. Calculation of Cfree values using the lithium tracer, San Diego peeper samples.

Equilibrium Correction of Porewater Concentration using Lithium Tracer

Sample ID	Sample Deployment Date	Sample Collection Date	Chemical Name	Chemical Abreviation	Report Result Text	Measured Concentration in Peeper	MDL in Peeper	Report Result Unit	Lab Qualifiers	Initial Li Concentration (µg/L)	Deployment Time (days)	Assumed Li Concentration External to Peeper (µg/L)	Sample-Specific Elimination Rate for Li (K_{Li}) (day^{-1})	Diffusion Coefficient for Analytes (Di) (* 10^{-5} cm^2/s)	Di ÷ D_{Li}	Sample-specific Elimination Rate for Analytes (K_i) (day-1)	Percent Equilibrium Reached (%)	Equilibrium Corrected Concentration (µg/L)	Equilibrium Corrected MDL (µg/L)	Equilibrium Corrected Result (µg/L) 2-sig figs
6-PW	10-4-22 10:54	10-14-22 12:49	Lithium	Li	17000	17000	42	µg/L		86000	10.08	100	0.161	0.90	1.00	0.161	80	--	--	**--**
6-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.08			0.63	0.70	0.113	68	0.00	0.32	**< 0.32**
6-PW			Chromium	Cr	ND	0	1.5	µg/L			10.08			0.52	0.58	0.093	61	0.00	2.46	**< 2.5**
6-PW			Copper	Cu	ND	0	1.1	µg/L			10.08			0.62	0.69	0.111	67	0.00	1.63	**< 1.6**
6-PW			Iron	Fe	3100	3100	28	µg/L			10.08			0.63	0.70	0.113	68	4558.01	41.17	**4600**
6-PW			Lead	Pb	ND	0	0.17	µg/L			10.08			0.83	0.92	0.149	78	0.00	0.22	**< 0.22**
6-PW			Manganese	Mn	150	150	1.3	µg/L			10.08			0.62	0.69	0.111	67	222.46	1.93	**220**
6-PW			Mercury	Hg	ND	0	0.13	µg/L			10.08			0.74	0.82	0.133	74	0.00	0.18	**< 0.18**
6-PW			Nickel	Ni	ND	0	0.52	µg/L			10.08			0.62	0.69	0.111	67	0.00	0.77	**< 0.77**
6-PW			Zinc	Zn	ND	0	2.9	µg/L			10.08			0.61	0.68	0.109	67	0.00	4.34	**< 4.3**
6-SW	10-4-22 10:54	10-14-22 12:49	Lithium	Li	180	180	0.83	µg/L		86000	10.08	100	0.692	0.90	1.00	0.692	100	--	--	**--**
6-SW			Cadmium	Cd	ND	0	0.22	µg/L			10.08			0.63	0.70	0.485	99	0.00	0.22	**< 0.22**
6-SW			Chromium	Cr	ND	0	1.5	µg/L			10.08			0.52	0.58	0.401	98	0.00	1.53	**< 1.5**
6-SW			Copper	Cu	4.8	4.8	1.1	µg/L			10.08			0.62	0.69	0.478	99	4.84	1.11	**4.8**
6-SW			Iron	Fe	ND	0	28	µg/L			10.08			0.63	0.70	0.485	99	0.00	28.21	**< 28**
6-SW			Lead	Pb	0.26	0.26	0.17	µg/L	J		10.08			0.83	0.92	0.639	100	0.26	0.17	**0.26**
6-SW			Manganese	Mn	6.9	6.9	1.3	µg/L			10.08			0.62	0.69	0.478	99	6.96	1.31	**7**
6-SW			Mercury	Hg	ND	0	0.33	µg/L			10.08			0.74	0.82	0.570	100	0.00	0.33	**< 0.33**
6-SW			Nickel	Ni	0.77	0.77	0.52	µg/L	J		10.08			0.62	0.69	0.478	99	0.78	0.52	**0.78**
6-SW			Zinc	Zn	10	10	2.9	µg/L			10.08			0.61	0.68	0.470	99	10.09	2.93	**10**
7-PW	10-4-22 9:59	10-14-22 15:33	Lithium	Li	9600	9600	21	µg/L		86000	10.23	100	0.215	0.90	1.00	0.215	89	--	--	**--**
7-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.23			0.63	0.70	0.151	79	0.00	0.28	**< 0.28**
7-PW			Chromium	Cr	ND	0	1.5	µg/L			10.23			0.52	0.58	0.125	72	0.00	2.08	**< 2.1**
7-PW			Copper	Cu	1.1	1.1	1.1	µg/L	J		10.23			0.62	0.69	0.148	78	1.41	1.41	**< 1.4**
7-PW			Iron	Fe	1200	1200	28	µg/L			10.23			0.63	0.70	0.151	79	1525.95	35.61	**1500**
7-PW			Lead	Pb	ND	0	0.17	µg/L			10.23			0.83	0.92	0.199	87	0.00	0.20	**< 0.2**
7-PW			Manganese	Mn	98	98	1.3	µg/L			10.23			0.62	0.69	0.148	78	125.46	1.66	**130**
7-PW			Mercury	Hg	ND	0	0.13	µg/L			10.23			0.74	0.82	0.177	84	0.00	0.16	**< 0.16**
7-PW			Nickel	Ni	0.77	0.77	0.52	µg/L	J		10.23			0.62	0.69	0.148	78	0.99	0.67	**0.99**
7-PW			Zinc	Zn	6.2	6.2	2.9	µg/L			10.23			0.61	0.68	0.146	78	7.99	3.74	**8**
7-SW	10-4-22 9:59	10-14-22 15:33	Lithium	Li	190	190	0.83	µg/L		86000	10.23	100	0.671	0.90	1.00	0.671	100	--	--	**--**
7-SW			Cadmium	Cd	ND	0	0.22	µg/L			10.23			0.63	0.70	0.470	99	0.00	0.22	**< 0.22**
7-SW			Chromium	Cr	ND	0	1.5	µg/L			10.23			0.52	0.58	0.388	98	0.00	1.53	**< 1.5**
7-SW			Copper	Cu	5.5	5.5	1.1	µg/L			10.23			0.62	0.69	0.463	99	5.55	1.11	**5.5**
7-SW			Iron	Fe	29	29	28	µg/L	J		10.23			0.63	0.70	0.470	99	29.24	28.23	**29**
7-SW			Lead	Pb	0.26	0.26	0.17	µg/L	J		10.23			0.83	0.92	0.619	100	0.26	0.17	**0.26**
7-SW			Manganese	Mn	7.5	7.5	1.3	µg/L			10.23			0.62	0.69	0.463	99	7.57	1.31	**7.6**
7-SW			Mercury	Hg	ND	0	0.13	µg/L			10.23			0.74	0.82	0.552	100	0.00	0.13	**< 0.13**
7-SW			Nickel	Ni	0.96	0.96	0.52	µg/L	J		10.23			0.62	0.69	0.463	99	0.97	0.52	**0.97**
7-SW			Zinc	Zn	13	13	2.9	µg/L			10.23			0.61	0.68	0.455	99	13.12	2.93	**13**

Table A2. Calculation of Cfree values using the bromide tracer, San Diego peeper samples.

Equilibrium Correction of Porewater Concentration using Bromide Tracer

Sample ID	Sample Deployment Date	Sample Collection Date	Chemical Name	Chemical Abreviation	Report Result Text	Measured Concentration in Peeper	MDL in Peeper	Report Result Unit	Lab Qualifiers	Initial Br Concentration (mg/L)	Deployment Time (days)	Assumed Br Concentration External to Peeper (mg/L)	Sample-Specific Elimintation Rate for Br (K_{Br}) (day^{-1})	Diffusion Coefficient for Analytes (Di) (* 10^{-5} cm^2/s)	Di ÷ D_{Br}	Sample-specific Elimination Rate for Analytes (K_i) (day-1)	Percent Equilibrium Reached (%)	Equilibrium Corrected Concentration (µg/L)	Equilibrium Corrected MDL (µg/L)	Equilibrium Corrected Result (µg/L) 2-sig figs
1A-PW	10-3-22 12:30	10-14-22 14:58	Bromide	Br	220	220	2.7	mg/L		980	11.10	65	0.160	1.82	1.00	0.160	83	--	--	**--**
1A-PW			Cadmium	Cd	ND	0	0.27	µg/L			11.10			0.63	0.35	0.055	46	0.00	0.59	**< 0.59**
1A-PW			Chromium	Cr	ND	0	1.9	µg/L			11.10			0.52	0.29	0.046	40	0.00	4.78	**< 4.8**
1A-PW			Copper	Cu	3.2	3.2	1.4	µg/L			11.10			0.62	0.34	0.054	45	7.05	3.08	**7.1**
1A-PW			Iron	Fe	220	220	35	µg/L			11.10			0.63	0.35	0.055	46	479.16	76.23	**480**
1A-PW			Lead	Pb	0.88	0.88	0.21	µg/L	J		11.10			0.83	0.46	0.073	56	1.59	0.38	**1.6**
1A-PW			Manganese	Mn	25	25	1.7	µg/L			11.10			0.62	0.34	0.054	45	55.09	3.75	**55**
1A-PW			Mercury	Hg	ND	0	0.13	µg/L			11.10			0.74	0.41	0.065	51	0.00	0.25	**< 0.25**
1A-PW			Nickel	Ni	ND	0	0.65	µg/L			11.10			0.62	0.34	0.054	45	0.00	1.43	**< 1.4**
1A-PW			Zinc	Zn	13	13	3.6	µg/L			11.10			0.61	0.34	0.054	45	28.99	8.03	**29**
1A-SW	10-3-22 12:30	10-14-22 14:58	Bromide	Br	120	120	2.7	mg/L		980	11.10	65	0.253	1.82	1.00	0.253	94	--	--	**--**
1A-SW			Cadmium	Cd	ND	0	0.36	µg/L			11.10			0.63	0.35	0.088	62	0.00	0.58	**< 0.58**
1A-SW			Chromium	Cr	20	20	2.6	µg/L			11.10			0.52	0.29	0.072	55	36.22	4.71	**36**
1A-SW			Copper	Cu	13	13	1.9	µg/L			11.10			0.62	0.34	0.086	62	21.09	3.08	**21**
1A-SW			Iron	Fe	110	110	46	µg/L			11.10			0.63	0.35	0.088	62	176.81	73.94	**180**
1A-SW			Lead	Pb	0.36	0.36	0.28	µg/L	J		11.10			0.83	0.46	0.115	72	0.50	0.39	**0.5**
1A-SW			Manganese	Mn	12	12	2.2	µg/L			11.10			0.62	0.34	0.086	62	19.47	3.57	**19**
1A-SW			Mercury	Hg	ND	0	0.33	µg/L			11.10			0.74	0.41	0.103	68	0.00	0.48	**< 0.48**
1A-SW			Nickel	Ni	29	29	0.86	µg/L			11.10			0.62	0.34	0.086	62	47.06	1.40	**47**
1A-SW			Zinc	Zn	23	23	4.8	µg/L			11.10			0.61	0.34	0.085	61	37.69	7.87	**38**
1B-PW	10-3-22 13:25	10-14-22 14:56	Bromide	Br	120	120	2.7	mg/L		980	11.06	65	0.254	1.82	1.00	0.254	94	--	--	**--**
1B-PW			Cadmium	Cd	ND	0	0.22	µg/L			11.06			0.63	0.35	0.088	62	0.00	0.35	**< 0.35**
1B-PW			Chromium	Cr	ND	0	1.5	µg/L			11.06			0.52	0.29	0.073	55	0.00	2.72	**< 2.7**
1B-PW			Copper	Cu	4.8	4.8	1.1	µg/L			11.06			0.62	0.34	0.087	62	7.79	1.78	**7.8**
1B-PW			Iron	Fe	4400	4400	28	µg/L			11.06			0.63	0.35	0.088	62	7072.31	45.01	**7100**
1B-PW			Lead	Pb	0.39	0.39	0.17	µg/L	J		11.06			0.83	0.46	0.116	72	0.54	0.24	**0.54**
1B-PW			Manganese	Mn	230	230	1.3	µg/L			11.06			0.62	0.34	0.087	62	373.22	2.11	**370**
1B-PW			Mercury	Hg	ND	0	0.13	µg/L			11.06			0.74	0.41	0.103	68	0.00	0.19	**< 0.19**
1B-PW			Nickel	Ni	1	1	0.52	µg/L			11.06			0.62	0.34	0.087	62	1.62	0.84	**1.6**
1B-PW			Zinc	Zn	20	20	2.9	µg/L			11.06			0.61	0.34	0.085	61	32.77	4.75	**33**
1B-SW	10-3-22 13:25	10-14-22 14:56	Bromide	Br	120	120	2.7	mg/L		980	11.06	65	0.254	1.82	1.00	0.254	94	--	--	**--**
1B-SW			Cadmium	Cd	ND	0	0.22	µg/L			11.06			0.63	0.35	0.088	62	0.00	0.35	**< 0.35**
1B-SW			Chromium	Cr	ND	0	1.5	µg/L			11.06			0.52	0.29	0.073	55	0.00	2.72	**< 2.7**
1B-SW			Copper	Cu	10	10	1.1	µg/L			11.06			0.62	0.34	0.087	62	16.23	1.78	**16**
1B-SW			Iron	Fe	ND	0	28	µg/L			11.06			0.63	0.35	0.088	62	0.00	45.01	**< 45**
1B-SW			Lead	Pb	0.45	0.45	0.17	µg/L	J		11.06			0.83	0.46	0.116	72	0.62	0.24	**0.62**
1B-SW			Manganese	Mn	5.2	5.2	1.3	µg/L			11.06			0.62	0.34	0.087	62	8.44	2.11	**8.4**
1B-SW			Mercury	Hg	ND	0	0.13	µg/L			11.06			0.74	0.41	0.103	68	0.00	0.19	**< 0.19**
1B-SW			Nickel	Ni	1	1	0.52	µg/L			11.06			0.62	0.34	0.087	62	1.62	0.84	**1.6**
1B-SW			Zinc	Zn	33	33	2.9	µg/L			11.06			0.61	0.34	0.085	61	54.07	4.75	**54**
1C-PW	10-3-22 13:50	10-14-22 11:51	Bromide	Br	230	230	2.7	mg/L		980	10.92	65	0.157	1.82	1.00	0.157	82	--	--	**--**
1C-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.92			0.63	0.35	0.054	45	0.00	0.49	**< 0.49**
1C-PW			Chromium	Cr	ND	0	1.5	µg/L			10.92			0.52	0.29	0.045	39	0.00	3.88	**< 3.9**
1C-PW			Copper	Cu	2.6	2.6	1.1	µg/L			10.92			0.62	0.34	0.053	44	5.88	2.49	**5.9**
1C-PW			Iron	Fe	230	230	28	µg/L			10.92			0.63	0.35	0.054	45	514.19	62.60	**510**
1C-PW			Lead	Pb	ND	0	0.17	µg/L			10.92			0.83	0.46	0.072	54	0.00	0.31	**< 0.31**
1C-PW			Manganese	Mn	36	36	1.3	µg/L			10.92			0.62	0.34	0.053	44	81.43	2.94	**81**
1C-PW			Mercury	Hg	ND	0	0.13	µg/L			10.92			0.74	0.41	0.064	50	0.00	0.26	**< 0.26**
1C-PW			Nickel	Ni	ND	0	0.52	µg/L			10.92			0.62	0.34	0.053	44	0.00	1.18	**< 1.2**
1C-PW			Zinc	Zn	5.6	5.6	2.9	µg/L			10.92			0.61	0.34	0.053	44	12.82	6.64	**13**
1C-SW	10-3-22 13:50	10-14-22 11:51	Bromide	Br	120	120	2.7	mg/L	^2	980	10.92	65	0.258	1.82	1.00	0.258	94	--	--	**--**
1C-SW			Cadmium	Cd	0.36	0.36	0.22	µg/L	J		10.92			0.63	0.35	0.089	62	0.58	0.35	**0.58**
1C-SW			Chromium	Cr	ND	0	1.5	µg/L			10.92			0.52	0.29	0.074	55	0.00	2.72	**< 2.7**
1C-SW			Copper	Cu	7.4	7.4	1.1	µg/L			10.92			0.62	0.34	0.088	62	12.01	1.78	**12**
1C-SW			Iron	Fe	ND	0	28	µg/L			10.92			0.63	0.35	0.089	62	0.00	45.01	**< 45**
1C-SW			Lead	Pb	0.17	0.17	0.17	µg/L	J		10.92			0.83	0.46	0.117	72	0.24	0.24	**< 0.24**
1C-SW			Manganese	Mn	6.6	6.6	1.3	µg/L			10.92			0.62	0.34	0.088	62	10.71	2.11	**11**
1C-SW			Mercury	Hg	ND	0	0.13	µg/L			10.92			0.74	0.41	0.105	68	0.00	0.19	**< 0.19**
1C-SW			Nickel	Ni	0.79	0.79	0.52	µg/L	J		10.92			0.62	0.34	0.088	62	1.28	0.84	**1.3**
1C-SW			Zinc	Zn	15	15	2.9	µg/L			10.92			0.61	0.34	0.086	61	24.58	4.75	**25**
2-PW	10-4-22 8:50	10-13-22 12:07	Bromide	Br	120	120	2.7	mg/L	^2	980	9.14	65	0.308	1.82	1.00	0.308	94	--	--	**--**
2-PW			Cadmium	Cd	ND	0	0.22	µg/L			9.14			0.63	0.35	0.107	62	0.00	0.35	**< 0.35**
2-PW			Chromium	Cr	ND	0	1.5	µg/L			9.14			0.52	0.29	0.088	55	0.00	2.72	**< 2.7**
2-PW			Copper	Cu	3.6	3.6	1.1	µg/L			9.14			0.62	0.34	0.105	62	5.84	1.78	**5.8**
2-PW			Iron	Fe	1400	1400	28	µg/L			9.14			0.63	0.35	0.107	62	2250.28	45.01	**2300**
2-PW			Lead	Pb	ND	0	0.17	µg/L			9.14			0.83	0.46	0.140	72	0.00	0.24	**< 0.24**
2-PW			Manganese	Mn	77	77	1.3	µg/L			9.14			0.62	0.34	0.105	62	124.95	2.11	**120**
2-PW			Mercury	Hg	ND	0	0.13	µg/L			9.14			0.74	0.41	0.125	68	0.00	0.19	**< 0.19**
2-PW			Nickel	Ni	ND	0	0.52	µg/L			9.14			0.62	0.34	0.105	62	0.00	0.84	**< 0.84**
2-PW			Zinc	Zn	3.1	3.1	2.9	µg/L	J		9.14			0.61	0.34	0.103	61	5.08	4.75	**5.1**

Table A2. Calculation of Cfree values using the bromide tracer, San Diego peeper samples.

Equilibrium Correction of Porewater Concentration using Bromide Tracer

Sample ID	Sample Deployment Date	Sample Collection Date	Chemical Name	Chemical Abreviation	Report Result Text	Measured Concentration in Peeper	MDL in Peeper	Report Result Unit	Lab Qualifiers	Initial Br Concentration (mg/L)	Deployment Time (days)	Assumed Br Concentration External to Peeper (mg/L)	Sample-Specific Elimintation Rate for Br (K_{Br}) (day^{-1})	Diffusion Coefficient for Analytes (Di) $(* 10^{-5} cm^2/s)$	Di ÷ D_{Br}	Sample-specific Elimination Rate for Analytes (K_i) (day-1)	Percent Equilibrium Reached (%)	Equilibrium Corrected Concentration (µg/L)	Equilibrium Corrected MDL (µg/L)	Equilibrium Corrected Result (µg/L) 2-sig figs
2-SW	10-4-22 8:50	10-13-22 12:06	Bromide	Br	110	110	2.7	mg/L	^2	980	9.14	65	0.330	1.82	1.00	0.330	95	--	--	**--**
2-SW			Cadmium	Cd	ND	0	0.22	µg/L			9.14			0.63	0.35	0.114	65	0.00	0.34	**< 0.34**
2-SW			Chromium	Cr	ND	0	1.5	µg/L			9.14			0.52	0.29	0.094	58	0.00	2.60	**< 2.6**
2-SW			Copper	Cu	6.6	6.6	1.1	µg/L			9.14			0.62	0.34	0.112	64	10.29	1.71	**10**
2-SW			Iron	Fe	ND	0	28	µg/L			9.14			0.63	0.35	0.114	65	0.00	43.24	**< 43**
2-SW			Lead	Pb	0.18	0.18	0.17	µg/L	J		9.14			0.83	0.46	0.150	75	0.24	0.23	**0.24**
2-SW			Manganese	Mn	6.3	6.3	1.3	µg/L			9.14			0.62	0.34	0.112	64	9.82	2.03	**9.8**
2-SW			Mercury	Hg	ND	0	0.13	µg/L			9.14			0.74	0.41	0.134	71	0.00	0.18	**< 0.18**
2-SW			Nickel	Ni	0.71	0.71	0.52	µg/L	J		9.14			0.62	0.34	0.112	64	1.11	0.81	**1.1**
2-SW			Zinc	Zn	11	11	2.9	µg/L			9.14			0.61	0.34	0.111	64	17.31	4.56	**17**
3-PW	10-3-22 15:00	10-14-22 14:02	Bromide	Br	230	230	2.7	mg/L	^2	980	10.96	65	0.156	1.82	1.00	0.156	82	--	--	**--**
3-PW			Cadmium	Cd	ND	0	0.36	µg/L			10.96			0.63	0.35	0.054	45	0.00	0.80	**< 0.8**
3-PW			Chromium	Cr	ND	0	2.6	µg/L			10.96			0.52	0.29	0.045	39	0.00	6.72	**< 6.7**
3-PW			Copper	Cu	ND	0	1.9	µg/L			10.96			0.62	0.34	0.053	44	0.00	4.30	**< 4.3**
3-PW			Iron	Fe	150	150	46	µg/L			10.96			0.63	0.35	0.054	45	335.34	102.84	**340**
3-PW			Lead	Pb	ND	0	0.28	µg/L			10.96			0.83	0.46	0.071	54	0.00	0.52	**< 0.52**
3-PW			Manganese	Mn	18	18	2.2	µg/L			10.96			0.62	0.34	0.053	44	40.72	4.98	**41**
3-PW			Mercury	Hg	ND	0	0.33	µg/L			10.96			0.74	0.41	0.064	50	0.00	0.66	**< 0.66**
3-PW			Nickel	Ni	1.1	1.1	0.86	µg/L	J		10.96			0.62	0.34	0.053	44	2.49	1.95	**2.5**
3-PW			Zinc	Zn	11	11	4.8	µg/L			10.96			0.61	0.34	0.052	44	25.18	10.99	**25**
3-SW	10-3-22 15:00	10-14-22 14:02	Bromide	Br	140	140	2.7	mg/L	^2	980	10.96	65	0.228	1.82	1.00	0.228	92	--	--	**--**
3-SW			Cadmium	Cd	ND	0	0.22	µg/L			10.96			0.63	0.35	0.079	58	0.00	0.38	**< 0.38**
3-SW			Chromium	Cr	ND	0	1.5	µg/L			10.96			0.52	0.29	0.065	51	0.00	2.94	**< 2.9**
3-SW			Copper	Cu	6.2	6.2	1.1	µg/L			10.96			0.62	0.34	0.078	57	10.81	1.92	**11**
3-SW			Iron	Fe	ND	0	28	µg/L			10.96			0.63	0.35	0.079	58	0.00	48.33	**< 48**
3-SW			Lead	Pb	ND	0	0.17	µg/L			10.96			0.83	0.46	0.104	68	0.00	0.25	**< 0.25**
3-SW			Manganese	Mn	6.5	6.5	1.3	µg/L			10.96			0.62	0.34	0.078	57	11.33	2.27	**11**
3-SW			Mercury	Hg	ND	0	0.13	µg/L			10.96			0.74	0.41	0.093	64	0.00	0.20	**< 0.2**
3-SW			Nickel	Ni	0.79	0.79	0.52	µg/L	J		10.96			0.62	0.34	0.078	57	1.38	0.91	**1.4**
3-SW			Zinc	Zn	10	10	2.9	µg/L			10.96			0.61	0.34	0.076	57	17.62	5.11	**18**
4-PW	10-4-22 10:34	10-14-22 14:20	Bromide	Br	130	130	2.7	mg/L	^2	980	10.16	65	0.260	1.82	1.00	0.260	93	--	--	**--**
4-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.16			0.63	0.35	0.090	60	0.00	0.37	**< 0.37**
4-PW			Chromium	Cr	ND	0	1.5	µg/L			10.16			0.52	0.29	0.074	53	0.00	2.83	**< 2.8**
4-PW			Copper	Cu	6.2	6.2	1.1	µg/L			10.16			0.62	0.34	0.089	59	10.44	1.85	**10**
4-PW			Iron	Fe	ND	0	28	µg/L			10.16			0.63	0.35	0.090	60	0.00	46.69	**< 47**
4-PW			Lead	Pb	0.2	0.2	0.17	µg/L	J		10.16			0.83	0.46	0.119	70	0.29	0.24	**0.29**
4-PW			Manganese	Mn	5.2	5.2	1.3	µg/L			10.16			0.62	0.34	0.089	59	8.76	2.19	**8.8**
4-PW			Mercury	Hg	ND	0	0.33	µg/L			10.16			0.74	0.41	0.106	66	0.00	0.50	**< 0.5**
4-PW			Nickel	Ni	1.1	1.1	0.52	µg/L			10.16			0.62	0.34	0.089	59	1.85	0.88	**1.9**
4-PW			Zinc	Zn	16	16	2.9	µg/L			10.16			0.61	0.34	0.087	59	27.22	4.93	**27**
4-SW	10-4-22 10:34	10-14-22 14:20	Bromide	Br	130	130	2.7	µg/L	^2	980	10.16	65	0.260	1.82	1.00	0.260	93	--	--	**--**
4-SW			Cadmium	Cd	ND	0	0.24	µg/L			10.16			0.63	0.35	0.090	60	0.00	0.40	**< 0.4**
4-SW			Chromium	Cr	ND	0	1.7	µg/L			10.16			0.52	0.29	0.074	53	0.00	3.21	**< 3.2**
4-SW			Copper	Cu	5.3	5.3	1.2	µg/L			10.16			0.62	0.34	0.089	59	8.93	2.02	**8.9**
4-SW			Iron	Fe	63	63	30	µg/L			10.16			0.63	0.35	0.090	60	105.06	50.03	**110**
4-SW			Lead	Pb	ND	0	0.18	µg/L			10.16			0.83	0.46	0.119	70	0.00	0.26	**< 0.26**
4-SW			Manganese	Mn	8.9	8.9	1.5	µg/L			10.16			0.62	0.34	0.089	59	14.99	2.53	**15**
4-SW			Mercury	Hg	ND	0	0.13	µg/L			10.16			0.74	0.41	0.106	66	0.00	0.20	**< 0.2**
4-SW			Nickel	Ni	1	1	0.56	µg/L	J		10.16			0.62	0.34	0.089	59	1.68	0.94	**1.7**
4-SW			Zinc	Zn	8.9	8.9	3.1	µg/L			10.16			0.61	0.34	0.087	59	15.14	5.27	**15**
5-PW	10-4-22 9:17	10-14-22 15:52	Bromide	Br	170	170	2.7	mg/L	^2	980	10.27	65	0.211	1.82	1.00	0.211	89	--	--	**--**
5-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.27			0.63	0.35	0.073	53	0.00	0.42	**< 0.42**
5-PW			Chromium	Cr	ND	0	1.5	µg/L			10.27			0.52	0.29	0.060	46	0.00	3.25	**< 3.3**
5-PW			Copper	Cu	1.8	1.8	1.1	µg/L	J		10.27			0.62	0.34	0.072	52	3.45	2.11	**3.5**
5-PW			Iron	Fe	1500	1500	28	µg/L			10.27			0.63	0.35	0.073	53	2844.38	53.10	**2800**
5-PW			Lead	Pb	ND	0	0.17	µg/L			10.27			0.83	0.46	0.096	63	0.00	0.27	**< 0.27**
5-PW			Manganese	Mn	110	110	1.3	µg/L			10.27			0.62	0.34	0.072	52	210.85	2.49	**210**
5-PW			Mercury	Hg	ND	0	0.13	µg/L			10.27			0.74	0.41	0.086	59	0.00	0.22	**< 0.22**
5-PW			Nickel	Ni	ND	0	0.52	µg/L			10.27			0.62	0.34	0.072	52	0.00	1.00	**< 1**
5-PW			Zinc	Zn	3	3	2.9	µg/L	J		10.27			0.61	0.34	0.071	52	5.81	5.62	**5.8**
5-SW	10-4-22 9:17	10-14-22 15:52	Bromide	Br	130	130	2.7	mg/L	^2	980	10.27	65	0.257	1.82	1.00	0.257	93	--	--	**--**
5-SW			Cadmium	Cd	ND	0	0.22	µg/L			10.27			0.63	0.35	0.089	60	0.00	0.37	**< 0.37**
5-SW			Chromium	Cr	ND	0	1.5	µg/L			10.27			0.52	0.29	0.074	53	0.00	2.83	**< 2.8**
5-SW			Copper	Cu	5.6	5.6	1.1	µg/L			10.27			0.62	0.34	0.088	59	9.43	1.85	**9.4**
5-SW			Iron	Fe	ND	0	28	µg/L			10.27			0.63	0.35	0.089	60	0.00	46.69	**< 47**
5-SW			Lead	Pb	0.23	0.23	0.17	µg/L	J		10.27			0.83	0.46	0.117	70	0.33	0.24	**0.33**
5-SW			Manganese	Mn	7.7	7.7	1.3	µg/L			10.27			0.62	0.34	0.088	59	12.97	2.19	**13**
5-SW			Mercury	Hg	ND	0	0.13	µg/L			10.27			0.74	0.41	0.105	66	0.00	0.20	**< 0.2**
5-SW			Nickel	Ni	0.97	0.97	0.52	µg/L	J		10.27			0.62	0.34	0.088	59	1.63	0.88	**1.6**
5-SW			Zinc	Zn	12	12	2.9	µg/L			10.27			0.61	0.34	0.086	59	20.41	4.93	**20**

Table A2. Calculation of Cfree values using the bromide tracer, San Diego peeper samples.

Equilibrium Correction of Porewater Concentration using Bromide Tracer

Sample ID	Sample Deployment Date	Sample Collection Date	Chemical Name	Chemical Abreviation	Report Result Text	Measured Concentration in Peeper	MDL in Peeper	Report Result Unit	Lab Qualifiers	Initial Br Concentration (mg/L)	Deployment Time (days)	Assumed Br Concentration External to Peeper (mg/L)	Sample-Specific Elimintation Rate for Br (K_{Br}) (day^{-1})	Diffusion Coefficient for Analytes (Di) (* 10^{-5} cm^2/s)	Di ÷ D_{Br}	Sample-specific Elimination Rate for Analytes (K_i) (day-1)	Percent Equilibrium Reached (%)	Equilibrium Corrected Concentration (µg/L)	Equilibrium Corrected MDL (µg/L)	Equilibrium Corrected Result (µg/L) 2-sig figs
6-PW	10-4-22 10:54	10-14-22 12:49	Bromide	Br	220	220	2.7	mg/L	^2	980	10.08	65	0.176	1.82	1.00	0.176	83	--	--	**--**
6-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.08			0.63	0.35	0.061	46	0.00	0.48	**< 0.48**
6-PW			Chromium	Cr	ND	0	1.5	µg/L			10.08			0.52	0.29	0.050	40	0.00	3.77	**< 3.8**
6-PW			Copper	Cu	ND	0	1.1	µg/L			10.08			0.62	0.34	0.060	45	0.00	2.42	**< 2.4**
6-PW			Iron	Fe	3100	3100	28	µg/L			10.08			0.63	0.35	0.061	46	6751.75	60.98	**6800**
6-PW			Lead	Pb	ND	0	0.17	µg/L			10.08			0.83	0.46	0.080	56	0.00	0.31	**< 0.31**
6-PW			Manganese	Mn	150	150	1.3	µg/L			10.08			0.62	0.34	0.060	45	330.51	2.86	**330**
6-PW			Mercury	Hg	ND	0	0.13	µg/L			10.08			0.74	0.41	0.072	51	0.00	0.25	**< 0.25**
6-PW			Nickel	Ni	ND	0	0.52	µg/L			10.08			0.62	0.34	0.060	45	0.00	1.15	**< 1.1**
6-PW			Zinc	Zn	ND	0	2.9	µg/L			10.08			0.61	0.34	0.059	45	0.00	6.47	**< 6.5**
6-SW	10-4-22 10:54	10-14-22 12:49	Bromide	Br	130	130	2.7	mg/L	^2	980	10.08	65	0.262	1.82	1.00	0.262	93	--	--	**--**
6-SW			Cadmium	Cd	ND	0	0.22	µg/L			10.08			0.63	0.35	0.091	60	0.00	0.37	**< 0.37**
6-SW			Chromium	Cr	ND	0	1.5	µg/L			10.08			0.52	0.29	0.075	53	0.00	2.83	**< 2.8**
6-SW			Copper	Cu	4.8	4.8	1.1	µg/L			10.08			0.62	0.34	0.089	59	8.08	1.85	**8.1**
6-SW			Iron	Fe	ND	0	28	µg/L			10.08			0.63	0.35	0.091	60	0.00	46.69	**< 47**
6-SW			Lead	Pb	0.26	0.26	0.17	µg/L	J		10.08			0.83	0.46	0.120	70	0.37	0.24	**0.37**
6-SW			Manganese	Mn	6.9	6.9	1.3	µg/L			10.08			0.62	0.34	0.089	59	11.62	2.19	**12**
6-SW			Mercury	Hg	ND	0	0.33	µg/L			10.08			0.74	0.41	0.107	66	0.00	0.50	**< 0.5**
6-SW			Nickel	Ni	0.77	0.77	0.52	µg/L	J		10.08			0.62	0.34	0.089	59	1.30	0.88	**1.3**
6-SW			Zinc	Zn	10	10	2.9	µg/L			10.08			0.61	0.34	0.088	59	17.01	4.93	**17**
7-PW	10-4-22 9:59	10-14-22 15:33	Bromide	Br	140	140	2.7	mg/L	^2	980	10.23	65	0.244	1.82	1.00	0.244	92	--	--	**--**
7-PW			Cadmium	Cd	ND	0	0.22	µg/L			10.23			0.63	0.35	0.085	58	0.00	0.38	**< 0.38**
7-PW			Chromium	Cr	ND	0	1.5	µg/L			10.23			0.52	0.29	0.070	51	0.00	2.94	**< 2.9**
7-PW			Copper	Cu	1.1	1.1	1.1	µg/L	J		10.23			0.62	0.34	0.083	57	1.92	1.92	**< 1.9**
7-PW			Iron	Fe	1200	1200	28	µg/L			10.23			0.63	0.35	0.085	58	2071.40	48.33	**2100**
7-PW			Lead	Pb	ND	0	0.17	µg/L			10.23			0.83	0.46	0.111	68	0.00	0.25	**< 0.25**
7-PW			Manganese	Mn	98	98	1.3	µg/L			10.23			0.62	0.34	0.083	57	170.88	2.27	**170**
7-PW			Mercury	Hg	ND	0	0.13	µg/L			10.23			0.74	0.41	0.099	64	0.00	0.20	**< 0.2**
7-PW			Nickel	Ni	0.77	0.77	0.52	µg/L	J		10.23			0.62	0.34	0.083	57	1.34	0.91	**1.3**
7-PW			Zinc	Zn	6.2	6.2	2.9	µg/L			10.23			0.61	0.34	0.082	57	10.92	5.11	**11**
7-SW	10-4-22 9:59	10-14-22 15:33	Bromide	Br	130	130	2.7	mg/L	^2	980	10.23	65	0.258	1.82	1.00	0.258	93	--	--	**--**
7-SW			Cadmium	Cd	ND	0	0.22	µg/L			10.23			0.63	0.35	0.089	60	0.00	0.37	**< 0.37**
7-SW			Chromium	Cr	ND	0	1.5	µg/L			10.23			0.52	0.29	0.074	53	0.00	2.83	**< 2.8**
7-SW			Copper	Cu	5.5	5.5	1.1	µg/L			10.23			0.62	0.34	0.088	59	9.26	1.85	**9.3**
7-SW			Iron	Fe	29	29	28	µg/L	J		10.23			0.63	0.35	0.089	60	48.36	46.69	**48**
7-SW			Lead	Pb	0.26	0.26	0.17	µg/L	J		10.23			0.83	0.46	0.118	70	0.37	0.24	**0.37**
7-SW			Manganese	Mn	7.5	7.5	1.3	µg/L			10.23			0.62	0.34	0.088	59	12.63	2.19	**13**
7-SW			Mercury	Hg	ND	0	0.13	µg/L			10.23			0.74	0.41	0.105	66	0.00	0.20	**< 0.2**
7-SW			Nickel	Ni	0.96	0.96	0.52	µg/L	J		10.23			0.62	0.34	0.088	59	1.62	0.88	**1.6**
7-SW			Zinc	Zn	13	13	2.9	µg/L			10.23			0.61	0.34	0.087	59	22.11	4.93	**22**

Table A3. Cfree of metals in sediment porewater and surface water from the San Diego field deployment, as determined with the lithium tracer (top) and bromide tracer (bottom).

Sample ID	Station	Description	Lithium corrected porewater concentration (µg/L)								
			Cd	**Cr**	**Cu**	**Fe**	**Pb**	**Mn**	**Hg**	**Ni**	**Zn**
1A-PW	1A	Sed porewater	< 0.39	< 3	**4.7**	**320**	**1.1**	**36**	< 0.17	< 0.95	**19**
1B-PW	1B	Sed porewater	< 0.23	< 1.6	**4.9**	**4500**	**0.39**	**240**	< 0.13	**1**	**21**
1C-PW	1C	Sed porewater	< 0.34	< 2.6	**4**	**350**	< 0.23	**56**	< 0.18	< 0.8	**8.7**
2-PW	2	Sed porewater	< 0.25	< 1.9	**4.2**	**1600**	< 0.18	**90**	< 0.14	< 0.61	**3.6**
3-PW	3	Sed porewater	< 0.54	< 4.4	< 2.9	**220**	< 0.37	**27**	< 0.46	**1.7**	**17**
4-PW	4	Sed porewater	< 0.22	< 1.5	**6.2**	< 28	**0.2**	**5.2**	< 0.33	**1.1**	**16**
5-PW	5	Sed porewater	< 0.31	< 2.4	**2.6**	**2100**	< 0.21	**160**	< 0.17	< 0.74	**4.3**
6-PW	6	Sed porewater	< 0.32	< 2.5	< 1.6	**4600**	< 0.22	**220**	< 0.18	< 0.77	< 4.3
7-PW	7	Sed porewater	< 0.28	< 2.1	< 1.4	**1500**	< 0.2	**130**	< 0.16	**0.99**	**8**
Sample ID	Station	Description	Lithium corrected sureface water concentration (µg/L)								
			Cd	**Cr**	**Cu**	**Fe**	**Pb**	**Mn**	**Hg**	**Ni**	**Zn**
1A-SW	1A	Surface water	< 0.36	**20**	**13**	**110**	**0.36**	**12**	< 0.33	**29**	**23**
1B-SW	1B	Surface water	< 0.22	< 1.5	**10**	< 28	**0.45**	**5.2**	< 0.13	**1**	**33**
1C-SW	1C	Surface water	**0.36**	< 1.5	**7.5**	< 28	< 0.17	**6.7**	< 0.13	**0.8**	**15**
2-SW	2	Surface water	< 0.22	< 1.5	**6.7**	< 28	**0.18**	**6.4**	< 0.13	**0.72**	**11**
3-SW	3	Surface water	< 0.22	< 1.5	**6.2**	< 28	< 0.17	**6.5**	< 0.13	**0.8**	**10**
4-SW	4	Surface water	< 0.24	< 1.7	**5.3**	**63**	< 0.18	**9**	< 0.13	**1**	**9**
5-SW	5	Surface water	< 0.22	< 1.5	**5.6**	< 28	**0.23**	**7.8**	< 0.13	**0.98**	**12**
6-SW	6	Surface water	< 0.22	< 1.5	**4.8**	< 28	**0.26**	**7**	< 0.33	**0.78**	**10**
7-SW	7	Surface water	< 0.22	< 1.5	**5.5**	**29**	**0.26**	**7.6**	< 0.13	**0.97**	**13**

Sample ID	Station	Description	Bromide corrected porewater concentration (µg/L)								
			Cd	**Cr**	**Cu**	**Fe**	**Pb**	**Mn**	**Hg**	**Ni**	**Zn**
1A-PW	1A	Sed porewater	< 0.59	< 4.8	**7.1**	**480**	**1.6**	**55**	< 0.25	< 1.4	**29**
1B-PW	1B	Sed porewater	< 0.35	< 2.7	**7.8**	**7100**	**0.54**	**370**	< 0.19	**1.6**	**33**
1C-PW	1C	Sed porewater	< 0.49	< 3.9	**5.9**	**510**	< 0.31	**81**	< 0.26	< 1.2	**13**
2-PW	2	Sed porewater	< 0.35	< 2.7	**5.8**	**2300**	< 0.24	**120**	< 0.19	< 0.84	**5.1**
3-PW	3	Sed porewater	< 0.8	< 6.7	< 4.3	**340**	< 0.52	**41**	< 0.66	**2.5**	**25**
4-PW	4	Sed porewater	< 0.37	< 2.8	**10**	< 47	**0.29**	**8.8**	< 0.5	**1.9**	**27**
5-PW	5	Sed porewater	< 0.42	< 3.3	**3.5**	**2800**	< 0.27	**210**	< 0.22	< 1	**5.8**
6-PW	6	Sed porewater	< 0.48	< 3.8	< 2.4	**6800**	< 0.31	**330**	< 0.25	< 1.1	< 6.5
7-PW	7	Sed porewater	< 0.38	< 2.9	< 1.9	**2100**	< 0.25	**170**	< 0.2	**1.3**	**11**
Sample ID	Station	Description	Bromide corrected surface water concentration (µg/L)								
			Cd	**Cr**	**Cu**	**Fe**	**Pb**	**Mn**	**Hg**	**Ni**	**Zn**
1A-SW	1A	Surface water	< 0.58	**36**	**21**	**180**	**0.5**	**19**	< 0.48	**47**	**38**
1B-SW	1B	Surface water	< 0.35	< 2.7	**16**	< 45	**0.62**	**8.4**	< 0.19	**1.6**	**54**
1C-SW	1C	Surface water	**0.58**	< 2.7	**12**	< 45	< 0.24	**11**	< 0.19	**1.3**	**25**
2-SW	2	Surface water	< 0.34	< 2.6	**10**	< 43	**0.24**	**9.8**	< 0.18	**1.1**	**17**
3-SW	3	Surface water	< 0.38	< 2.9	**11**	< 48	< 0.25	**11**	< 0.2	**1.4**	**18**
4-SW	4	Surface water	< 0.4	< 3.2	**8.9**	**110**	< 0.26	**15**	< 0.2	**1.7**	**15**
5-SW	5	Surface water	< 0.37	< 2.8	**9.4**	< 47	**0.33**	**13**	< 0.2	**1.6**	**20**
6-SW	6	Surface water	< 0.37	< 2.8	**8.1**	< 47	**0.37**	**12**	< 0.5	**1.3**	**17**
7-SW	7	Surface water	< 0.37	< 2.8	**9.3**	**48**	**0.37**	**13**	< 0.2	**1.6**	**22**

Appendix B: DGT Calculation Sheets

Table B1. Cfree calculation of metals in surface water from the San Diego field deployment, as determined in DGT.

Sample ID	1. Deployment Date/Time	1. Collection Date/Time	Exposure Duration (Days)	Exposure Duration (s)	3. M - Mass of metal in the resin gel (from Laboratory)								
					Hg (ng)	Cd (µg)	Cr (µg)	Cu (µg)	Fe (µg)	Mn (µg)	Ni (µg)	Pb (µg)	Zn (µg)
2-ME	10-4-22 8:50	10-13-22 12:05	9.14	789300	-	0.0029	0.0053	0.13	0.21	0.23	0.042	0.014	0.59
3-ME	10-3-22 15:00	10-14-22 14:01	10.96	946860	-	0.0044	0.0053	0.11	0.075	0.33	0.052	0.013	0.73
4-ME	10-4-22 10:34	10-14-22 14:18	10.16	877440	-	0.0043	0.0053	0.12	0.14	0.28	0.049	0.014	0.78
5-ME	10-4-22 9:17	10-14-22 15:50	10.27	887580	-	0.004	0.0053	0.12	0.34	0.27	0.038	0.014	0.6
6-ME1	10-4-22 10:54	10-14-22 12:49	10.08	870900	-	0.0041	0.0053	0.11	0.075	0.32	0.045	0.012	0.68
6-ME2	10-4-22 10:54	10-14-22 12:49	10.08	870900	-	0.0038	0.0053	0.11	0.075	0.24	0.043	0.012	0.64
7-ME	10-4-22 9:59	10-14-22 15:32	10.23	883980	-	0.004	0.0053	0.14	0.075	0.19	0.044	0.016	0.75
1A-HG1	10-3-22 12:30	10-14-22 14:58	11.10	959280	0.1	-	-	-	-	-	-	-	-
1A-HG2	10-3-22 12:30	10-14-22 14:58	11.10	959280	0.1	-	-	-	-	-	-	-	-
1B-HG1	10-3-22 13:25	10-14-22 14:57	11.06	955920	0.27	-	-	-	-	-	-	-	-
1B-HG2	10-3-22 13:25	10-14-22 14:57	11.06	955920	0.1	-	-	-	-	-	-	-	-
1C-HG1	10-3-22 13:50	10-14-22 11:51	10.92	943260	0.1	-	-	-	-	-	-	-	-
1C-HG2	10-3-22 13:50	10-14-22 11:51	10.92	943260	0.1	-	-	-	-	-	-	-	-
2-HG	10-4-22 8:50	10-13-22 12:06	9.14	789360	0.1	-	-	-	-	-	-	-	-
3-HG	10-3-22 15:00	10-14-22 14:02	10.96	946920	0.1	-	-	-	-	-	-	-	-
4-HG	10-4-22 10:34	10-14-22 14:20	10.16	877560	0.1	-	-	-	-	-	-	-	-
5-HG	10-4-22 9:17	10-14-22 15:52	10.27	887700	0.1	-	-	-	-	-	-	-	-
7-HG	10-4-22 9:59	10-14-22 15:33	10.23	884040	0.1	-	-	-	-	-	-	-	-

Red values are method detection limits.

Table B1. Cfree calculation of metals in surface water from the San Diego field deployment, as determined in DGT.

2. Average Temperature of Deployment (°C)	**15**

4. Thickness of the diffusive gel (mm)	**4. Thickness of the Membrane (mm)**	**Δg (cm):**	**A - exposure area (cm2):**	**D - Diffusion coefficient of metal in the resin gel (temperature and metal specific)**								
				Hg	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
				6	4.57	3.79	4.68	4.59	4.39	4.33	6.03	4.56
				Final Porewater Concentration								
				[Hg] ng/L	**[Cd] µg/L**	**[Cr] µg/L**	**[Cu] µg/L**	**[Fe] µg/L**	**[Mn] µg/L**	**[Ni] µg/L**	**[Pb] µg/L**	**[Zn] µg/L**
0.8	0.14	0.094	3.14	-	0.024	0.053	1.054	1.74	1.99	0.37	0.088	4.91
0.8	0.14	0.094	3.14	-	0.030	0.044	0.743	0.52	2.38	0.38	0.068	5.06
0.8	0.14	0.094	3.14	-	0.032	0.048	0.875	1.04	2.18	0.39	0.079	5.84
0.8	0.14	0.094	3.14	-	0.030	0.047	0.865	2.50	2.07	0.30	0.078	4.44
0.8	0.14	0.094	3.14	-	0.031	0.048	0.808	0.56	2.51	0.36	0.068	5.13
0.8	0.14	0.094	3.14	-	0.029	0.048	0.808	0.56	1.88	0.34	0.068	4.82
0.8	0.14	0.094	3.14	-	0.030	0.047	1.013	0.55	1.47	0.34	0.090	5.57
0.8	0.14	0.094	3.14	0.520	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	0.520	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	1.409	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	0.522	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	0.529	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	0.529	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	0.632	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	0.527	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	0.569	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	0.562	-	-	-	-	-	-	-	-
0.8	0.14	0.094	3.14	0.564	-	-	-	-	-	-	-	-

Red values are concentrations associated with the method detection limits.

Appendix C: Field Notes and Forms

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Deployment Field Form

Project Number: PNG7584 - ER20-5261 **Project Name:** ESTCP Peeper

Site: Paleta Creek – San Diego

Date	Station ID	Sample ID	Pole Deployment		Water depth (ft)	Anchor Direction	Lat	Lon	Notes
			Times	Duration (min)					
10-3-22	1	SPW-1A	12:52 – 13:18	26	24.0	SW	32.40 25.039	117.06 58.693	2 agarose DGTs (For Hg)
10-3-22	1	SPW-1B	13:28 – 13:33	5	24.4	SW	32.40 25.060	117.06 58.079	2 agarose DGTs. Station 1B 5ft S of 1A
10-3-22	1	SPW-1C	13:55 – 13:58	3	25.2	NE	32.40 25.174	117.06 58.623	2 agarose DGTs.
10-3-22	3	SPW-3	14:58 – 15:06	8	28.0	SW	32.40 23.915	117.06 58.833	1 agarose, 1 Chelex DGT. 5 poles
10-4-22	2	SPW-2	08:50 – 08:55	5	25.0	SW	32.40 23.907	117.06 58.064	1 agarose, 1 CHELEX DGT 5 poles
10-4-22	5	SPW-5	09:13 – 09:17	4	28.0	SW	32.40 23.427	117.06 59.051	1 agarose, 1 Chelex DGT 5 poles
10-4-22	8	SPW-8	09:32 – 09:40	8	27.9	S	32.40 23.058	117.06 59.640	1 agarose, 1 Chelex DGT ☆ 5 poles
10-4-22	7	SPW-7	09:59 – 10:05	6	26.3	NW	32.40 23.874	117.06 59.816	1 agarose, 1 Chelex DGT 5 poles
10-4-22	4	SPW-4	10:28 – 10:34	6	25.1	N	32.40 24.489	117.06 59.771	1 agarose, 1 Chelex 5 poles
10-4-22	6	SPW-6	10:51 – 10:54	3	25.8	N	32.40 24.044	117.06 59.293	2 Chelex DGTs

Notes & Observations

☆ Station 8 – Took GPS reading after leaving station, so GPS coordinates are uncertain at this station.

Peeper Deployment Notes
Jason Conder

10-3-22
ESTCP Peeper Project
Navy Base San Diego, San Diego, CA
Deployment Day 1

0745: Met at Pepper Park boat ramp; unload vehicle and load boat (Pi Environmental). Onboard health and safety meeting. Organize gear, peeper materials, equipment. Personnel present: Jason Conder, Flo Risacher, and Michaela Lawrence (Geosyntec); Brent Mardian and Mason (Pi Environmental); Gunther Rosen (US Navy NIWC). Weather – calm wind, cloudy, low 70°F. Unpack, prepare, and organize field gear and plan for the day with team.

1025: Left Pepper Park for Site – mouth of Paleta Creek in Navy Base San Diego.

1100: At Site in Paleta Creek. Had a little trouble getting through security barrier into the Base (clearing up and communicating access agreement and etc.). When on Site, had to wait for maintenance vessel (Port) to move some things around (booms) near Site. We used this time to prep the sandwich bag sand anchors and anchor lines.

1132: Position/anchor on Station 1.

1148: On Station 1; break for lunch.

1230: Station 1 – load up peeper frame with peepers and DGTs (2 Agarose DGTs for Hg), and then deployed frame into sediment for sample frame 1A. Had a few minor challenges with the pole and peeper frame disconnecting – the top of the frame kept getting hung on the bottom of the pole. This was because the frame was pushed too deeply into the sediment. Took 4 tries to insert the frame. Used 4 pole sections.

1325: Station 1 – sample frame 1B setup and load with peepers and DGTs (2 Agarose DGTs for Hg). Only took 1 try for insertion of frame into sediment (only took 5 minutes). The 1B location was approximately 5 feet to the southeast of where 1A was inserted. The Go Pro camera was having a bad connection and could not be used, so we used Pi Environmental's "Fishsens" (SondeCAM HD) underwater camera, which was superior and rugged and was able to connect to everyone's cell phone after installing the App.

1350: Station 1 – sample frame 1C setup and load with peepers and DGTs (2 Agarose DGTs for Hg). Only took 3 minutes to insert peeper. The 1C location was on the opposite side of the boat from 1A and 1B, approximately 12 feet northeast of 1A insertion point.

1405: Moved off of Station 1 to Station 3; applied 3-point anchor to secure in place.

1442: On Station 3. Anchoring was difficult due to light afternoon west wind an very soft sediment in the area. Important to plan sequence of stations and anchoring to avoid entangling anchor lines from the vessel and anchor lines from the peeper frames that had already been deployed.

1444: Assembling peepers and DGTs into frame for Station 3. Note – on 1A, 1B, and 1C, only the agarose DGTs (for Hg) were used in these frames. So we will get 6 Hg DGT samples from these 3 sample locations, but no regular metals (i.e., Chelex DGTs). Note that the Agarose and Chelex DGTs look identical, so all Chelex DGTs were notched on the edge with snips to we can differentiate them from the Agarose DGTs.

1458: Started on Station 3. Had to use 5 poles since the water depth was 28 feet (tide was rising, and tides during the day were all positive). 30 feet deep is about the maximum depth for working with push poles since deeper water would require 6 poles, which would not be feasible for 1-2 people to operate safely. Got peeper frame for 3 deployed in 1 try.

1510: Moving to Station 2. Could not get Navy Base on radio to inform them of our plans to work more in the day, so we decided to stop work.

1515: Left Site for Pepper Park. After arriving at Pepper Park, left gear in the boat.

1535: Left Pepper Park; end of day.

10-4-22
ESTCP Peeper Project
Navy Base San Diego, San Diego, CA
Deployment Day 2

0731: At Pepper Park to ready boat. Onboard health and safety meeting. Organize gear, peeper materials, equipment. Personnel present: Jason Conder, Flo Risacher, and Michaela Lawrence (Geosyntec); Brent Mardian and Mason (Pi Environmental); Gunther Rosen (US Navy NIWC). Weather – calm wind, cloudy, low 70°F.

0745: Left Pepper Park for Site.

0758: Arrived at Base barrier gate to wait on tug to open gate to base.

0820: Gate finally open; accessing Navy Base San Diego.

0826: At Site. Navigate to Station 2. Floating dock was partly in the way, so we got as close as possible.

0840: At Station 2; build peeper frame- load up peeper frame with peepers and DGTs (1 Agarose DGT for Hg and 1 Chelex DGT for metals).

0850: Frame and pole ready; begin pole assembly and insertion. Had to use 5 poles.

0855: Complete insertion. Got good video.

0859: Navigate and anchor at Station 5. Marked the station location with a marker buoy.

0908: Anchored at Station 5; build peeper frame- load up peeper frame with peepers and DGTs (1 Agarose DGT for Hg and 1 Chelex DGT for metals).

0917: Station 5 complete. Navigated to Station 8. Dropped buoy marker.

0930: On Station 8; build peeper frame- load up peeper frame with peepers and DGTs (1 Agarose DGT for Hg and 1 Chelex DGT for metals).

0932: Started insertion at Station 8. Took 8 minutes. When pulling up pole, anchor line got hung on pole, so we re-threw sand bag anchor. We do not think the frame was dislodged from the sediment.

0942: Moving to Station 7, but then went back to Station 8 to record GPS location. Reported GPS coordinates may be a little off from where frame was inserted.

0949: Dropped marker buoy at Station 7; build peeper frame- load up peeper frame with peepers and DGTs (1 Agarose DGT for Hg and 1 Chelex DGT for metals).

0956: On Station 7. Three-point anchoring (as at all stations today). Wind was calm, so that helped a lot in anchoring.

0959: Inserted peeper frame at Station 7. Boat swung off station a bit, so we might be 15-20 feet from the actual planned station.

1009: Moved from Station 7. Took a break to drill out the holes (for the cotter pin) on the push poles a little more so they would accommodate the pin more easily. Headed to Station 4.

1018: On Station 4; build peeper frame- load up peeper frame with peepers and DGTs (1 Agarose DGT for Hg and 1 Chelex DGT for metals).

1028: Started deployment of frame at Station 4.

1034: Finished Station 4 frame insertion. Moving to Station 6. Start build peeper frame- load up peeper frame with peepers and DGTs (2 Chelex DGT for metals – NO AGAROSE DGT here). Saved 4 Chelex DGTs for use in blank analysis, as needed. No more agarose DGTs are available (they were all deployed).

1039: On Station 6. Saved 8 peepers for blanks and 4 Chelex DGTs for blanks.

1048: Re-positioning boat and re-anchor for Station 6.

1051: On Station 6. Start deployment. Always check to make sure anchor line not caught on pole before/as pulling pole away from inserted peeper frame.

1054: Finished Station 6. Deployed ROV, but not well configured today to view peeper frames or bottom.

1116: Started breaking down poles and equipment and pulling anchors.

1128: Left Site.

1140: Exited gate at Base. Visited areas nearby Coronado Bridge.

1154: Headed back to Pepper Park.

1205: At Pepper Park to unload and de-mobe from the boat.

1216: Finished de-mobe. End of day.

* * *

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DGT Retrieval Field Form

Project Number: PNG7584 - ER20-5261 **Project Name:** ESTCP Peeper

Site: Paleta Creek – San Diego

Recorded by: Jason Conde

Station ID	Sample ID	Retrieval		Notes
		Date	Time	
1A	1A-HG1	10-14-22	14:55	
1A	1A-HG2	10-14-22	14:55	
1B	1B-HG1	10-14-22	14:57	
1B	1B-HG2	10-14-22 ~~10-14-22~~	14:57 ~~11:50~~	
1C	1C-HG1	10-14-22	11:50	
1C	1C-HG2	10-14-22	11:50	
2	2-HG	10-13-22	12:05	Snagged with hook.
2	2-ME	10-13-22	12:05	Snagged with hook.
3	3-HG	10-14-22	14:01	
3	3-ME	10-~~13~~14-22	14:01	
4	4-HG	10-14-22	14:18	
4	4-ME	10-14-22	14:18	
5	5-HG	10-14-22	15:50	
5	5-ME	10-14-22	15:50	
6	6-ME1	10-~~13~~14-22	12:49	
6	6-ME2	10-~~13~~14-22	12:49	
7	7-HG	10-14-22	15:32	
7	7-ME	10-14-22	15:32	
8	8-HG	—	—	Did not locate Station 8 array
8	8-ME	—	—	Did not locate Station 8 array

Notes and Observations:

Geosyntec consultants

Peeper Retrieval and Processing Field Form

Project Number: PNG7584 - ER20-5261 **Project Name:** ESTCP Peeper

Site: Paleta Creek – San Diego

Recorded by: Jason Conder

Station ID	Sample ID	Retrieval ★		Processing ★★		Mtls (mL)	Br (mL)	Notes
		Date	Time	Date	Time			
1A	1A-PW	10-14-22	14:58	10-14-22	17:39	40	20	1 peeper had sediment particles
1A	1A-SW	10-14-22	14:58	10-14-22	17:43	20	20	1 peeper was punctured 1 peeper had a 0.5-cm diameter orange/brown blob
1B	1B-PW	10-14-22	14:56	10-14-22	17:18	60	20	
1B	1B-SW	10-14-22	14:56	10-14-22	17:13	60	20	
1C	1C-PW	10-~~13~~ 14-22	11:51	10-14-22	18:16	60	20	
1C	1C-SW	10-~~13~~ 14-22	11:51	10-14-22	18:10	60	20	
2	2-PW	10-~~13~~ 13-22	12:07	10-13-22	16:18	60	20	Snagged with grapple hook
2	2-SW	10-13-22	12:06	10-13-22	16:11	60	20	Snagged with grapple hook
3	3-PW	10-14-22	14:02	10-~~13~~ 14-22	17:32	~~40~~ 20	20	Only got 3, 1 was punctured, 1 had particles in the peeper
3	3-SW	10-14-22	14:02	10-14-22	17:48	60	20	

★ time noted is when peepers placed in storage bags with oxy munchers.

★★ time note is when sample bottles closed.

Geosyntec consultants

Peeper Retrieval and Processing Field Form

Station ID	Sample ID	Retrieval		Processing		Mtls (mL)	Br (mL)	Notes
		Date	Time	Date	Time			
4	4-PW	10-14-22	14:20	10-14-22	17:52	40	20	1 ~~may have~~ has sed in it.
4	4-SW	10-14-22	14:20	10-14-22	17:56	40	20	1 had particles
5	5-PW	10-14-22	15:52	10-14-22	17:07	60	20	
5	~~5-PW~~ 5-SW	10-14-22	15:52	10-14-22	17:02	60	20	
6	6-SW	10-14-22	12:49	10-14-22	18:07	40 ~~60~~	20 ~~20~~	Only got 3 peepers, 1 was punctured
6	6-PW	10-14-22	12:49	10-14-22	18:04	60	20	
7	7-PW	10-14-22	15:33	10-14-22	18:00	60	20	1 had 0.5-cm orange blob in it, but was included in the Br sample (20 mL)
7	7-SW	10-14-22	15:33	10-14-22	17:27	60	20	
8	8-PW	—	—	—	—	0	0	Did not locate station 8 array
8	8-SW	—	—	—	—	0	0	Did not locate Station 8 array

Notes & Observations

X	FB	NA (Field Blank)	10-13-22	16:02	60	20	

Peeper Retrieval Notes
Jason Conder

10-13-22
ESTCP Peeper Project
Navy Base San Diego, San Diego, CA
Retrieval Day 1

0744: Arrived at Pepper Park boat ramp; unload vehicle and load boat (Pi Environmental). Onboard health and safety meeting. Organize gear, peeper materials, equipment. Personnel present: Jason Conder, Flo Risacher, and Michaela Lawrence (Geosyntec); Brent Mardian and Mason (Pi Environmental); Gunther Rosen (US Navy NIWC). Weather – calm wind, cloudy, high 60s°F.

0817: Left Pepper Park for Site – mouth of Paleta Creek in Navy Base San Diego, San Diego, CA.

0824: At security barrier gate to Navy Base San Diego to request access.

0838: Accessed Base.

0848: At Site, cruised to Station 1A/1B/1C area; looked at sonar.

0858: At Station 1 area. Booms were in the way, partly.

0902: First throw of grappling hook to snag station 1 peeper arrays. Various techniques tried, but overall, no success. Even tried 2 grappling hooks at the same time. Added weight (2 pound or so) to top of hook to make sure it sinks well and scrapes bottom, but that did not seem to help much. The issue was that the anchor lines were too short – the lines were only about 5 to 10 feet out from the peeper arrays, which does not make a large target to snag with the hooks given the uncertainty around GPS locations and vessel positioning. Need to have at least 30 to 40 feet of rope for the anchor line, so if the water depth is 30 feet, plan on an anchor line of 60-70 feet so that the anchor weight (sand bag) can be thrown 30 feet or so from the vessel.

1204: After tying up to floating bumpers/infrastructure at Station 2, was able to snag the Station 2 peeper array. Packaged up peepers and DGTs for Station 2. No fouling on peepers or DGTs at Station 2 (and this was consistent for the remainder of the peeper and DGTs recovered).

1212: Break for lunch. Spent some time working with the underwater drop camera and ROV, but was not able to see anything at any of the stations.

1235: Moved back to Station 1 area and tried to retrieve. Also tried a few more Stations (1, 3, 5, etc.). Could not snag any arrays with the grappling hooks.

1415: Gave up grappling and left the Site. Will return tomorrow with scuba diver.

1422: Exited Base; headed to Pepper Park boat launch.

1434: Back at Pepper Park to unload.

1503: Went to San Diego Geosyntec office (2355 Northside Dr Suite 250, San Diego, CA) to obtain bottles.

1537: Set up processing station in parking lot at Geosyntec San Diego so we could process Station 2 samples and Field Blank samples.

1620: Finished processing. All samples (2-PW for sediment porewater, 2-SW for surface water, and FB field blank) were obtained; each sample had 1 sample for bromide and 1 sample for target metals (including lithium). Samples placed in cooler. Packed up processing materials and table.

1628: End of day.

10-14-22
ESTCP Peeper Project
Navy Base San Diego, San Diego, CA
Retrieval Day 2

0740: Arrived at Pepper Park boat ramp. Pi Environmental put boat in water. Unload vehicle and load boat (Pi Environmental). Organize gear, peeper materials, equipment. Personnel present: Jason Conder, Flo Risacher, and Michaela Lawrence (Geosyntec); Brent Mardian and Mason (Pi Environmental); Gunther Rosen (US Navy NIWC).

0835: Left Pepper Park to get 3 scuba tanks from a local dive shop. Rest of crew went to the Site to try to locate and retrieve peeper arrays using grappling hook and the side scan sonar to help better visualize. Was not successful.

1103: Back at Pepper Park with scuba tanks. Boat returned shortly thereafter and we loaded tanks on boat. Took a brief break for lunch at Pepper Park.

1120: Left Pepper Park for Site.

1142: On Site. Navigated to Station 1 to mark it with a marker buoy.

1147: Diver entered the water from the boat, swam to the marker buoy, and descended along the marker buoy line.

1149: Diver returned to the surface with the peeper array for Station 1C. Pulled anchor and moved to Station B location.

1154: Dropped buoy at Station 1B.

1156: Diver down at Station 1B.

1158: Diver up at 1B. Did not find array. Station 1B coordinates (from deployment) are suspect. 1B should be 5 to 10 feet away from 1A and 1C, but GPS coordinates indicate it is 50 feet away. Most likely this was an error in GPS or recording the coordinates.

1206: Dropped marker buoy at Station 7, but re-pulled buoy since it did not appear to be on target.

1212: Dropped marker buoy at Station 7, 2nd attempt.

1213: Diver down at Station 7. Spent 6 minutes looking for array.

1222: Moved buoy to Station 6.

1225: Diver down at Station 6.

1241: Re-dropped anchor at Station 6. Diver down Station 6.

1250: Diver up with Station 6 array. Packaged peepers and DGTs from Station 6 and headed to 5. The key to retrieval is having accurate GPS with good refresh rates and dropping the marker buoy accurately.

1255: Dropped buoy at Station 5. Took a short (~25 minute) break. During this break, we rigged up a 60-foot line with a sand bag anchor weight at each end. One bag was dropped adjacent to the boat (about 25-30 feet water depth). Once that bag was on the bottom, the other bag was thrown from the boat, and it landed in the water approximately 30 feet away – much farther than we had been able to throw the sand bag during last week's deployment. After this, a grappling hook was thrown in the water about 20 feet from the boat in the approximate area of the line. The hook snagged the anchor line on the first try and the 60-ft line was easily retrieved. The key to this method is to have a very long line that can be thrown as far as possible from the boat (at least 30 feet), such that there is a very long linear (horizontal) length of line extending from the array insertion point to the sand bag. Recording the direction of the throw is also critical. Ideally one can record basic cardinal direction for the throw (like NW, SE, etc.), but having a handheld GPS or compass to record the direction in degrees might be even more helpful.

1309: Diver in the water for surface swim to Station 5.

1311: Diver down at Station 5.

1320: Diver back at surface; array not located.

1322: Diver back on board. Took a break for about 10 minutes.

1330: Diver back in water to try Station 5 again.

1332: Diver down at Station 5.

1342: Diver back at surface; array not located.

1344: Diver back on board; head to Station 3.

1348: Dropped marker buoy at Station 3.

1351: Diver down at Station 3.

1400: Diver back with peeper array from Station 3.

1405: Moved to Station 4 to drop buoy.

1411: Marked buoy at Station 4.

1413: Diver in the water at Station 4. Diver down at Station 4.

1417: Diver back with peeper array from Station 4.

1420: Pulled anchor buoy. Moved boat back to Station 1A. Dropped anchor buoy.

1425: Diver down at Station 1A.

1435: Diver back at surface; array not located. Re-positioned buoy, as we believed it may be off target.

1442: Dropped buoy for 2nd time at Station 1A. Diver down at Station 1A.

1453: Diver back with peeper arrays from Station 1A and 1B. Peeper arrays were entangled in/blocked by underwater debris (a sunken oil boom/barrier). Packed up peepers and DGTs, pulled buoy marker, and moved to Station 8.

1507: Dropped marker buoy at Station 8. Diver in the water.

1509: Diver down at Station 8.

1519: Diver back at surface; array not located. Pulled buoy and moved to Station 7.

1523: Dropped buoy at Station 7.

1524: Diver down at Station 7.

1530: Diver back with peeper array from Station 7.

1540: Dropped buoy at Station 5 again. Diver down at Station 5.

1548: Diver back with peeper array from Station 5. Packed DGTs and peepers for Station 5. GPS coordinates for Station 8 (which was tried) are believed to be suspect because we did not get coordinates on the push pole at time of deployment (went back to location after moving boat and took a reading, as this was best we could do).

1555: Left Site.

1617: Back at Pepper Park to unload boat.

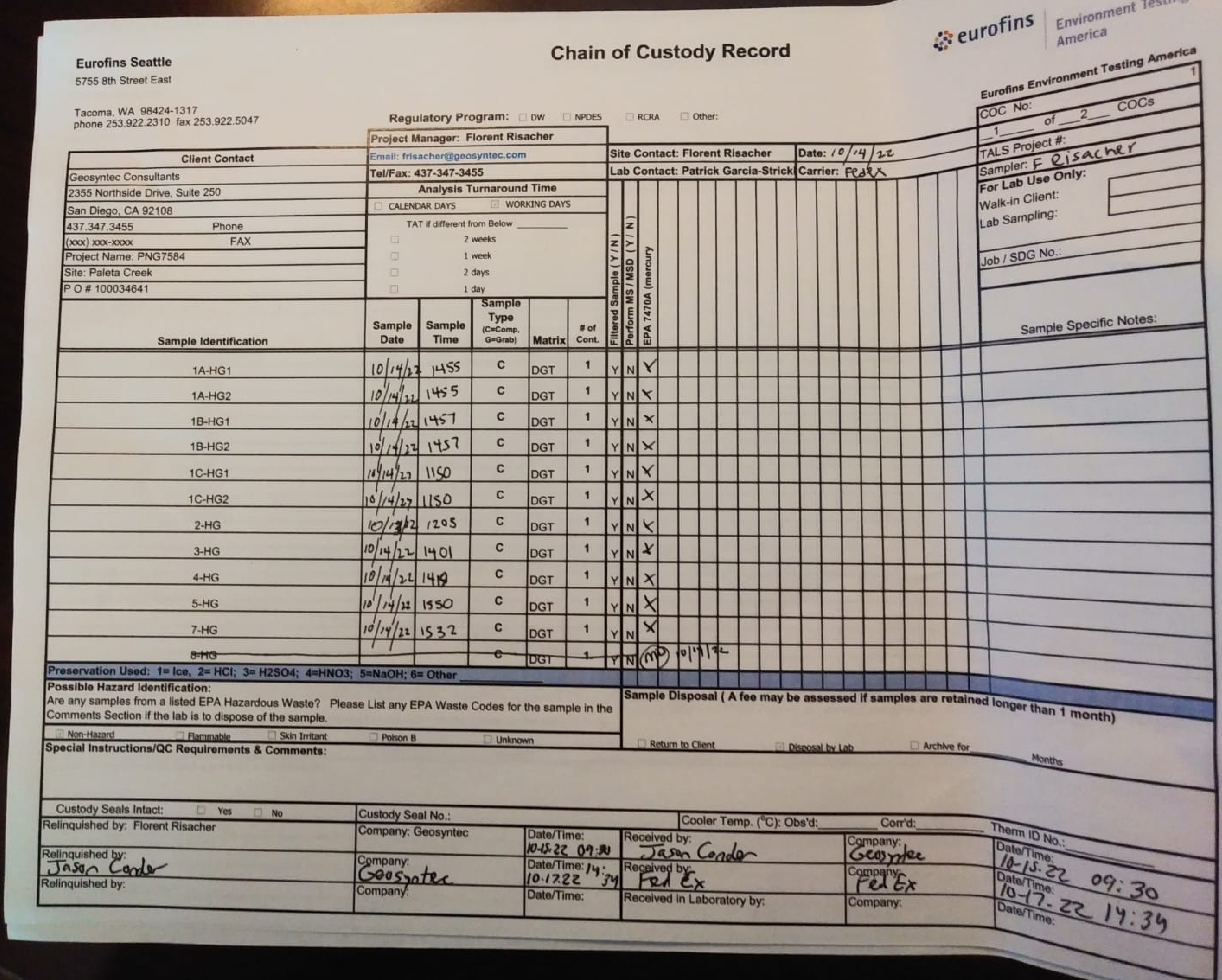
1632: Set up processing station at Pepper Park parking lot. Prepared bottle labels and organized processing materials, then filled out chain or custody forms.

1700: Start processing of peeper samples. Have 8 sediment porewater (PW) and 8 surface water (SW) samples to do.

1814: Finished processing of last sample. Begin packing up field table and materials.

1829: Finished packing and de-mobe. Left Pepper Park. End of day.

Appendix D: Chain of Custody



Chain of Custody Record

eurofins | Environment Testing America

Eurofins Seattle
5755 8th Street East
Tacoma, WA 98424-1317
phone 253.922.2310 fax 253.922.5047

Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☐ Other:

Eurofins Environment Testing America 1
COC No:
1 of 2 COCs
TALS Project #:
Sampler: F Risacher
For Lab Use Only:
Walk-in Client:
Lab Sampling:
Job / SDG No.:

Client Contact	Project Manager: Florent Risacher
Geosyntec Consultants	Email: frisacher@geosyntec.com
2355 Northside Drive, Suite 250	Tel/Fax: 437-347-3455
San Diego, CA 92108	**Analysis Turnaround Time**
437.347.3455 Phone	☐ CALENDAR DAYS ☑ WORKING DAYS
(xxx) xxx-xxxx FAX	TAT if different from Below
Project Name: PNG7584	☐ 2 weeks
Site: Paleta Creek	☐ 1 week
P O # 100034641	☐ 2 days
	☐ 1 day

Site Contact: Florent Risacher
Date: 10/14/22
Lab Contact: Patrick Garcia-Strick
Carrier: FedEx

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)	EPA 7470A (mercury)	Sample Specific Notes:
1A-HG1	10/14/22	1455	C	DGT	1	Y	N	X	
1A-HG2	10/14/22	1455	C	DGT	1	Y	N	X	
1B-HG1	10/14/22	1457	C	DGT	1	Y	N	X	
1B-HG2	10/14/22	1457	C	DGT	1	Y	N	X	
1C-HG1	10/14/22	1150	C	DGT	1	Y	N	X	
1C-HG2	10/14/22	1150	C	DGT	1	Y	N	X	
2-HG	10/13/22	1205	C	DGT	1	Y	N	X	
3-HG	10/14/22	1401	C	DGT	1	Y	N	X	
4-HG	10/14/22	1418	C	DGT	1	Y	N	X	
5-HG	10/14/22	1550	C	DGT	1	Y	N	X	
7-HG	10/14/22	1532	C	DGT	1	Y	N	X	
~~8-HG~~			~~C~~	~~DGT~~	~~1~~	~~Y~~	~~N~~	MD 10/14/22	

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other

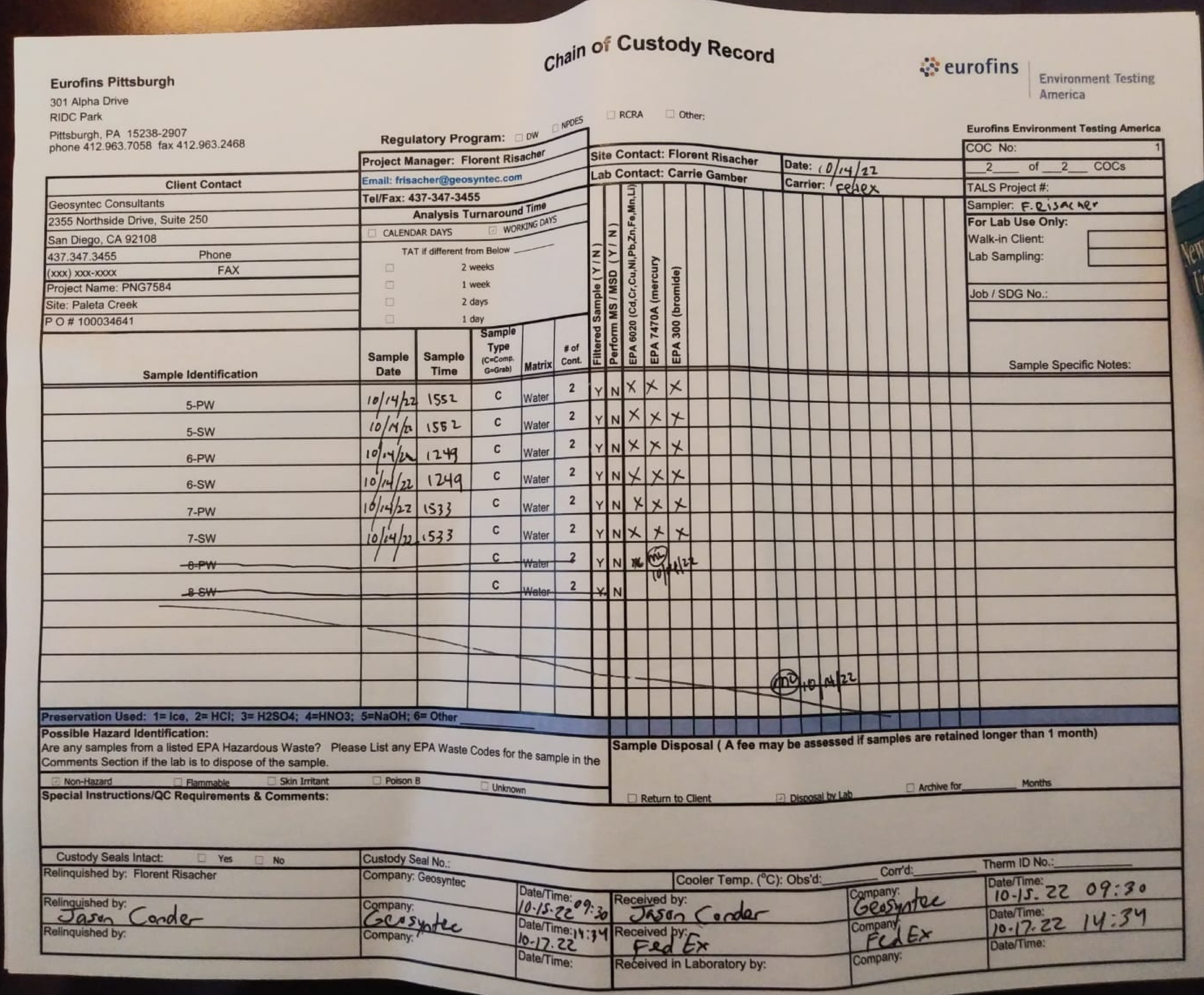
Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.
☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)
☐ Return to Client ☑ Disposal by Lab ☐ Archive for ____ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No
Custody Seal No.:
Cooler Temp. (°C): Obs'd:____ Corr'd:____ Therm ID No.:

Relinquished by: Florent Risacher	Company: Geosyntec	Date/Time: 10-15-22 09:30	Received by: Jason Conder	Company: Geosyntec	Date/Time: 10-15-22 09:30
Relinquished by: Jason Conder	Company: Geosyntec	Date/Time: 10-17-22 14:34	Received by: Fed Ex	Company: Fed Ex	Date/Time: 10-17-22 14:34
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time:



Chain of Custody Record

eurofins | Environment Testing America

Eurofins Pittsburgh
301 Alpha Drive
RIDC Park
Pittsburgh, PA 15238-2907
phone 412.963.7058 fax 412.963.2468

Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☐ Other:

Eurofins Environment Testing America

Client Contact	
Geosyntec Consultants	
2355 Northside Drive, Suite 250	
San Diego, CA 92108	
437.347.3455	Phone
(xxx) xxx-xxxx	FAX
Project Name: PNG7584	
Site: Paleta Creek	
P O # 100034641	

Project Manager: Florent Risacher
Email: frisacher@geosyntec.com
Tel/Fax: 437-347-3455

Analysis Turnaround Time
☐ CALENDAR DAYS ☑ WORKING DAYS
TAT if different from Below ______
☐ 2 weeks
☐ 1 week
☐ 2 days
☐ 1 day

Site Contact: Florent Risacher
Lab Contact: Carrie Gamber
Date: 10/14/22
Carrier: FedEx

COC No: 1
2 of 2 COCs
TALS Project #:
Sampler: F. Risacher
For Lab Use Only:
Walk-in Client:
Lab Sampling:
Job / SDG No.:

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)	EPA 6020 (Cd,Cr,Cu,Ni,Pb,Zn,Fe,Mn,Li)	EPA 7470A (mercury)	EPA 300 (bromide)	Sample Specific Notes:
5-PW	10/14/22	1552	C	Water	2	Y	N	X	X	X	
5-SW	10/14/22	1552	C	Water	2	Y	N	X	X	X	
6-PW	10/14/22	1249	C	Water	2	Y	N	X	X	X	
6-SW	10/14/22	1249	C	Water	2	Y	N	X	X	X	
7-PW	10/14/22	1533	C	Water	2	Y	N	X	X	X	
7-SW	10/14/22	1533	C	Water	2	Y	N	X	X	X	
~~8-PW~~			C	~~Water~~	~~2~~	Y	N		ML 10/14/22		
~~8-SW~~			C	~~Water~~	2	~~Y~~	N				

ML 10/14/22

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other ______

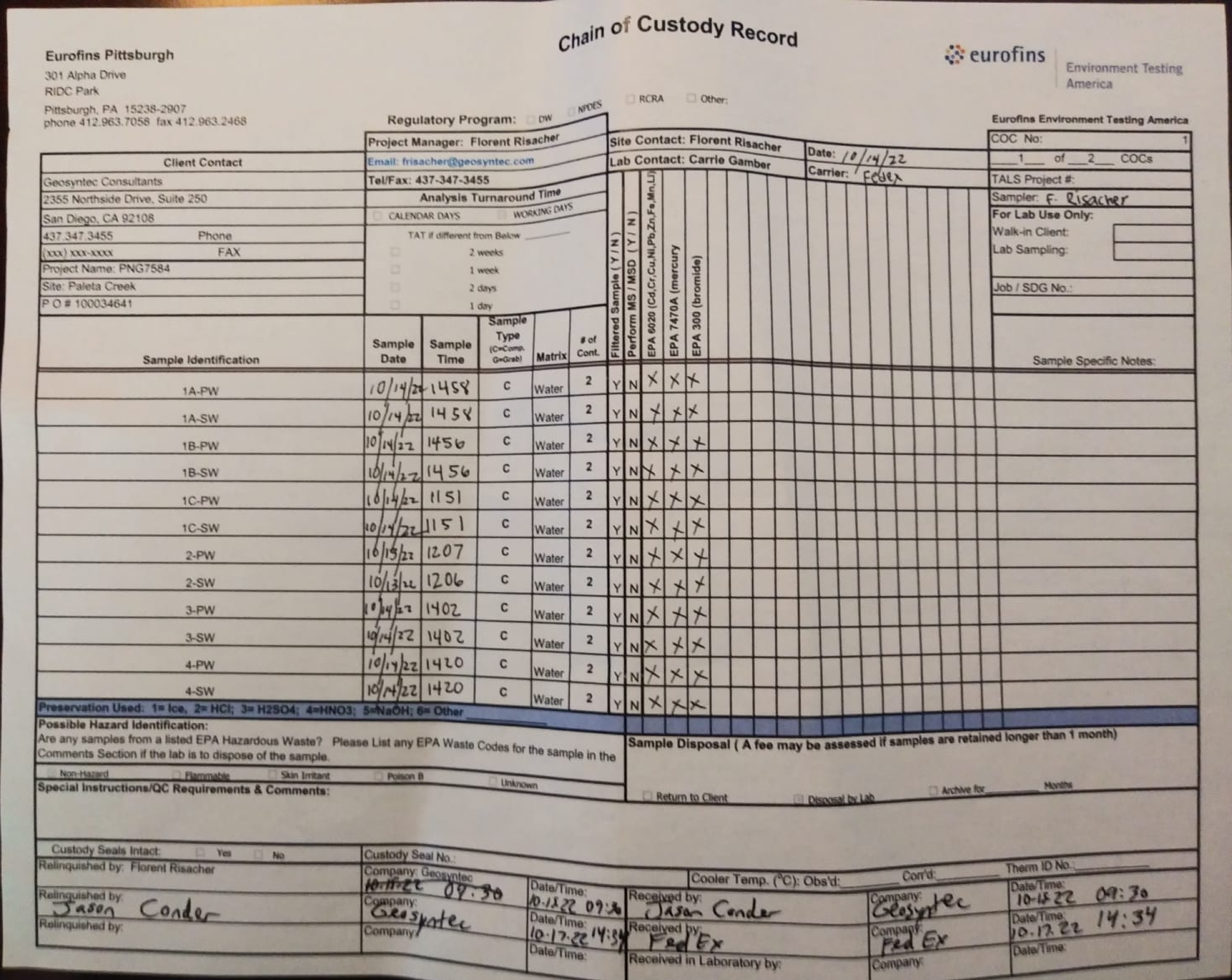
Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.
☑ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)
☐ Return to Client ☑ Disposal by Lab ☐ Archive for ______ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No
Custody Seal No.:
Cooler Temp. (°C): Obs'd: ______ Corr'd: ______ Therm ID No.: ______

Relinquished by: Florent Risacher	Company: Geosyntec	Date/Time: 10-15-22 09:30	Received by: Jason Conder	Company: Geosyntec	Date/Time: 10-15-22 09:30
Relinquished by: Jason Conder	Company: Geosyntec	Date/Time: 10-17-22 14:34	Received by: FedEx	Company: FedEx	Date/Time: 10-17-22 14:34
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time:



Chain of Custody Record

Eurofins Pittsburgh
301 Alpha Drive
RIDC Park
Pittsburgh, PA 15238-2907
phone 412.963.7058 fax 412.963.2468

eurofins | Environment Testing America

Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☐ Other:

Eurofins Environment Testing America

Client Contact	
Geosyntec Consultants	
2355 Northside Drive, Suite 250	
San Diego, CA 92108	
437.347.3455	Phone
(xxx) xxx-xxxx	FAX
Project Name: PNG7584	
Site: Paleta Creek	
P O # 100034641	

Project Manager: Florent Risacher
Email: frisacher@geosyntec.com
Tel/Fax: 437-347-3455

Analysis Turnaround Time
☐ CALENDAR DAYS ☐ WORKING DAYS
TAT if different from Below ______
☐ 2 weeks
☐ 1 week
☐ 2 days
☐ 1 day

Site Contact: Florent Risacher
Lab Contact: Carrie Gamber
Date: 10/14/22
Carrier: FedEx

COC No: 1
1 of 2 COCs
TALS Project #:
Sampler: F. Risacher
For Lab Use Only:
Walk-in Client:
Lab Sampling:
Job / SDG No.:

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)	EPA 6020 (Cd,Cr,Cu,Ni,Pb,Zn,Fe,Mn,Li)	EPA 7470A (mercury)	EPA 300 (bromide)	Sample Specific Notes:
1A-PW	10/14/22	1458	C	Water	2	Y	N	X	X	X	
1A-SW	10/14/22	1458	C	Water	2	Y	N	X	X	X	
1B-PW	10/14/22	1456	C	Water	2	Y	N	X	X	X	
1B-SW	10/14/22	1456	C	Water	2	Y	N	X	X	X	
1C-PW	10/14/22	1151	C	Water	2	Y	N	X	X	X	
1C-SW	10/14/22	1151	C	Water	2	Y	N	X	X	X	
2-PW	10/15/22	1207	C	Water	2	Y	N	X	X	X	
2-SW	10/13/22	1206	C	Water	2	Y	N	X	X	X	
3-PW	10/14/22	1402	C	Water	2	Y	N	X	X	X	
3-SW	10/14/22	1402	C	Water	2	Y	N	X	X	X	
4-PW	10/14/22	1420	C	Water	2	Y	N	X	X	X	
4-SW	10/14/22	1420	C	Water	2	Y	N	X	X	X	

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other ______

Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.

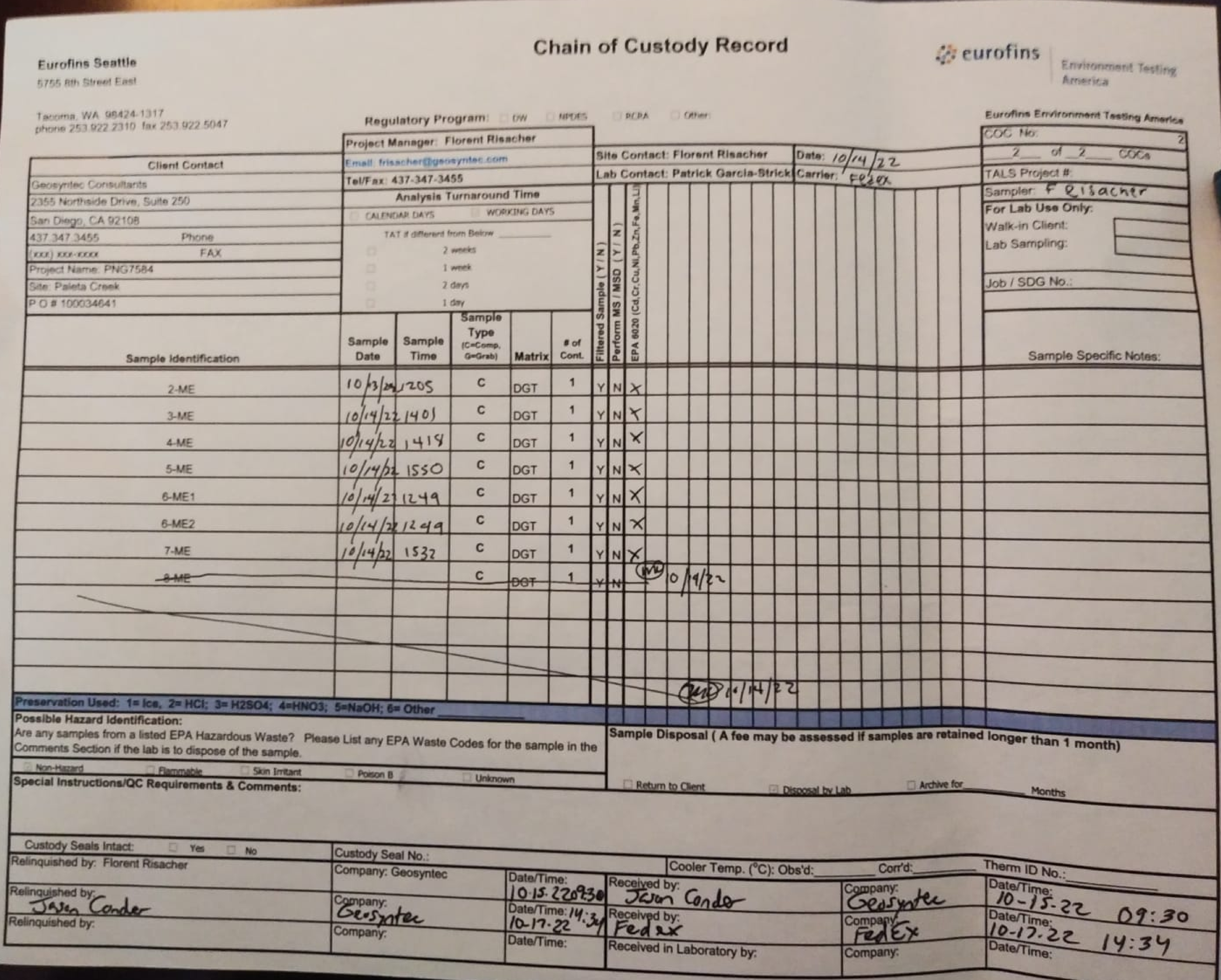
☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)
☐ Return to Client ☐ Disposal by Lab ☐ Archive for ______ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No
Custody Seal No.:
Cooler Temp. (°C): Obs'd: ______ Corr'd: ______ Therm ID No.: ______

Relinquished by: Florent Risacher	Company: Geosyntec ~~10.15.22~~ 09:30	Date/Time:	Received by: Jason Conder	Company: Geosyntec	Date/Time: 10-15-22 09:30
Relinquished by: Jason Conder	Company: Geosyntec	Date/Time: 10.15.22 09:30	Received by: FedEx	Company: Fed Ex	Date/Time: 10.17.22 14:34
Relinquished by:	Company:	Date/Time: 10.17.22 14:34	Received in Laboratory by:	Company:	Date/Time:



Eurofins Seattle
5755 8th Street East

Tacoma, WA 98424-1317
phone 253.922.2310 fax 253.922.5047

Chain of Custody Record

eurofins | Environment Testing America

Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☐ Other:

Eurofins Environment Testing America

Client Contact	**Project Manager:** Florent Risacher
Geosyntec Consultants	Email: frisacher@geosyntec.com
2355 Northside Drive, Suite 250	**Tel/Fax:** 437-347-3455
San Diego, CA 92108	**Analysis Turnaround Time**
437.347.3455 Phone	☐ CALENDAR DAYS ☐ WORKING DAYS
(xxx) xxx-xxxx FAX	TAT if different from Below ________
Project Name: PNG7584	☐ 2 weeks
Site: Paleta Creek	☐ 1 week
P O # 100034641	☐ 2 days ☐ 1 day

Site Contact: Florent Risacher — **Date:** 10/14/22

Lab Contact: Patrick Garcia-Strick — **Carrier:** FedEx

COC No: 2

2 of 2 COCs

TALS Project #:

Sampler: F Risacher

For Lab Use Only:
Walk-in Client:
Lab Sampling:

Job / SDG No.:

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)	EPA 6020 (Cd,Cr,Cu,Ni,Pb,Zn,Fe,Mn,Li)	Sample Specific Notes:
2-ME	10/13/22	1205	C	DGT	1	Y	N	X	
3-ME	10/14/22	1401	C	DGT	1	Y	N	X	
4-ME	10/14/22	1418	C	DGT	1	Y	N	X	
5-ME	10/14/22	1550	C	DGT	1	Y	N	X	
6-ME1	10/14/22	1249	C	DGT	1	Y	N	X	
6-ME2	10/14/22	1249	C	DGT	1	Y	N	X	
7-ME	10/14/22	1532	C	DGT	1	Y	N	X	
~~8-ME~~			C	~~DGT~~	1	~~Y~~	~~N~~	10/14/22	

10/14/22

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other ________

Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.
☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☐ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)
☐ Return to Client ☐ Disposal by Lab ☐ Archive for ________ Months

Special Instructions/QC Requirements & Comments:

Custody Seals Intact: ☐ Yes ☐ No — Custody Seal No.: — Cooler Temp. (°C): Obs'd: ________ Corr'd: ________ — Therm ID No.: ________

Relinquished by: Florent Risacher	Company: Geosyntec	Date/Time: 10.15.22 0930	Received by: Jason Conder	Company: Geosyntec	Date/Time: 10-15-22 09:30
Relinquished by: Jason Conder	Company: Geosyntec	Date/Time: 10-17-22 14:34	Received by: Fedex	Company: FedEx	Date/Time: 10-17-22 14:34
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time:

Appendix E: Analytical Laboratory Reports

Field demonstration analytical reports can be found attached to this document.

Appendix F: Peeper Deployment, Retrieval and Processing Method

Peeper Deployment, Retrieval, and Processing Method

OVERVIEW

- Peepers are a small chamber containing deionized water capped with a semi-permeable membrane. The water may be spiked with lithium and/or bromine tracer.
- Peepers should be shipped in a plastic or mylar zipseal bag. The bags may have a few milliliters of water in them to keep peepers moist. The bags should be kept after deployment to store peepers during retrieval
- Peeper (within their bags) should ship from the laboratory in a cooler for ultimate protection during shipping.
- Prior to deployment, the peepers do not need to be refrigerated; however, they should be kept (ideally within their protective cooler) at temperatures above freezing (i.e., 32°F or 0°C) and below excessively hot temperatures (i.e., 100 °F or 38°C).
- A portion of the peeper water (e.g., at least 20 mL) from the peepers may be used for bromine tracer analysis while the remainder (e.g., 20 to 60 mL) is used for metal analysis (including lithium tracer).
- After retrieval, peepers should be processed, limiting exposure of the peeper to air to 10 minutes or less.
- If rapid processing is not possible, peeper should be stored in a plastic or mylar zipseal bag with oxygen absorbing packets within approximately 10 minutes or less after removal from sediment or water.
- At least 1 sample for blank analysis of metals and tracer should be created using a set of peepers that have not been deployed at the site (store them in the cooler in a safe location during the field deployment).

DEPLOYMENT

Materials for Deployment:

- Peepers– please ensure that extra peepers (approximately 10% extra, plus additional for Trip Blanks) are shipped to the field, as peepers can be damaged during transport and handling
- Peeper frame (if deployed in array)
- Polyester rope
- Laminated sample ID card
- Zip-ties
- Electrical tape & duct tape
- Handheld GPS unit with 1 second (or less) refresh rate and accuracy of 1-2 m or better
- Plastic or mylar bags for peepers storage

Deployment

1. If deployment is made from a vessel using divers, the vessel should be anchored to maintain the location and stability if possible.
2. Confirm the water depth at the location where the peepers will be deployed using vessel instruments (i.e., sonar) or a marked anchor line.
3. If peepers are deployed in a frame, take out the frame and put it together.
4. Label each peeper by attaching a laminated sample ID card to the frame with a zip-tie. If peepers are not deployed in a frame, attach the laminated card later directly to the peeper.
5. Attach a polyester rope to an attachment point at the top corner of the peeper frame or to the peeper itself. This rope can be attached to a sand bag or weight and serve as an anchor line. The length of rope should be long enough to facilitate the retrieval of the peepers by divers or with a grappling hook; ideally the length of the rope should extend at least 30 feet from the insertion point. Alternatively, if the deployment is close to an accessible shoreline the rope can be tied to a tree or a stake. If tied to shore, make sure the location has limited public access.
6. Remove the peepers from the bag. Note, there may be ~0.5 L of water in the bag surrounding the peepers; this is not leakage from the peepers. The extra water is included in the bag to assure the peepers stay moist. **Keep the plastic or mylar bags, as they will be used for retrieval of the peepers.** Inspect the peepers to make sure the water inside does not contain bubbles, and inspect the membrane of each peepers to make sure it wasn't damaged during transport. A damaged membrane (below, left) will appear wrinkled or punctured; a secure membrane will appear smooth (below, right):

A **wrinkle** in the peeper membrane due to damage or mishandling; do not use the peeper for field deployment, although it can be used as a Trip Blank if needed

A smooth peeper membrane

If a peeper has a damaged membrane or contains bubbles in the peeper water, do not use it for field sampling as it may negatively impact sampling performance. It can be used to create a Trip Blank sample, however.

7. Secure the peeper into the frame, being sure to not touch the peeper membranes. If no frames are used, attached a label to the peeper.
8. Insert the peeper frame or peeper into the sediment with the membrane facing the side. This can be achieved using divers, or by wading if the location is shallow enough. A diverless push pole apparatus can also be used. If full insertion cannot be achieved pull up the frame or peepers and retry insertion a few feet away.
9. The anchor line should be extended from the insertion point and the direction of the extension should be noted. If using divers, the diver can swim from the insertion point and drop the anchor a few feet (10 to 30 feet) away. If the peeper is being deployed from the surface (from a vessel) using a push pole or other apparatus, the anchor line should be tossed so that it enters the water approximately 30 feet (or more) away. This methods requires a longer anchor line (length equal to 30 feet plus water depth at station).
10. Using a handheld GPS unit, note (and/or mark) GPS coordinates of deployed peepers.

RETRIEVAL

Materials for Retrieval:

- Bags for peeper storage (use peeper bags from deployment)
- Oxygen absorbing packets
- Coolers with wet ice

Note: Before retrieving the peepers, ensure that you are ready to process them right away or that you have the supplies to preserve them until processing. If working from a boat, preserving the peepers and processing them on shore may be the best approach. After removal from the sediment, peepers should be exposed to surface water and air for as little time as possible (ideally 10 minutes or less). This can be achieved by having the plastic/mylar bags and oxygen absorbing packets ready to be used as soon as the peeper is retrieved at the surface. Note that once the oxygen absorbing packets are removed from their vacuum packed bag, they need to be used on the same day or be discarded.

Retrieval

1. Position the vessel at or near the location of the deployed peepers using the GPS coordinates from the deployment. Use of a handheld GPS system with a graphical display and "navigate to point" is extremely helpful.
2. If divers are retrieving the peepers, drop a buoy with an anchor to mark the retrieval location for the diver, then send the diver down to do a search around the buoy, starting adjacent and circling further around until the peepers are found. Once found, return the peeper frame as quickly as possible to the surface via diver or a tender line to the vessel.

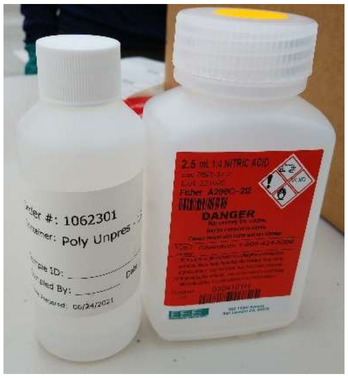
3. If retrieval is being attempted using grappling hooks from the surface of the boat, catch the weighted rope by tossing the hook in a direction perpendicular to that in which the anchor and anchor line were deployed. Drag the grappling hook on the bottom of the sediment until snagged on the rope. Pull the boat or platform above the hook and pull everything straight up.
4. If retrieval is being attempted via wading, safely wade into the water and remove the peeper frame from the sediment. Return the peepers to the shore or vessel.
5. Once retrieved, quickly remove the peepers from the frame and place in the plastic/mylar bag. Peepers do not need to be cleaned or rinsed. Be careful in positioning the peepers so that they do not bump against each other's membrane, this can be achieved by storing them flat in the bag, side by side, with the membrane up. Do not stack the peepers on top of each other. Add 2-3 oxygen absorbing packets in the bag before sealing it.
6. Label the outside of the storage bag according to the sample nomenclature.
7. Store the bags with the peepers in a cooler, on wet ice until they can be processed.
8. Processing should ideally occur on the same day after retreival (laboratory research is ongoing to confirm the timing of this recommendation).

⚠ **Special Note: Once removed from the sediment, the peepers and peeper frames should be visually inspected to confirm they were fully inserted during the deployment duration. This can be seen from the different coloration of the frame between parts that were exposed to surface water and parts that were in the sediments.**

PROCESSING

Peeper Processing in Field or Field Lab

1. Prepare a clean workstation (i.e. table), ideally in a sheltered area. Essential elements include:
    a. Serological pipettes tips
    b. Pipette pump compatible with serological pipettes tips
    c. Several gallons of DI or distilled water (e.g., approximately 1 gallon per 20 samples)
    d. Plastic spray bottle of DI or distilled water
    e. Laboratory supplied sample bottles to contain waters transferred from the peepers; two bottles are needed for each sample:
        i. An empty HPDE bottle for the bromine sample (if bromine is being used as a tracer)
        ii. An HDPE bottle for the metals sample, containing a small amount of nitric acid (i.e., 2.5 mL 1:4 concentrated nitric acid) for preservative



    f. Nitrile gloves
    g. Eye protection
    h. Roll of paper towels or box of Kimwipes
    i. Garbage bag or container to contain waste
    j. Cooler with peepers retrieved from the field and peepers for the Trip Blank
    k. Additional ice (as needed) to maintain cool temperatures
    l. Zipseal bags for packaging sample bottles
    m. Processing forms and chain of custody forms
    n. Tape for securing the cooler for shipment

Special Note: Once removed from the protective bag, peepers should be processed within 10 minutes so that contact with the atmosphere is minimized (oxygen will diffuse into the water contained within the peepers and could compromise sample integrity)

2. Two people are recommended for processing. A designated person ("dirty hands") should be responsible to clean peepers, while another person ("clean hands") should be

responsible for transferring water from the peepers into the sample bottles and recording processing information on the processing form. If this is not possible, it is recommended to change gloves between cleaning peepers and transferring the water to the sample bottles.

3. Attach the pipette pump to a fresh serological pipette tip. One pipette tip is needed to transfer the water from the multiple peepers used to create a sample (change out the pipette tip when processing peepers being combined for a separate sample).
4. Removal from storage, open the bag and remove one peeper; take note of the sampling location.
5. Rinse the top of the peeper membrane with DI water to clean off any sediment. Ensure to flush thoroughly around the membrane and cap. A paper towel or Kimwipe can be used to assist removal of sediment as needed, although care must be taken as the membrane is fragile. The membrane should be free of visible grains of sediment.
6. Inspect the peeper for contamination by sediments. To ensure sample integrity, peepers should be inspected for sediments by looking inside from the bottom of the vial. If sediment particles can be seen floating inside against the membrane of the peeper, the peeper should not be sampled, as it may have allowed solid particles into the sampler during sampling, and this may not represent freely-dissolved metal concentrations.

Sediment grains that have entered the peeper; they are observable by swirling the water and turning the peeper upside down

Peeper with no observable sediment grains

7. Once cleaned off, use the serological pipette tip to puncture the membrane, angle the serological pipette tip towards the bottom of the vial and drawn up all water from the peeper into the pipette.

8. Dispense at least 5 mL from the peeper in the sample container for the bromine analysis (if bromine is being used as a tracer).
9. Dispense the rest of the peeper water in the sample container for the metal analysis. The vial for metal analysis should already contain a small volume of nitric acid so that the sample will be acidified.
10. In total, ~20 mL or more should be collected for bromine analysis and ~60 mL or more for metal analysis (consult your analytical lab to confirm ideal and minimum sample volumes).
11. Cap all sample bottles, label, and store in a cooler on wet ice.
12. Note the processing date and time and approximate volume of peeper water used for the bromine sample (ideally ≥ 20 mL) and the metals sample (ideally ≥ 60 mL).
13. Remove the pipette tip from the pipette pump and attach a new pipette tip for use for the next set of peepers that will be used for the next sample.
14. Do not to forget to prepare blank samples using unexposed peepers. This will be used as the Trip Blank sample for bromine and metals.
15. Once all peeper samples have been processed, prepare the samples for laboratory submission (e.g. fill out chain of custody, initiate transfer of samples to receiving laboratory for analysis, etc.).

Appendix D: Peeper Preparation Standard Operating Procedure

Peeper Preparation Method

OVERVIEW

- Peepers are a small chamber containing deionized water capped with a semi-permeable membrane. The water may be spiked with lithium and/or bromide tracer.

PREPARATION

Materials for Preparation:

- A large plastic bin to contain a weak acid bath.
- Materials for Peepers: Vials and caps, approximately 15-mL; e.g., 1/2 oz. Natural Polypropylene (PP) Straight-Sided Thick Wall Round Jar with 43/400 Neck and 43/400 White Polypropylene (PP) Unlined Ribbed Cap (US Plastics, https://www.usplastic.com/
- Nitrile gloves.
- 1.25-inch diameter hole saw drill bit and drill press
- 0.45-µm pore size Polyethersulfone (PES) filters, 47-mm diameter
- Lithium bromide (LiBr)
- 70% Nitric Acid (trace metal grade)
- Laboratory Detergent
- Reverse osmosis (RO) water
- Deionized water: Ultrapure 18.2 MΩ/cm deionized (DI) water
- Chemical waste container
- Mylar zipseal storage bags
- Additional personal protective equipment as needed (eye protection, etc.)

Preparation of Peeper Vials

1. Drill out the center of each cap of the peeper caps with the hole saw (drill press), leaving a 1.25-inch diameter hole in the center of the cap.

Cleaning of Peepers

1. Clean the vials and caps with laboratory-grade detergent and RO water, followed with an RO water rinse, and a final DI water rinse.
2. Place vials and caps (and any other peeper support material) in a large plastic tote.
3. Rinse bin and its contents, with DI water three times.
4. Prepare a 5% trace metal grade nitric acid bath using concentrated nitric acid and DI water, and place in the bin with its contents.
5. Soak contents in the bin for 24 hours.
6. Drain bin and dispose of acid bath solution in the appropriate waste container.
7. Rinse the bin and its contents 5 times with DI water.
8. Repeat steps 5-8 once more, for a second acid wash.
9. Fill the bin with DI water and let soak for 24 hours.
10. After the 24-hour soak, drain the bin.
11. Rinse the bin and its contents 3 times with DI water.

Peeper Water Preparation

1. Calculate the mass of lithium bromide (LiBr) necessary to obtain the desired concentration of LiBr: 1 g/L (deployments in marine water) or 0.1 g/L (deployments in freshwater) of LiBr for the volume of water needed to fill the peepers.
2. Add LiBr to an acid-cleaned bottle or flash and bring to volume with DI water; mix until all solids have dissolved.

Peeper Assembly

1. Gather all necessary components needed for peeper construction (e.g., PES membranes, Mylar bags, caps and vials, LiBr solution)
2. Fill the peepers with LiBr solution such that the solution beads up above the lip of the vial.
3. Gently place the 0.45-µm PES filter on top of the vial opening and tighten the cap over the vial, ensuring no bubbles are present in the solution.
4. Ensure a seal has been made between the vial and the cap via the membrane by visually inspecting the peeper.
5. Check to make sure that there are no rips, tears, or wrinkles in the membrane. Any deformities in the membrane could prevent the peeper performing correctly.
6. Repeat above steps with remaining vials.

7. Final example product:

8. Once peepers have been prepared, place in a mylar zipseal storage bag. Include approximately 5 to 10 mL of the LiBr solution in the mylar bag so the atmosphere in the mylar bag remains moist.
9. In the mylar bag, ensure peepers are lying flat within the bag so the filter membranes are not punctured by the bottom of another peeper.
10. Repeat above until all peeper required for the project have been constructed.
11. Store peepers in their mylar bags, lying flat, under ambient conditions (20-25°C) or in cold conditions (4°C) until shipment.

Appendix E: Peeper Deployment, Retrieval, and Processing Standard Operating Procedure

Peeper Deployment, Retrieval, and Processing Method

OVERVIEW

- Peepers are a small chamber containing deionized water capped with a semi-permeable membrane. The water may be spiked with lithium and/or bromide tracer.
- Peepers should be shipped in a plastic or mylar zipseal bag. The bags may have a few milliliters of water in them to keep peepers moist. The bags should be kept after deployment to store peepers during retrieval
- Peeper (within their bags) should ship from the laboratory in a cooler for ultimate protection during shipping.
- Prior to deployment, the peepers do not need to be refrigerated; however, they should be kept (ideally within their protective cooler) at temperatures above freezing (i.e., 32°F or 0°C) and below excessively hot temperatures (i.e., 100 °F or 38°C).
- A portion of the peeper water (e.g., at least 20 mL) from the peepers may be used for bromide tracer analysis while the remainder (e.g., 20 to 60 mL) is used for metal analysis (including lithium tracer).
- After retrieval, peepers should be processed, limiting exposure of the peeper to air to 10 minutes or less.
- If rapid processing is not possible, peeper should be stored in a plastic or mylar zipseal bag with oxygen absorbing packets within approximately 10 minutes or less after removal from sediment or water. Peepers stored in this manner should be processed within approximately 8 hours of collection.
- At least 1 sample for blank analysis of metals and tracer should be created using a set of peepers that have not been deployed at the site (store them in the cooler in a safe location during the field deployment).

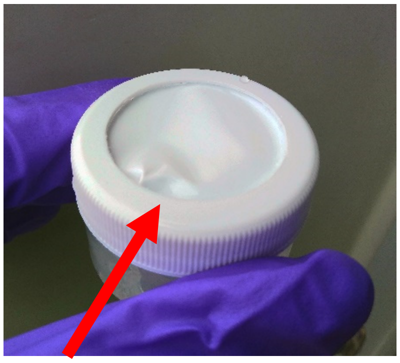
DEPLOYMENT

Materials for Deployment:

- Peepers– please ensure that extra peepers (approximately 10% extra, plus additional for Trip Blanks) are shipped to the field, as peepers can be damaged during transport and handling
- Peeper frame (if deployed in array)
- Polyester rope
- Laminated sample ID card
- Zip-ties
- Electrical tape & duct tape
- Handheld GPS unit with 1 second (or less) refresh rate and accuracy of 1-2 m or better
- Plastic or mylar bags for peepers storage

Deployment

1. If deployment is made from a vessel using divers, the vessel should be anchored to maintain the location and stability if possible.
2. Confirm the water depth at the location where the peepers will be deployed using vessel instruments (i.e., sonar) or a marked anchor line.
3. If peepers are deployed in a frame, take out the frame and put it together.
4. Label each peeper by attaching a laminated sample ID card to the frame with a zip-tie. If peepers are not deployed in a frame, attach the laminated card later directly to the peeper.
5. Attach a polyester rope to an attachment point at the top corner of the peeper frame or to the peeper itself. This rope can be attached to a sand bag or weight and serve as an anchor line. The length of rope should be long enough to facilitate the retrieval of the peepers by divers or with a grappling hook; ideally the length of the rope should extend at least 30 feet from the insertion point. Alternatively, if the deployment is close to an accessible shoreline the rope can be tied to a tree or a stake. If tied to shore, make sure the location has limited public access.
6. Remove the peepers from the bag. Note, there may be ~0.5 L of water in the bag surrounding the peepers; this is not leakage from the peepers. The extra water is included in the bag to assure the peepers stay moist. **Keep the plastic or mylar bags, as they will be used for retrieval of the peepers.** Inspect the peepers to make sure the water inside does not contain bubbles, and inspect the membrane of each peepers to make sure it wasn't damaged during transport or handling. A damaged membrane (below, left) will appear wrinkled or punctured; a secure membrane will appear smooth (below, right):



A **wrinkle** in the peeper membrane due to damage or mishandling; do not use the peeper for field deployment, although it can be used as a Trip Blank if needed

A smooth peeper membrane

If a peeper has a damaged membrane or contains bubbles in the peeper water, do not use it for field sampling as it may negatively impact sampling performance. It can be used to create a Trip Blank sample, however.

7. Secure the peeper into the frame, being sure to not touch the peeper membranes. If no frames are used, attached a label to the peeper.
8. Insert the peeper frame or peeper into the sediment with the membrane facing the side. This can be achieved using divers, or by wading if the location is shallow enough. A diverless push pole apparatus can also be used. If full insertion cannot be achieved pull up the frame or peepers and retry insertion a few feet away.
9. The anchor line should be extended from the insertion point and the direction of the extension should be noted. If using divers, the diver can swim from the insertion point and drop the anchor a few feet (at least 30 feet) away. If the peeper is being deployed from the surface (from a vessel) using a push pole or other apparatus, the anchor line should be tossed so that it enters the water approximately 30 feet (or more) away. This methods requires a longer anchor line (length equal to 30 feet plus water depth at station).
10. Using a handheld GPS unit, note (and/or mark) GPS coordinates of deployed peepers.

RETRIEVAL

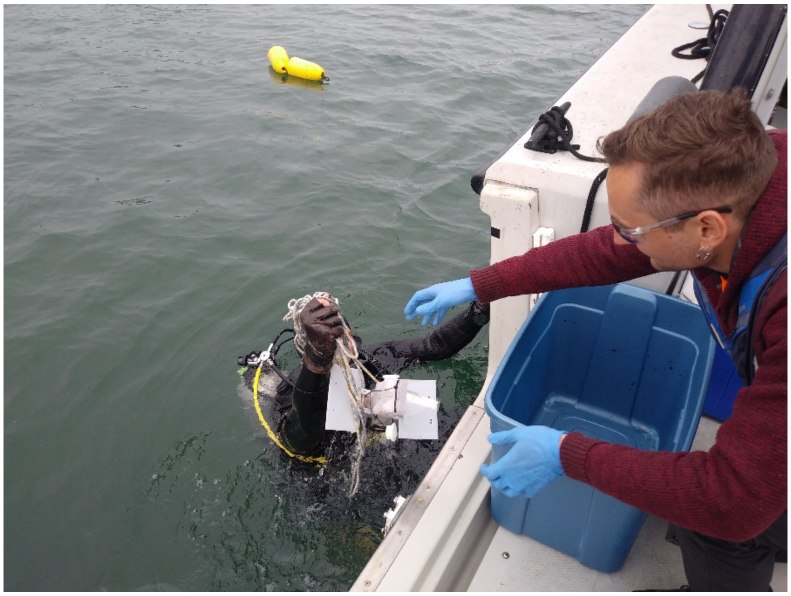
Materials for Retrieval:

- Bags for peeper storage (use peeper bags from deployment)
- Oxygen absorbing packets, “500-cc”, at least 2-3 per peeper sample
- Coolers with wet ice

Note: Before retrieving the peepers, ensure that you are ready to process them right away or that you have the supplies to preserve them until processing. If working from a boat, preserving the peepers and processing them on shore may be the best approach. After removal from the sediment, peepers should be exposed to surface water and air for as little time as possible (ideally 10 minutes or less). This can be achieved by having the plastic/mylar bags and oxygen absorbing packets ready to be used as soon as the peeper is retrieved at the surface. Note that once the oxygen absorbing packets are removed from their vacuum packed bag, they need to be used on the same day or be discarded.

Retrieval

1. Position the vessel at or near the location of the deployed peepers using the GPS coordinates from the deployment. Use of a handheld GPS system with a graphical display and “navigate to point” is extremely helpful.
2. If divers are retrieving the peepers, drop a buoy with an anchor to mark the retrieval location for the diver, then send the diver down to do a search around the buoy, starting adjacent and circling further around until the peepers are found. Once found, return the peeper frame as quickly as possible to the surface via diver or a tender line to the vessel.



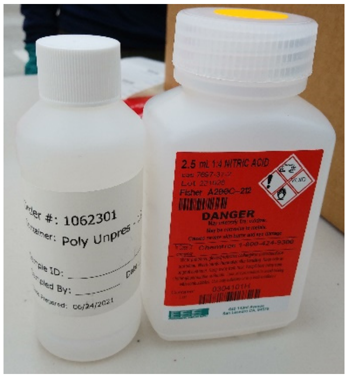
3. If retrieval is being attempted using grappling hooks from the surface of the boat, catch the weighted rope by tossing the hook in a direction perpendicular to that in which the anchor and anchor line were deployed. Drag the grappling hook on the bottom of the sediment until snagged on the rope. Pull the boat or platform above the hook and pull everything straight up.
4. If retrieval is being attempted via wading, safely wade into the water and remove the peeper frame from the sediment. Return the peepers to the shore or vessel.
5. Once retrieved, quickly remove the peepers from the frame and place in the plastic/mylar bag. Peepers do not need to be cleaned or rinsed. Be careful in positioning the peepers so that they do not bump against each other’s membrane, this can be achieved by storing them flat in the bag, side by side, with the membrane up. Do not stack the peepers on top of each other. Add 2-3 “500-cc” oxygen absorbing packets in the bag before sealing it.
6. Label the outside of the storage bag according to the sample nomenclature.
7. Store the bags with the peepers in a cooler, on wet ice until they can be processed.
8. Processing should ideally occur on the same day, within approximately 8 hours after retreival (addditional research would be reccommended to confirm longer storage times).

⚠ **Special Note: Once removed from the sediment, the peepers and peeper frames should be visually inspected to confirm they were fully inserted during the deployment duration. This can be seen from the different coloration of the frame between parts that were exposed to surface water and parts that were in the sediments.**

PROCESSING

Peeper Processing in Field or Field Lab

1. Prepare a clean workstation (i.e. table), ideally in a sheltered area. Essential elements include:
    a. Serological pipettes tips
    b. Pipette pump compatible with serological pipettes tips
    c. Several gallons of DI or distilled water (e.g., approximately 1 gallon per 20 samples)
    d. Plastic spray bottle of DI or distilled water
    e. Laboratory supplied sample bottles to contain waters transferred from the peepers; two bottles are needed for each sample:
        i. An empty 100-mL HPDE bottle for the bromide sample (if bromide is being used as a tracer)
        ii. For metals (typical focus of peeper investigations): a 100-mL or 125-mL HDPE bottle for the metals sample, containing a small amount of nitric acid (i.e., 2.5 mL 1:4 concentrated nitric acid:water or 1 mL 1:1 concentrated nitric acid:water) for preservative



    f. Nitrile gloves
    g. Eye protection
    h. Roll of paper towels or box of Kimwipes
    i. Garbage bag or container to contain waste
    j. Cooler with peepers retrieved from the field and peepers for the Trip Blank
    k. Additional ice (as needed) to maintain cool temperatures
    l. Zipseal bags for packaging sample bottles
    m. Processing forms and chain of custody forms
    n. Tape for securing the cooler for shipment

⚠ **Special Note: Once removed from the protective bag, peepers should be processed within 10 minutes so that contact with the atmosphere is minimized (oxygen will diffuse into the water contained within the peepers and could compromise sample integrity)**

2. Two people are recommended for processing. A designated person ("dirty hands") should be responsible to clean peepers, while another person ("clean hands") should be responsible for transferring water from the peepers into the sample bottles and recording processing information on the processing form. If this is not possible, it is recommended to change gloves between cleaning peepers and transferring the water to the sample bottles.
3. Attach the pipette pump to a fresh serological pipette tip. One pipette tip is needed to transfer the water from the multiple peepers used to create a sample (change out the pipette tip when processing peepers being combined for a separate sample).
4. Removal from storage, open the bag and remove one peeper; take note of the sampling location.
5. Rinse the top of the peeper membrane with DI water to clean off any sediment. Ensure to flush thoroughly around the membrane and cap. A paper towel or Kimwipe can be used to assist removal of sediment as needed, although care must be taken as the membrane is fragile. The membrane should be free of visible grains of sediment.
6. Inspect the peeper for contamination by sediments. To ensure sample integrity, peepers should be inspected for sediments by looking inside from the bottom of the vial. If sediment particles can be seen floating inside against the membrane of the peeper, the peeper should not be sampled, as it may have allowed solid particles into the sampler during sampling, and this may not represent freely-dissolved metal concentrations.

Sediment grains that have entered the peeper; they are observable by swirling the water and turning the peeper upside down

Peeper with no observable sediment grains

7. Once cleaned off, use the serological pipette tip to puncture the membrane, angle the serological pipette tip towards the bottom of the vial and drawn up all water from the peeper into the pipette.

8. Dispense at least 5 mL from the peeper in the sample container for the bromide analysis (if bromide is being used as a tracer).
9. Dispense the rest of the peeper water in the sample container for the metal analysis. The vial for metal analysis should already contain a small volume of nitric acid so that the sample will be acidified.
10. In total, ~20 mL or more should be collected for bromide analysis and ~60 mL or more for metal analysis (consult your analytical lab to confirm ideal and minimum sample volumes).
11. Cap all sample bottles, label, and store in a cooler on wet ice.
12. Note the processing date and time and approximate volume of peeper water used for the bromide sample (ideally ≥ 20 mL) and the metals sample (ideally ≥ 60 mL).
13. Remove the pipette tip from the pipette pump and attach a new pipette tip for use for the next set of peepers that will be used for the next sample.
14. Do not to forget to prepare blank samples using unexposed peepers. This will be used as the Trip Blank sample for bromide and metals.
15. Once all peeper samples have been processed, prepare the samples for laboratory submission (e.g. fill out chain of custody, initiate transfer of samples to receiving laboratory for analysis, etc.).

Appendix F: Peeper Pre-equilibrium Calculation Spreadsheets
(Provided as Excel file attachment to PDF)