A review of peeper passive sampling approaches to measure the availability of inorganics in sediment porewater

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ABSTRACT

Sediment porewater dialysis passive samplers, also known as “peepers,” are inert containers with a small volume of water (usually 1-100 mL) capped with a semi-permeable membrane. When exposed to sediment over a period of days to weeks, chemicals (typically inorganics) in sediment porewater diffuse through the membrane into the water. Subsequent analysis of chemicals in the peeper water sample can provide a value that represents the concentrations of freely-dissolved chemicals in sediment, a useful measurement for understanding fate and risk. Despite more than 45 years of peeper uses in peer-reviewed research, there are no standardized methods available, which limits the application of peepers for more routine regulatory-driven decision making at sediment sites. In hopes of taking a step towards standardizing peeper methods for measuring inorganics in sediment porewater, over 85 research documents on peepers were reviewed to identify example applications, key methodological aspects, and potential uncertainties. The review found that peepers could be improved by optimizing volume and membrane geometry to decrease the necessary deployment time, decrease detection limits, and provide sufficient sample volumes needed for commercial analytical laboratories using standardized analytical methods. Several methodological uncertainties related to the potential impact of oxygen presence in peeper water prior to deployment and oxygen accumulation in peepers after retrieval from sediment were noted, especially for redox-sensitive metals. Additional areas that need further development include establishing the impact of deionized water in peeper cells when used in marine sediment and use of pre-equilibration sampling methods with reverse tracers allowing shorter deployment periods. Overall, it is expected that highlighting these technical aspects and research needs will encourage work to address critical methodological challenges, aiding in the standardization of peeper methods for measuring porewater concentrations at contaminated regulatory-driven sediment sites.

Keywords

Peepers, passive sampling, porewater, sediment, metals, inorganic

1. INTRODUCTION

Contaminated sediments are a major environmental concern of the 21st century, with more than 70 Superfund sites in the United States, each requiring cleanup of more than 10,000 cubic yards (approximately five acres) of impacted sediment (United States Environmental Protection Agency [USEPA], 2020). Aquatic sediment 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 (USEPA, 2001). Total bulk sediment measurements for metals can overestimate the portion of biologically available inorganics in sediment (Peijnenburg et al., 2014). Assessing the bulk sediment concentrations alone can result in overly protective and inaccurate site-specific sediment management decisions impacting stakeholder resources.

Biologically available inorganics in sediment related to sediment toxicity can be 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). This measurement can be obtained in several ways. Mechanical sediment porewater analysis usually consists of collecting large volumes of bulk sediment which are then mechanically squeezed or centrifuged to produce a supernatant liquid (porewater) that then is filtered to extract the water to be analyzed (Gruzalski et al., 2016). Porewater can also be mechanically collected through suction. The mechanical process presents challenges due to the heterogeneity of sediments, high reactivity of some inorganic analytes, and chemical and physical disturbances of the sediments that can cause the concentration of dissolved inorganics obtained from analysis of a mechanically-extracted sample to deviate from the concentration in *in situ* 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-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 to provide a measurement of availability

that has a low impact on the surrounding geochemistry of sediment and sediment porewater and enable a more accurate measurement ((USEPA, 2001; 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 sediment. Peepers (Figure 1) are inert containers with a small volume (1-100 mL) of purified water ("peeper water") capped with a semi-permeable membrane. Peepers usually feature a protective cap or structure that secures the membrane to the peeper. The peeper water is sometimes deoxygenated prior to placement into the peeper, and in some cases, the peeper is maintained in a deoxygenated atmosphere or in deoxygenated water until deployment (Carignan et al., 1994).

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. It is assumed that the peeper insertion does not alter geochemical conditions that affect freely-dissolved inorganics. It is also 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 at the end of the deployment time. After an equilibration period, the peeper is retrieved and brought to the surface. After retrieval, the peeper water is transferred as quickly as possible 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 (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). In general, direct comparisons of porewater samples obtained from mechanical extraction methods and measurements of porewater in peepers

have generally indicated peepers are more accurate in terms of predicting metal availably 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 reflect more accurately 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).

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, there is no standard guidance method for peepers, and uncertainties remain regarding aspects of peeper field methodology, equilibration dynamics, and device materials that hinder the use of peepers for more routine applications at sediment sites under regulatory oversight. A wide variety of methods and formats for peepers exists, and selecting a set of best practices for sampling sediment porewater can be challenging. The goal of our research was to conduct a comprehensive literature review of sediment passive sampling of inorganics using peepers, specifically to identify past and present best practices for peeper preparation, deployment, retrieval, and data analysis, as well as data gaps that, if addressed, would further improve peeper methods and facilitate steps towards standardization.

2. APPROACH

The review evaluated over 85 peer-reviewed and grey literature documents that detail the applications of peepers to measure freely-dissolved inorganics in sediment porewater (Supplementary Material, Table S1). 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 for inorganics at contaminated sediment sites. The review was 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 sediment sites. Key aspects included: 1) peeper design; 2) pre-equilibrium sampling methods; and 3) pre- and post-sampling 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.

3. PEEPER DESIGN

3.1 Overview of Peeper Design

In the several decades since peepers were first reported in the literature (Hesslein, 1976), a variety of peeper designs have been developed to meet project-specific application needs. Most of the designs are close adaptations of the original multi-chamber Hesslein (1976) design, which consists of an acrylic sampler body with multiple peeper water sample chambers. 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. 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), Passeport et al. (2016) and, Xu and Baddar (2022). The vials are usually filled with deionized water, and the membrane is held in place using the vial cap (through which openings have been made) or an o-ring.

3.2 Peeper Chamber Material and Volume

Peeper chambers have been constructed from a variety of materials representing a variety of volumes (Figure 2). It is common for multi-chambered Hesslein (1976) peepers to be constructed out of rigid plastics (e.g., acrylic, polycarbonate, polypropylene) because such materials are

relatively inexpensive, strong, and easy to customize. 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 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 volume to membrane area ratio) and lower resolution compared to smaller multi-chambered designs.

Peeper chamber material should be relatively inert with regards to the potential sorption of freely-dissolved inorganics in water. The 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 so that it depletes the mass of available inorganics surrounding the sampler. Similarly, the material should not act as a sink that will significantly sorb inorganics from peeper water, which is important for the period in which the peeper water remains inside the peeper during deployment and after retrieval from the sediment. For contaminated sediment with 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 relatively inert with regards to sorption. Studies evaluating the sorption of dissolved metals to materials used in sample containers have yielded inconsistent results, such as that significant sorption to materials can occur within minutes (Sekaly et al., 1999), or sorption does not occur in 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 materials with low sorption of metals (Sekaly et al., 1999; USEPA, 1996; USEPA, 1998), but can be also 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 attributed to the durability and relative inertness of the material. However, the authors noted that samples stored in glass bottles that were acid-cleaned or treated overnight with bromine chloride presented "excellent" mercury speciation results. Moreover, Parker and Bloom (2005) indicated a preference for glass bottles ("certified clean for trace metals sampling" I-CHEM® level 300) over PTFE due to the 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). 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, finding no artifacts with their methods. However, other studies 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). Methylmercury passive sampling using peepers differs from other metals and metalloids and is not evaluated in this paper.

Ultimately, peeper material type may be an inconsequential issue for sorption of inorganics, as even if the peeper material does sorb metals from the surrounding porewater matrix, the metal sorbed from the porewater would be replaced by desorption and geochemical equilibrium processes over the many days or weeks of peeper deployment (Peijnenburg et al., 2014). 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 period between the end of deployment and transfer of the peeper water from the peeper chamber is minimized (e.g., less than 24 hours).

Overall, the selection of appropriate materials for contact with and/or storage of water samples for trace metal analysis is fairly well characterized by existing inorganic analysis methods for aqueous samples, and suggests materials typically used for most peeper designs do not present artifacts to the sampling process. In addition, longer contact times between peeper and surrounding sediment

as well as between peeper and peeper water may negate any artifact. This review suggests that the best candidate materials are polymers ideal for trace metal analysis of water samples (i.e., polyethylene, polycarbonate, polypropylene, or FEP/PTFE) as a standard peeper material. Among these materials, FEP/PFTE is considered to be the most inert. However, as FEP/PFTE can represent considerable additional costs, and an empirical comparison of sample results with a less expensive material (i.e., HPDE) would be helpful.

3.3 Peeper Membrane Material and Pore Size

A variety of materials with pore size diameters of approximately 0.2- to 1-micrometer (µm) have been used as peeper membranes (Figure 3). Polysulfone and polyethersulfone are similar in performance and are the most commonly-used membrane types, and have been used for most recent studies because of their chemical inertness and resistance to biofouling (Teasdale et al., 1995; Doig and Liber, 2000; Teasdale et al., 2003; MacDonald et al., 2013; Passeport et al., 2016). Other membrane types have been evaluated in several studies. For example, Carignan (1984) compared the performance of raw cellulose, cellulose acetate, PVC, and polysulfone membranes in measuring porewater concentrations of inorganics in lake sediment 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. 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. Nylon membranes have also been used in instances in which peepers were driven into cohesive sediments and stronger membranes were required to prevent tearing during insertion (Doussan et al., 1998; Jackson et al., 2005; Larson et al., 2012).

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 (Figure 3). The largest membrane pore size identified in the literature review was a 1.0-µm polycarbonate membrane (Serbst et al., 2003), which were used to compare equilibration times for cadmium in a vial peeper design 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, smaller pore sizes (i.e., 0.2-µm) would better prevent inorganics sorbed to fine particulate material, which are not truly dissolved, from entering the peeper. Smaller pore sizes may also be better for limiting entry of metals that are bound to colloids, which have sizes in the 0.001- to 1-µm size range (Buffle et al., 1998). However, Carignan et al. (1985) noted that peeper results with seven metals for peepers with a 0.45-µm membranes were identical to those obtained with a much finer pore size of 0.03-µm. Thus, a pore size of 0.45-µm is likely reasonable for limiting the entry of particulate inorganics and some proportion of colloids. Additionally. the 0.45-µm pore size is the most commonly used pore size for peeper membranes (Figure 3), 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. Overall, 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 for peepers.

3.4 Peeper Chamber Design Factor

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 is an important consideration for peeper design. Larger chamber volumes allow for higher water sample volumes, which allows more analytes to be measured and generally lower detection limits. Higher

specific surface areas for a given volume (i.e., smaller F values) allow for faster equilibration of peeper water with porewater, resulting in shorter deployment times. Design factor also affects the spatial vertical resolution of sampling. For example, if a circular peeper membrane diffusional area is 5 centimeters (cm) in diameter, the peeper integrates the porewater sampling over a 5-cm depth interval when inserted into the sediment (a spatial vertical resolution of 5 cm).

Method detection limits for peeper water samples are inversely related to peeper chamber volumes – larger sample 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, commercial analytical laboratories can use smaller volumes, although reductions in sample volumes affect the number of metals than can be analyzed in a single sample and may affect the method detection limit. For example, the relationship between a hypothetical method detection limit in water for copper versus sample volume size (peeper chamber volume) is shown in Figure 4. The lowest detection limit (0.3 µg/L) is for a peeper volume of 100 mL. Assuming 100 mL is the minimum volume needed for optimal analysis, 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 saltwater 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 4, 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 less than and greater than the AWQC. However, allowing for larger volumes because of variability in the detection limit, potential pre-equilibrium sampling conditions (which can increase the equilibrium-corrected detection limit), and extra capacity for added precision, attaining lower detection limits could be ideal. For example, in the example shown in Figure 4, only peeper volumes 50 mL and greater could attain typical commercial analytical laboratory detection limits that were five times lower than the copper AWQC.

For widespread and routine application at contaminated sites under regulatory oversight, it would be 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, although as noted above, this is affected by the amount of equilibration attained during deployment and the actual performance of the commercial analytical laboratory. Peeper volumes have varied based on project-specific objectives but have ranged from less than 1 mL to over 100 mL (Figure 5). Attaining peeper volumes necessary to match commercial analytical laboratory volume requirements is feasible, as peeper volumes can be 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) and have been successfully implemented with deployment periods of approximately 14 to 28 days. However, as shown in Figure 5, 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 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 US state or federal regulatory oversight.

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 5). Few experiments have confirmed the 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) 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 6). 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). However, full equilibration is not required, as pre-equilibration results can be corrected to equilibrium using modeling. Nonetheless, even when using pre-equilibrium sampling, achieving as much equilibration as possible within the peeper deployment period is generally preferred.

As noted above, 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) can be controlled when designing the peepers (Carignan, 1984; Teasdale et al., 1995; Webster et al., 1998). Decreasing the F value will reduce the time required to reach equilibrium. As shown in Figure 7, 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 time by approximately 50%. Typically, F values for peeper designs are approximately 1 mL/cm^2 or higher. Values for commercially-available multi-chamber peeper samplers 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.

Lower F values can be achieved by reducing the volume of the peeper chamber, given a fixed membrane area. To avoid analytical disadvantages of low captured volumes mentioned above, it is possible to decrease sampling time via combining (compositing volume) 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 4), 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 due to longer times of constructing, deploying, and processing multiple peepers.

Another approach to decrease the F is by increasing the membrane area, given a fixed volume. However, this increases the spatial vertical resolution of sediment porewater 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 (vertical resolution), preventing the evaluation of freely-dissolved measurements at very precise scales (e.g., 1- to 3-cm layer resolution). Another technique 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 or length of the peeper body, which can lead to more difficult deployment and potential 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 in sediment investigations.

Overall, peeper chamber shape and design influences analyte method detection limits, peeper deployment periods, and spatial resolution of samples. 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 vertical scale. 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 vertical resolution in the sediment. However, smaller peepers require compositing multiple chamber volumes to attain the 50-100 mL necessary for commercial labs. Additional experimentation is needed for peepers with lower F values to evaluate the potential advantages of compositing peepers versus one peeper of 50-100 mL and/or large peepers with small design factors to identify the optimal peeper design.

3.5 Peeper Water Salinity

Peeper 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) which can result in a great difference between the high salinity and density of the marine sediment porewater compared to the deionized water in the peeper. 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. This approach was used to

prevent 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 sediment. Webster et al. (1999) specifically tested equilibration dynamics of peepers containing deionized water in marine sediment 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 the initial period of equilibration (e.g., first 1-5 days).

The effect of initial peeper water salinity on peeper results for metals over longer periods and reverse tracer equilibration has not been studied adequately. 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 sediment porewater salinity is likely to vary from site to site, so any attempts to match the initial salinity in the peeper water is unlikely to be successful. Additional experiments would be necessary to understand the impact of using saltwater versus deionized water in peeper chambers.

4. PRE-EQUILIBRIUM SAMPLING METHODS

As noted in Section 2, the equilibration period of peepers can last several weeks and depends 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 for passive samplers have been applied to measure freely-dissolved organic chemicals in sediment (USEPA, 2017).

Although the equilibrium concentration of an analyte in sediment can be evaluated by examining analyte results for peepers deployed for multiple periods (i.e., a time series), this is impractical for typical field investigations. This would require several mobilizations to the site to retrieve samplers at multiple events. Alternately, reverse tracers (referred to as a performance reference compound when used with organic compound passive sampling) can be used to evaluate the percentage of equilibrium reached by a passive sampler. For example, a reverse tracer can be added to the peeper

425 water at a concentration of 100 mg/L. After deployment in sediment, if the concentration of the
426 reverse tracer is determined to be 50 mg/L, one can infer that the peeper has reached 50% of
427 equilibration. Assuming that the diffusion of a target analyte (which has diffused into the peeper
428 during deployment) has related properties to that of the reverse tracer, a measured concentration
429 of a target analyte can be corrected to the predicted concentration at complete equilibrium.

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

436 $$C_0 = \frac{C_{p,t}}{1 - e^{-Kt}}$$

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

439 $$K = K_{tracer}\left(\frac{D}{D_{tracer}}\right)$$

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

442 $$K_{tracer} = -\frac{1}{t}\ln\left(\frac{C_{p,t}}{C_{p,i}}\right)$$

443 The exponential decay equations detailed above were evaluated alongside comparatively complex
444 analytical approximations based on an infinite plane source and an infinite point source. The study
445 concluded that the point source correction resulted in significant inaccuracy at low values of K_{Tracer},
446 while both the plane source and exponential decay corrections improved estimations of porewater
447 concentrations. The authors recommended using the exponential decay correction in the interest
448 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 rigorously 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., freshwater sediment and marine sediment) would also be useful, as salinity may affect equilibration dynamics. Although temperature also affects the diffusivity of the bromide tracer and inorganic analytes of interest, it is assumed that the ratio of bromide diffusivity and target analyte diffusivity 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 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.

5. OXYGEN CONTAMINATION

5.1 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 have the potential to diffuse out of the sediment into the water (Hesslein, 1976; Peijnenburg et al., 2014). 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 sediment is that some inorganics can react with oxygen 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 enhance the dissolution of oxidized metal sulfide complexes (Wise, 2009). These reactions can also affect the solubility of other inorganics, even those 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 introduced into the sediment from the peeper during deployment, and 2) oxygen exposure of the peeper water during peeper retrieval and processing.

5.2 Oxygen Contamination During Deployment

Oxygen contamination from peepers 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 iron and manganese compared to acrylic peepers. Carignan (1984) attributed this issue to oxygen diffusing out of the polycarbonate into the chamber and causing precipitation of iron and manganese, which are less soluble in oxygenated sediment porewater (Simpson et al., 2022). Dissolved oxygen present in the peeper water 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 to concentrations of freely-available metal. Additional investigation by Carignan (1984), showed that deoxygenation of the peeper and peeper water had the highest impact on concentrations 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.

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

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

528 Despite the lack of consensus in the literature regarding the importance of deoxygenating peepers
529 prior to deployment, commonly applied procedures for peeper preparation tend to err on the side
530 of caution and follow the recommendations of Carignan (1984). Of the 82 papers reviewed in our
531 paper that conducted empirical experiments with peepers (Table S1), 64 of the papers (78%)
532 deoxygenated peepers prior to deployment (usually via maintaining peepers in deoxygenated water
533 prior to deployment).

Deoxygenating peepers and isolating peepers from oxygen prior to deployment is challenging since our atmosphere is composed of 21% oxygen. Additionally, most surface waters overlying sediments are relatively well oxygenated, so it is questionable that deoxygenated peepers can truly remain completely deoxygenated during their deployment. Procedures to deoxygenate peepers increase the time and costs required to prepare peepers in the laboratory due to the lengthy deoxygenation of the peeper water and plastic as well as the 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 deoxygenated 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 risks. 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 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.

5.3 Oxygen Contamination After Deployment

The second major issue related to oxygen is the oxygen contamination during and after retrieval from the sediment. Given the rapid kinetics of oxygen-sensitive species and potential effects on geochemical conditions within the peeper, oxygen contamination could hypothetically affect results. For example, upon removal from 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

563 suggest that peeper waters could reach relatively oxygenated levels (i.e., 5 to 7 mg/L) within
564 approximately 30 to 60 minutes during exposure of the peeper to air depending on volume to
565 membrane surface area ratio. Removal of the membrane or covering of the peeper water (i.e., to
566 facilitate removal of the peeper water) could further speed this process. Hypothetically, oxygen
567 entering the peeper could trigger precipitation reactions that could remove dissolved inorganics
568 from the solution, forming a precipitate. In some cases, this precipitate would be transferred to the
569 storage vial where it is preserved and would be ultimately quantified in the analysis once the
570 sample is acidified. However, it is also possible that the precipitate could adhere to the interior of
571 the peeper vial and would not be transferred to the storage vial, resulting in an underestimation of
572 the original dissolved concentration within the peeper at the time of retrieval from the sediment.

573 Despite these hypotheses, the effects on peeper water oxygen contamination after removal from
574 sediment have not been rigorously evaluated, leading researchers to take considerable precautions
575 to avoid oxygen contamination. Rapid processing of the peeper water and stabilization of redox
576 sensitive species have been used to minimize the reactions of anoxic peeper water after it is
577 removed from the sediment (Burbridge et al., 2012). Several papers reviewed in this effort (Table
578 S1) noted that the processing was conducted quickly (generally less than 5 to 10 minutes after
579 retrieval of the peeper from sediment) to avoid potential oxygen contamination of samples during
580 transfer of the sample from the peeper to the storage container, in which the peeper sampler is
581 usually preserved via acidification. However, immediate processing of peeper water is not always
582 feasible, practical, or ideal. Conditions for processing peepers in the field are often not as ideal as
583 in an analytical chemistry laboratory and can result in higher probabilities of inadvertent sample
584 contamination or other sample handling errors. If peeper water cannot be transferred to storage
585 containers within minutes after retrieval, peepers are often stored in oxygen free containers, such
586 as bags or containers purged with inert gases. This requires the use of compressed inert gases,
587 which complicate field sampling, especially on vessels or in remote locations. Maintaining inert
588 atmospheres in typical sample storage containers can be difficult and can complicate shipping, so
589 often peepers are transferred to storage containers in the field or temporary shelters.

590 As noted above, concern regarding the potential for oxygen to enter the peeper after exposing it
591 directly to the air before transfer to the storage container has necessitated complicated transfer
592 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 the removal of the liquid such that oxygen is not introduced into the peeper during transfer. 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.

Alternatively, 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. Of the 82 papers reviewed in our paper that conducted empirical experiments with peepers (Table S1), 13 of the papers (16%) noted that transfer of the peeper water to storage containers was conducted in an inert (usually nitrogen) atmosphere. The reliance on inert gases in the field also presents complications as described previously. Wise (2009) showed that working in an anaerobic chamber was not necessary as it did not provide a significant difference in concentrations of redox sensitive constituents; this result could be attributed to the short contact time with the atmosphere if the processing of the peeper water is rapid.

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 for small volume peeper samplers in Xu et al. (2012). However, freezing larger volume porewater samples within minutes or hours of removal from sediment at most field sites would be extremely difficult, and the steps required to thaw and process the sample for analysis are complicated and may be redundant. Overall, there is uncertainty in the need to preserve peepers from oxygen contamination after they are retrieved from sediment, and considerable variation in approaches for preserving peeper samplers.

6. CONCLUSIONS AND RECOMMENDATIONS

The review in this paper 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 basic peeper design deserve

additional empirical evaluation to further provide confidence in their use in contaminated sediment site investigations. First, the sorption of metal analytes to peeper materials has a low potential to represent an artifact to sample results for most commonly used plastics. Further research needs could evaluate various standard materials, comparing performance to FEP or PTFE. The potential effects of storing unpreserved peeper samples for a period typical of field programs and commercial analytical laboratory processing times could also be beneficial if sorption or material interaction is of concern. Size and shape of peeper chambers (i.e., design factors) could be better optimized. As noted in this review, commercial analytical laboratories desire large sample volumes, compared to academic research, when analyzing inorganics using standard regulatory chemical analysis methods. Thus, for routine commercial application of peepers, there is work to be done 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.

Typical peeper membrane materials (i.e., polysulfone and polyethersulfone) have been shown to be inert with regards to typical inorganic analytes. The 0.45-µm pore size of these membranes is somewhat standardized, and the fraction of metals in water passing through a 0.45-µm filter has been traditionally considered to be dissolved by regulatory organizations. This assumption would benefit for more rigorous empirical evaluation, perhaps following research to address and streamline the methodological aspects of peeper sampling such as sample handling and preservation. Comparisons of peeper measurements of availability to measurements of bioaccumulation of inorganics by sediment organisms would be especially useful.

The time required for peeper deployment also deserves more optimization. Obtaining results quickly is often paramount for regulatory driven investigations, and typical time periods required to reach full peeper equilibration can strain the patience of stakeholders. The use of pre-equilibration sampling methods with peepers containing reverse tracers can reduce peeper deployment times. A robust demonstration and validation of the approach with metals typically evaluated at sediment sites would establish additional confidence in the methods. It is also unknown if the peeper equilibration process in marine sediment is affected by the use of deionized water typically used in peepers, as the salinity difference may affect sampling kinetics thus altering deployment time.

Lastly, the potential artifactual effects of oxygen on the peeper sampling process has been an uncertainty throughout the history of peeper uses. Oxygen present in peepers prior to deployment and oxygen contamination of peeper water after removal from sediment has been assumed to potentially affect the results, particularly for redox-sensitive analytes that are often the focus of peeper investigations. Methods traditionally used to prevent oxygen contamination before and after deployment are complicated, expensive, and potentially impractical for many investigation scenarios. Thus, the need for these methods should be evaluated to confirm if these protective approaches are truly necessary to ensure high data quality and establish confidence in peeper results.

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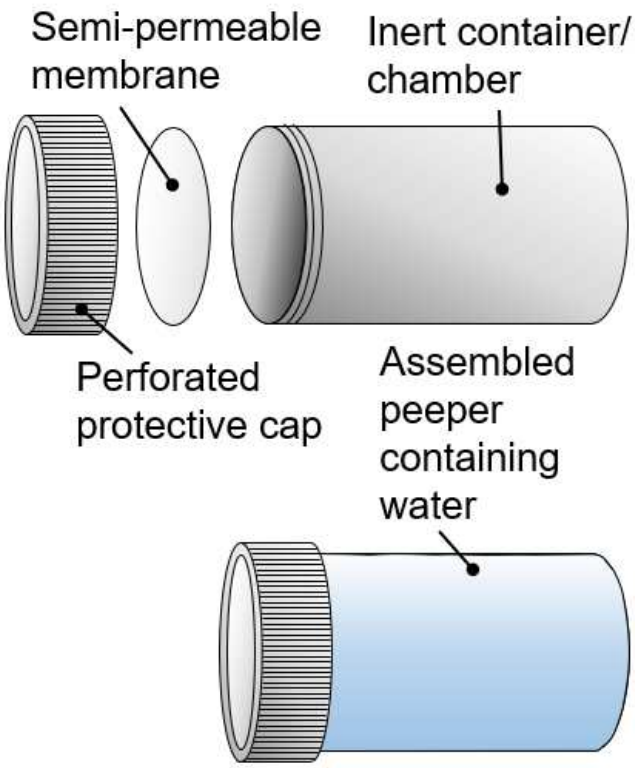


Figure 1. Conceptual illustration of peeper construction showing (top, left to right) the peeper cap (optional), peeper membrane and peeper chamber, and an assembled peeper containing peeper water (bottom).

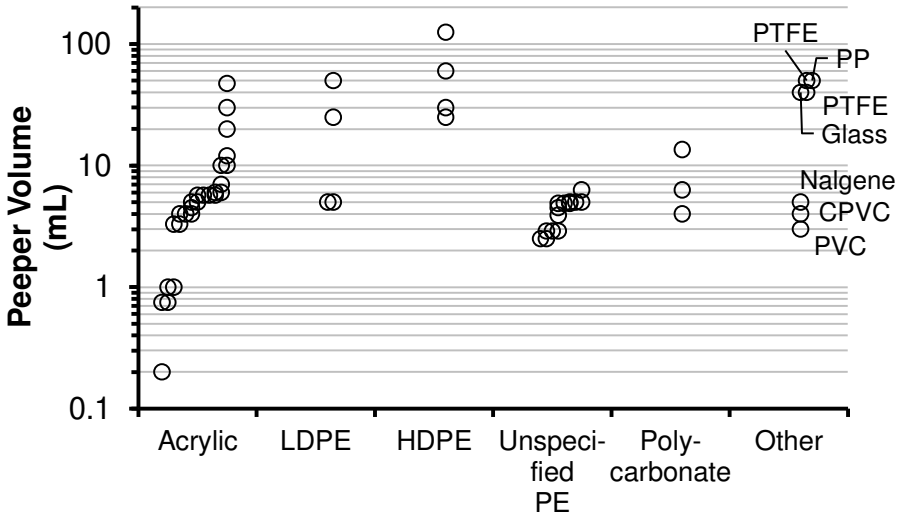


Figure 2. Peeper chamber volume by peeper material type. Labels next to each symbol represent the peeper water volume (milliliters [mL]) and material type (for the peepers in the "Other" category).

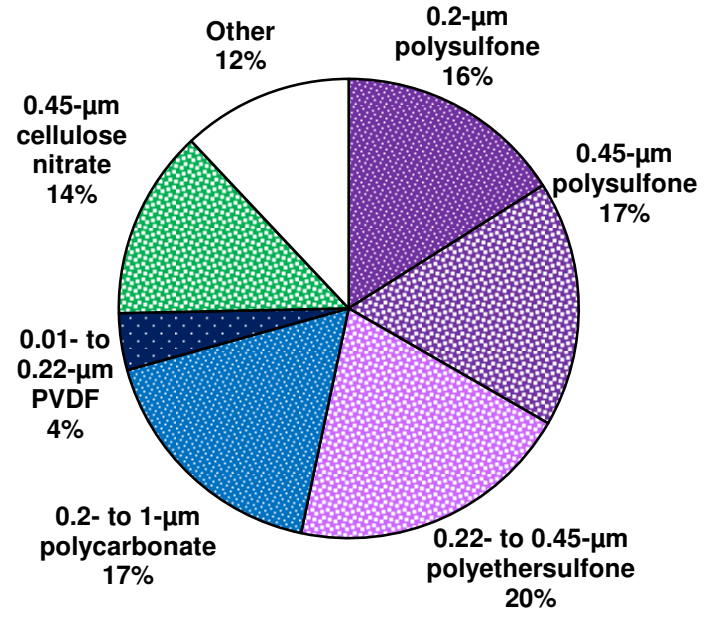


Figure 3. Peeper membrane types of the 75 studies reporting membrane details. Values reflect the percentage of studies using peepers with the specified membrane type.

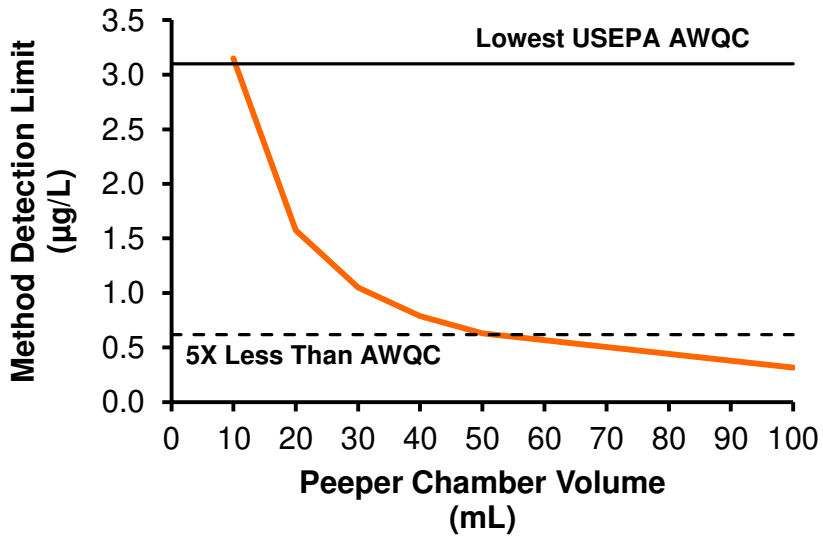


Figure 4. Hypothetical commercial analytical laboratory method detection limits for copper (orange line) for various peeper chamber volumes. The USEPA saltwater chronic Ambient Water Quality Criterion (AWQC) for copper (3.1 µg/L) is shown as the solid line. The dotted line represents a threshold five times less than the AWQC.

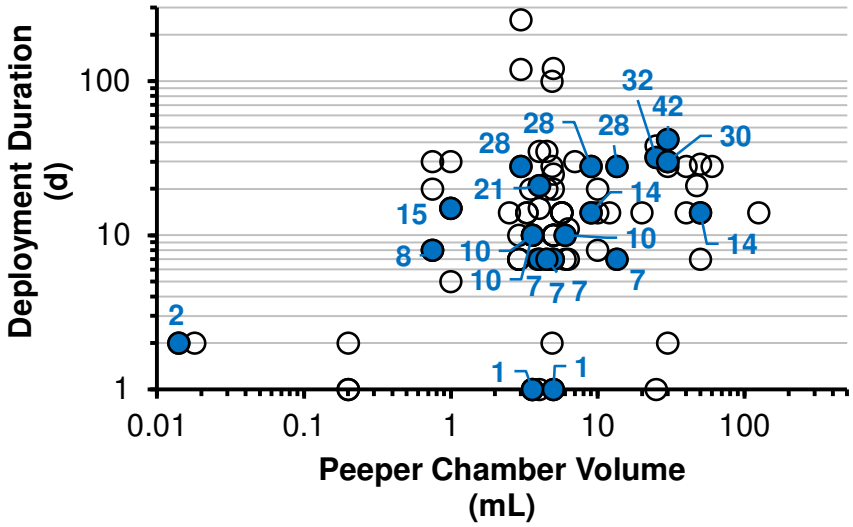


Figure 5. Deployment duration versus peeper chamber volume. The figure is on a logarithmic scale. Blue-filled symbols indicate peepers that were confirmed to be at equilibrium at the deployment time indicated by the blue label (note that equilibration may have been reached prior to the deployment time). Hollow symbols represent peepers that were not at equilibration or instances in which equilibration status was not confirmed.

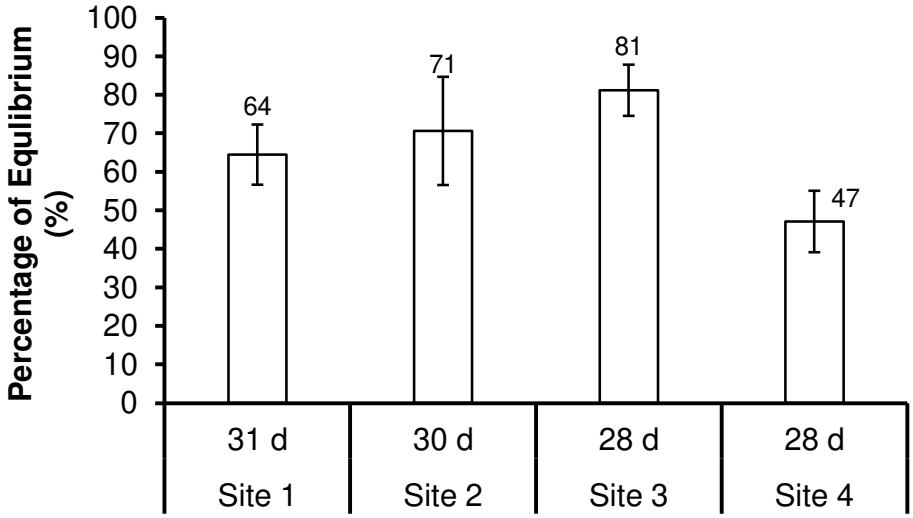


Figure 6. Percentage of equilibration (mean ± standard deviation) measured with a bromide tracer in four different site sediments (60-mL peeper with F = 8 mL/cm^2, unpublished data courtesy of SiREM). Labels next to each column represent the mean value.

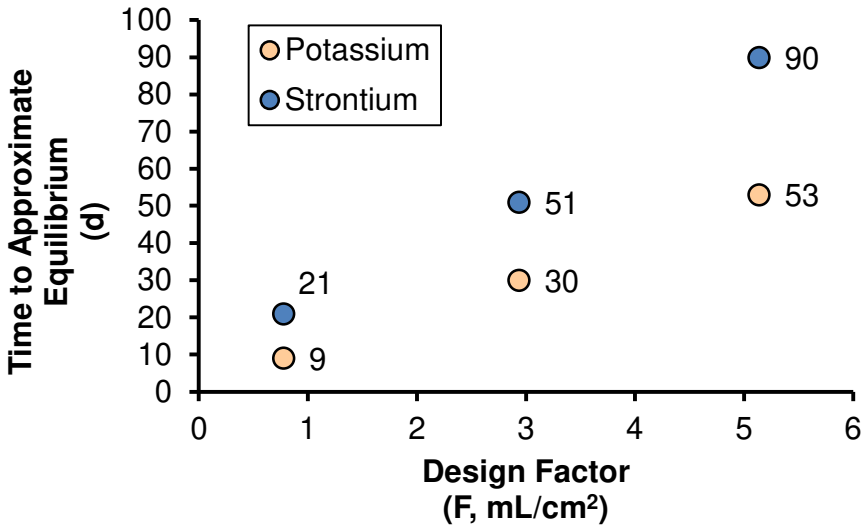
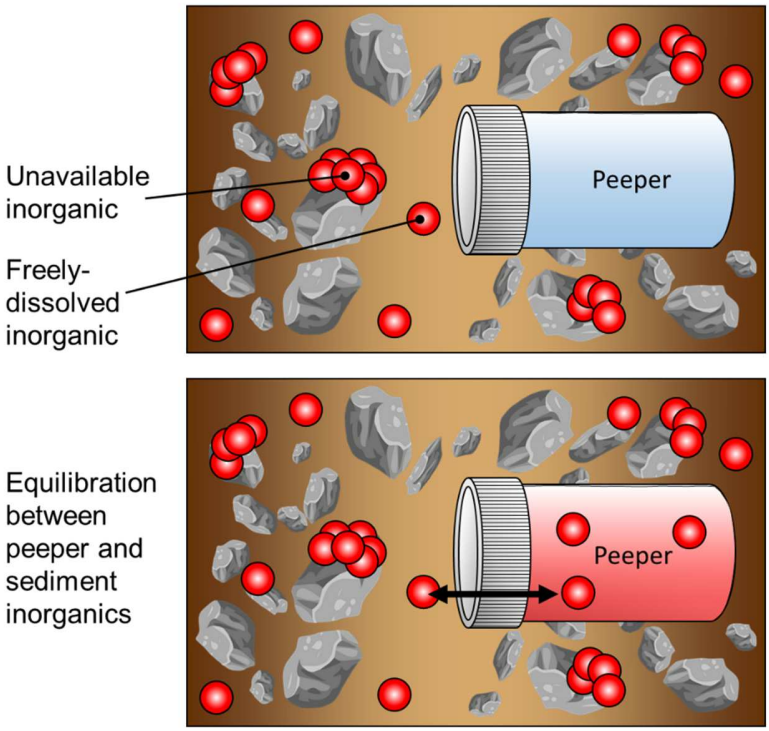


Figure 7. Time required to reach approximate equilibrium (90% of equilibrium) for strontium and potassium in sediment using three peepers with different design factors. Figure created from data in Webster et al. [1998]. Labels next to each symbol represent the time to approximate equilibrium.

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 chamber material	• 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 materials versus FEP or PTFE and evaluate effects of typical storage times (i.e., days to weeks).
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.	Evaluate the relationship between the metals that pass through 0.45-µm polysulfone/polyethersulfone membranes and true measures of bioavailability.
Peeper chamber 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). • Samplers with a lower design factor F increase equilibration speed, reducing deployment times and allowing finer spatial vertical resolution in the sediment. • 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 factor.
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 saline 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 the ability of reverse tracers to predict concentrations at equilibrium.
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, affecting results for redox-sensitive analytes.	Evaluate effects of deoxygenation on peeper results, peeper materials, and storage time for deoxygenated peepers.
Oxygen contamination after deployment	• Oxygen has the potential to contaminate the peeper water after the peeper is removed from sediment, potentially altering the results for redox-sensitive analytes.	Evaluate best procedures for transferring peeper water to storage container and hold time for peepers removed from sediment.



Graphical Abstract. 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).