# Synthetic Iron Oxides for Documenting Sulfide in Marsh Pore Water

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In estuarine systems, naturally occurring soluble $S^{2-}$ is an indicator of anaerobic decomposition by the $SO_4^{2-}$ reduction pathway and can, at high concentrations, be detrimental to plant communities. Depth distributions of soluble $S^{2-}$ in marsh pore water are typically measured using either equilibrium dialysis samplers (peepers) or pore water extractors (sippers). The former technique provides concentrations equilibrated over one or more weeks at centimeter-scale resolution, while the latter allows rapid sampling and analysis but with a coarser vertical resolution (5–10 cm). We report on a novel technology for documenting marsh pore water $S^{2-}$ concentrations based on reactive synthetic Fe oxides and image analysis, which allows rapid sampling but still captures small-scale spatial resolution. During the last few years, this new technology associated with synthetic Fe oxides known as IRIS (Indicator of Reduction In Soils) has been developed to aid in documenting reducing conditions in wetland soils. Our recent work has shown that IRIS technology can be used to document and measure $H_2S$ levels in marsh soil pore water. The data obtained can provide detailed, quantitative information on $S^{2-}$ concentrations with millimeter-scale spatial resolution.

**Abbreviations:** IRIS, Indicator of Reduction In Soils; IT, Image Tool; PVC, polyvinyl chloride.

The factors necessary for $SO_4^{2-}$ reduction have been well documented (Rabenhorst and James, 1992) and include a source of oxidizable organic matter, a source of $SO_4^{2-}$, $SO_4^{2-}$–reducing microorganisms, and reducing conditions. All these requirements are met in estuarine (brackish or saline) marsh environments, making the dissimilatory reduction of $SO_4^{2-}$ perhaps the most distinctive biogeochemical process in these ecosystems. Aside from imparting saline tidal wetlands with the familiar aroma of $H_2S$, $SO_4^{2-}$ reduction has important implications for ecosystem processes. For example, $SO_4^{2-}$ reduction dominates anaerobic decomposition in brackish marshes, inhibiting $CH_4$ production and regulating soil C storage in these systems (Megonigal et al., 2003). Soluble $S^{2-}$ can be detrimental or even toxic to many organisms at the levels found in estuarine marshes, and it has been shown to limit the growth of common marsh grasses such as *Spartina alterniflora* Loisel. (Koch et al., 1990; Mendelssohn and McKee, 1988). For these reasons, there has been interest in measuring the levels of soluble $S^{2-}$ in marsh pore water, and a rapid assessment approach for these measurements is especially valuable.

Sulfide in pore water is usually measured using two basic methods. Pore water extractors (sippers) inserted into the marsh soil are put under suction and the pore water is collected in a syringe or similar device (e.g., Marsh et al., 2005, Keller et al., 2009). The water sample is then transported to the laboratory and $S^{2-}$ measured using any number of techniques (Eaton et al., 1995). This approach is relatively rapid, but has the limitation of providing poor resolution because the sample is drawn from a soil volume of uncertain dimensions. It is probably not reasonable to expect vertical resolution better than about 10 cm using this method. A second approach uses equilibrium dialysis samplers (peepers; Hesslein, 1976). In this method, a device containing a vertical series of chambers is filled with deoxygen-

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ated, distilled water, covered with a semipermeable membrane, inserted into the marsh soil, and allowed to equilibrate during an extended period. When sufficient time has allowed the soluble constituents in the pore water to reach equilibrium with those in the chambers (usually 1 wk or longer), the device is extracted and the water in the chambers is analyzed in the laboratory. This method has superior resolution to the sippers (1–2 cm) but has the limitation of requiring a relatively long time to equilibrate (Teasdale et al., 1995).

High spatial variability in natural systems is a ubiquitous characteristic that has important consequences for biogeochemical cycling. This is particularly true in wetland soils, where aerobic microsites near roots or animal burrows are hotspots for regenerating terminal electron acceptors (Gribsholt et al., 2003; Megonigal et al., 2003). Existing methods of measuring pore water constituents do a poor job of describing the spatial variability in the root zone (surface 50 cm), where these processes are most active. Although microelectrodes provide high spatial resolution, the information is confined to the upper several centimeters of the soil profile.

In the last few years, a new technology based on the reduction of synthetic Fe oxides, known as IRIS, has been developed to aid in evaluating wetland soils (Rabenhorst and Burch, 2006; Rabenhorst and Castenson, 2005; Castenson and Rabenhorst, 2006; Jenkinson and Franzmeier, 2006). Using this approach, polyvinyl chloride (PVC) tubes coated with an Fe oxide paint are inserted into the soil. In wetland systems with actively respiring microbes, the Fe oxides will become reduced, soluble, and visibly stripped from the tubes, providing a simple documentation of reducing soil conditions. It was inadvertently discovered that when these IRIS tubes were placed into wetland systems that contained soluble $S^{2-}$, black Fe sulfide coatings formed on the tubes that later faded when exposed to the air (Stolt, 2005).

The observed reaction can be described with the following equations, where $S^{2-}$ chemically reduces Fe(III) to Fe(II):

$$H_2S + 2FeOOH \rightarrow 2Fe^{2+} + S^0 + 4OH^- \quad [1]$$

and further reacts with $S^{2-}$ to form insoluble FeS:

$$2H_2S + 2Fe^{2+} \rightarrow 2FeS + 4H^+ \quad [2]$$

The combined reaction is

$$3H_2S + FeOOH \rightarrow 2FeS + S^0 + 4H_2O \quad [3]$$

Iron monosulfide (FeS) is a poorly crystalline metastable phase (possibly similar to the mineral makinawite) and is a black pigment. On the IRIS tubes, the FeS forms a dark gray to black coating. The FeS phase is very labile and thermodynamically unstable under oxidizing conditions, and thus the dark color will fade over a period of minutes to hours when exposed to the air. In the reducing marsh environment, the black FeS remains metastable, but with time it generally converts to the more stable disulfide form $FeS_2$—pyrite.

The objectives of this study were to assess the feasibility of using IRIS technology to describe the spatial variability and quantitatively measure $S^{2-}$ concentrations in marsh pore water. We compared data obtained from this novel methodology to $S^{2-}$ concentrations measured using traditional sipper and peeper techniques.

## MATERIALS AND METHODS

An Fe oxide suspension of the appropriate mineralogical composition (approximately 40% goethite and 60% ferrihydrite) was synthesized following the procedure described in Rabenhorst and Burch (2006). The IRIS tubes were constructed using 60-cm lengths of 1.27 cm (1/2 inch) Schedule 40 PVC tubing (21-mm [0.84-inch] o.d.) that had been cleaned and lightly sanded, to which a single coat of Fe oxide paint was evenly applied to the lower 50 cm while rotating the tube using a lathe device (Jenkinson and Franzmeier, 2006). The same Fe oxide paint was applied to the lower 50 cm of 0.635-cm (1/4-inch) PVC panels 20 by 60 cm in size (these were cut from large PVC sheets available from standard plastics suppliers) that had been cleaned and lightly sanded, using a single stroke with a 23-cm-wide soft foam brush to improve the evenness of application. The paint was similarly applied to small 0.635-cm (1/4-inch) PVC chips that were 2.5 by 8 cm in size.

To create a series of standards, duplicate painted chips were placed into $Na_2S$ solutions (adjusted to pH 7.5) of known concentration (3, 6, 9, 12, 15, 23, 30, 38, 45, 60, 75, 90, 120, 150, 225, and 300 mg/L $S^{2-}$) for periods of 1, 5, 60, and 360 min. After the allotted time, each chip was removed from the solution and quickly rinsed with water and patted dry (still moist). The color was measured using a CR-300 Minolta digital colorimeter, immediately after which a color image of the chip was obtained using a flatbed scanner. The total time for these two analyses was approximately 90 s.

### Field and Laboratory Methods

Preliminary testing of the IRIS tubes was conducted at several marsh sites around Chesapeake Bay to learn approximately how long the tubes should be left in place. After testing periods ranging from 1 through 7 d, we concluded that <24 h was required to document noticeable reactions. We therefore decided to use installation times of 5, 60, and 360 min. It was during the preliminary testing that we decided to use large flat panels rather than the cylindrical tubes so that images could be quickly and easily recorded using a flatbed scanner.

Two marsh sites were selected at the Smithsonian Environmental Research Center (SERC) near Edgewater, MD, which is located on the Rhode River, a tributary of Chesapeake Bay. The average salinity of Rhode River is approximately 7 g/kg. One site was located close to a major tidal stream and had greater mineral sediment inputs and, being dominated by a stand of *Phragmites australis* (Cav.) Trin. ex Steud., was named the Phragmites site (38°52′37.70″ N, 76°32′39.03″ W). The second site was located in a more interior portion of the marsh and, being dominated by *Schoenoplectus americanus* (Pers.) Volkart ex Schinz & R. Keller (formerly *Scirpus olneyi* A. Gray), was named the Schoenoplectus marsh (38°52′30.47″ N, 76°32′42.93″ W). The soils at both sites were dominated by organic materials and both fell within the range of the Transquaking soil series (euic, mesic Typic Sulfihemists). The soil at the Phragmites site that was closer to the tidal stream had dramatically more mineral sediment (as shown by less organic material) in the upper 20 to

**Table 1. Soil properties at the two marsh study sites. Both soils fall within the range of the Transquaking series (euic, mesic Typic Sulfihemists).**

| Horizon | Depth | Description | Organic C |
|---|---|---|---|
| | cm | | g/kg |
| Schoenoplectus site | | | |
| Oe1 | 0–20 | 7.5YR 2.5/2 (very dark brown) mucky peat; many fine and medium roots; rubbed fiber content 65%; very dense root mat | 449 |
| Oe2 | 20–44 | 7.5YR 3/3 (dark brown) mucky peat; many fine roots; rubbed fiber content 70%; firm root mat | 440 |
| Oe3 | 44–165 | 10YR 2/2 (very dark brown) mucky peat; rubbed fiber content 25% | 476 |
| Oa | 165–200 | 5Y 2.5/1 (black); rubbed fiber content 5% | 121 |
| Phragmites site | | | |
| Oa1 | 0–13 | 2.5Y 3/2 (very dark grayish brown) muck; 35% phragmites rhizomes | 221 |
| Oa2 left | 13–23 | 5Y 3/1 (very dark gray) muck | 181 |
| Oa2 right | 13–32 | 10YR 3/2 (very dark grayish brown) muck | 154 |
| Oe1 | 23(32)–49 | 7.5YR 3/2 (dark brown) mucky peat; 15% phragmites rhizomes; rubbed fiber content 25% | 420 |
| Oe2 | 49–180 | 10YR 2/1 (black) mucky peat; rubbed fiber content 18% | 502 |
| Oe3 | 180–200 | 10YR2/2 (very dark brown) mucky peat; rubbed fiber content 18% | 500 |

30 cm than the soil at the Schoenoplectus site, and it is probable that the sediment came with overbank flow during flood tides (Table 1).

Duplicate equilibrium dialysis samplers (peepers) with chambers at 1-cm intervals and extending to a depth of 42 cm were installed at each site on 28 Sept. 2006 and were removed and analyzed from the Schoenoplectus site on 10 Oct. 2006 (after 12 d) and from the Phragmites site on 11 Oct. 2006 (after 13 d). Using sippers, water samples were collected at depths of 5, 15, 25, 35, and 45 cm on 2 Oct. 2006 and again on 11 Oct. 2006 near the locations where the peepers were installed. All pore water samples were collected in the field using syringes (30-mL volume for sippers, 10-mL volume for peepers) equipped with two-way stopcocks, and transported on ice to the SERC laboratory for analysis. Upon returning to the laboratory, 2 mL of pore water sample was added to 2 mL of alkaline antioxidant (2 mol/L NaOH, 0.2 mol/L $Na_2H_2$ethylenediaminetetraacetic acid, 0.2 mol/L ascorbic acid; Eaton et al., 1995), which had been prepared before field sampling in deoxygenated water. Sulfide concentrations were measured as quickly as possible using an ion-selective electrode (Lazar Research Laboratories, Los Angeles; Eaton et al., 1995). The electrode was calibrated using prepared $S^{2-}$ standards ranging from 0.1 through 200 mg/L $S^{2-}$. In all cases, a logarithmic function was used to generate a standard curve between $S^{2-}$ concentration and millivolt output from the electrode.

The IRIS panels were initially used on 2 Oct. 2006, but due to difficulties with the scanner, an incomplete data set was collected. Therefore the panels were installed and analyzed again on 9 Oct. 2006, which was between the dates on which measurements were made using sippers and between the dates of installation and removal of the peepers. At each site, duplicate panels were installed in the vicinity of the peepers (within 1 m) for periods of 5, 60, and 360 min. To facilitate the insertion of the panels, a pilot hole was first made using a 2.5-cm-thick PVC wedge (25 cm wide by 60 cm tall) that was sharpened on one edge to help cut through the root mat and to minimize compaction, and was driven 50 cm into the marsh. Because of suction, a winch mounted on a tripod was required to extract the wedge from the marsh before introducing the panel. The panels were inserted carefully to minimize abrasion and were secured in place using a shim inserted behind the panel. After the allotted time, the shim was removed and the panel was carefully removed. To minimize oxidation of the Fe sulfides on the panels during the brief transport period to the scanner (approximately 1–2 min), each panel was slipped into a plastic bag that was sealed close against the wet painted face of the panel to exclude atmospheric $O_2$. Each panel was briefly rinsed to remove any adhering marsh soil material (the black sulfide precipitate is stable and not affected by rinsing) and quickly blotted dry and placed on a flatbed scanner powered using an DC–AC inverter. Due to the length of the panels (60 cm), two scans were required to capture the full area of each panel, which were later composited using Adobe Photoshop software. The total processing time was approximately 2 min.

## Image Analysis

Scanned images of both standards and the field data were processed using Adobe Photoshop CS2 version 9.0.2 software. To prepare the images for quantitative analysis, they were converted from color to grayscale. Complications emerged during this conversion because of variations in the thickness of the original Fe oxide paint, which when initially viewed as a grayscale image, falsely appeared as differences in $S^{2-}$. This problem was ameliorated by using the channel mixer function to effectively isolate and remove contributions caused by the reddish-colored paint. This was accomplished by using a gray (monochrome) output channel and setting the source channels at red = 140%, green = 0%, and blue = 0%. In this way, the gray and black colors of the precipitated FeS were preserved in the images without confounding shades of gray contributed from the red-colored paint.

Grayscale images were analyzed using Image Tool 3 (IT) image analysis software (University of Texas Health Science Center in San Antonio, 1995). The images obtained from the chips placed in the standard $S^{2-}$ solutions were evaluated using the threshold tool (in IT). The threshold was manually adjusted to optimally distinguish the level of gray or black on the standard chip. The threshold levels were then plotted against the $S^{2-}$ concentration. Using a least squares approach, an exponential function best fit the data.

On the field panels, the black to gray continuum was split into four classes that could be visually distinguished. These corresponded to threshold levels of 121, 188, 232, and 245, which were then used throughout the study to maintain uniformity (the threshold scale ranges from 0 to 255, essentially splitting the black–white continuum into 256 increments). Separate images were generated identifying those areas with gray colors falling within these thresholds. The binary images that were generated were then quantified using the software. Using the best-

fit exponential equations developed from the standards for the length of time the panels were in place, these threshold values of 121, 188, 232, and 245 correspond to $S^{2-}$ concentrations of 192, 84, 48, and 41 mg/L (60 min) and 68, 32, 20, and 17 mg/L (360 min). By joining the quantified areas for each grayscale threshold with the $S^{2-}$ concentrations represented by that threshold, the overall $S^{2-}$ concentration in the pore water could be quantified. To obtain a depth function, these calculations were made on each 5-cm increment through the 50 cm that the panels extended into the soil profile.

## RESULTS AND DISCUSSION

The IRIS panels allowed quantification of the pore water $S^{2-}$ concentrations in both marshes. The Fe oxide coated PVC chips placed in different $S^{2-}$ solutions showed a systematic change in color as a function of $S^{2-}$ concentration and as a function of time exposed. These trends are clear from visual assessment (Fig. 1) and are demonstrated from colorimeter measurements. The color of the original chips was approximately 8.7YR 6.5/7.7, and although there was no systematic change in Munsell hue, both Munsell value and chroma decreased monotonically with both higher $S^{2-}$ concentration and longer exposure, at least at concentrations >6 mg/L (Fig. 2). The scanned images of these chips showed exponential relationships between the IT threshold value and the $S^{2-}$ concentration (Fig. 3), and these relationships were used as standards for evaluating $S^{2-}$ reactions on IRIS panels used in the marsh.

Examination of the panels after they were removed from the sites indicated that the 60- and 360-min panels showed adequate $S^{2-}$ formation for analysis. Figure 4 provides an example of a panel that was in the Schoenoplectus site for 60 min and then scanned, processed, and analyzed using the specified IT threshold values (i.e., 121, 188, 232, and 245) as described above.

The IRIS panels capture a very fine spatial resolution (<1 mm) in the depiction of the marsh pore water $S^{2-}$ concentration. The analyzed images from the IRIS panels demonstrate that there is a great deal of microsite variability in the pore water concentration of $S^{2-}$ (Fig. 5). Small zones (pores) carrying water with a $S^{2-}$ concentration of nearly 200 mg/L are only a few millimeters away from other zones where the $S^{2-}$ concentration is not detectable. Because water flows more readily through macropores, when pore water analysis is conducted on bulk water samples (such as when using sippers), it may entirely miss reactive hotspots within the soil that can be very important in wetland $S^{2-}$ dynamics.

To generate depth concentration profiles, the image of each IRIS panel was divided into 5-cm vertical increments for detailed quantitative analysis. Within each 5-cm increment, the area covered by a given threshold range was measured following the protocols described above. Using the percentage area for each threshold range and multiplying this by the $S^{2-}$ concentration for that threshold range, the weighted contribution to the total pore water $S^{2-}$ concentration was calculated. These contributions were then summed for each 5-cm increment to estimate the average pore water $S^{2-}$ concentration within a given zone.

### Comparison of Methodologies

Sulfide concentrations from duplicate sets of peepers, sippers, and IRIS panels exhibited considerable variability (Fig. 6). The values for the 60- and 360-min IRIS panels were fairly similar in the upper portion of the profile (down to about 30 cm) where the $S^{2-}$ levels reached approximately 40 to 50 mg/L. Below this depth, $S^{2-}$ values for the 60-min panels continued to increase, while values for the 360-min panels remained constant. A similar threshold of color development was also observed in the test chips, where no additional change in color (decrease in value or chroma) was observed in the 360-min samples when the $S^{2-}$ concentrations were raised above 40 to 50 mg/L (Fig. 2). Therefore, if the pore water contains $S^{2-}$ levels that are >50 mg/L, measurements should be made using a 60-min exposure rather than 360 min. (Unpublished data [2007] indicate that temperature variations in the range likely to be encountered during field sampling have a relatively small effect on the reaction forming FeS relative to the $S^{2-}$ concentration or to the duration of installation.)

In the Schoenoplectus marsh, which had relatively homogeneous soils, the replications of the same method were closer than in the Phragmites site. Nevertheless, all three methods showed significant variation among duplicates (Table 2). To make meaningful comparisons between methods and replicates, the $S^{2-}$ values from the peepers were first integrated (averaged) across vertical distances of 5 or 10 cm. These could then be compared with the values determined by the other methods, which had a 5- or 10-cm

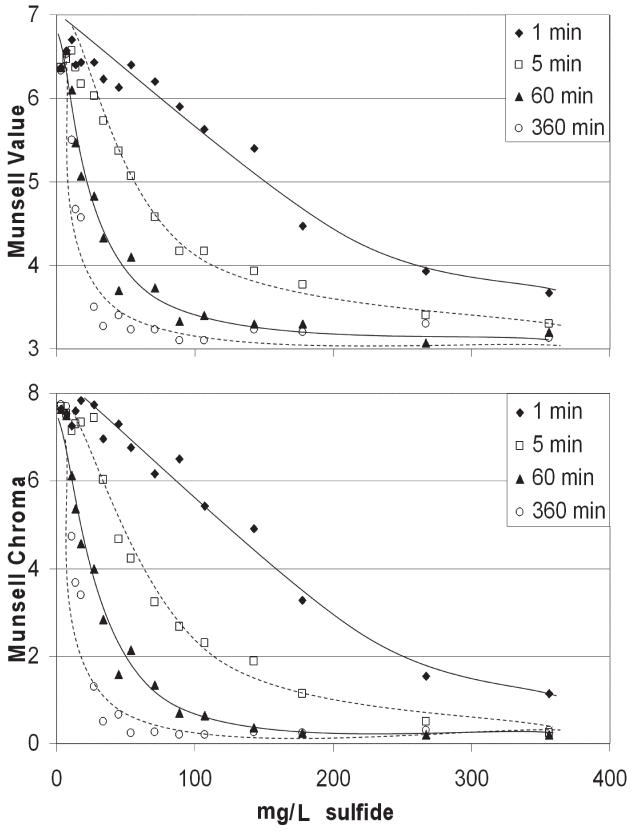


**Fig. 2. Munsell value and chroma measured on Fe oxide coated test chips placed in $Na_2S$ solutions for periods of 1, 5, 60, and 360 min.**

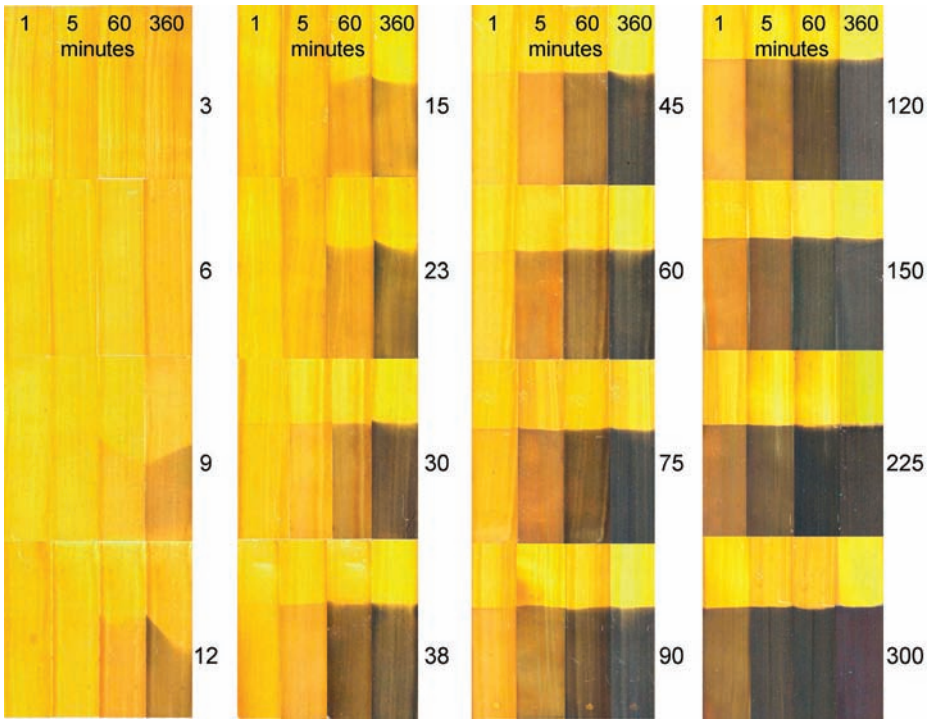


**Fig. 1. Standards for comparison were prepared from polyvinyl chloride chips coated with an Fe oxyhydroxide paint that were placed into pH 7.5 $Na_2S$ solutions ranging in concentration from 3 to 300 mg/L, for time periods ranging from 1 to 360 min.**

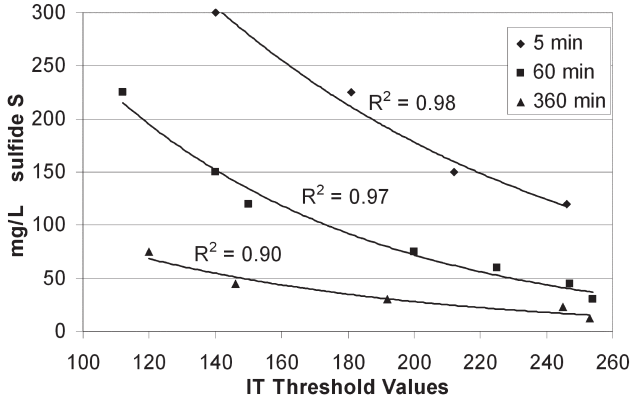


**Fig. 3. Exponential functions relating the concentration of soluble $S^{2-}$ to the Image Tool (IT) threshold value corresponding to the equivalent color of gray or black that formed when the standard chip was placed in the $S^{2-}$ solution for 5, 60, or 360 min.**

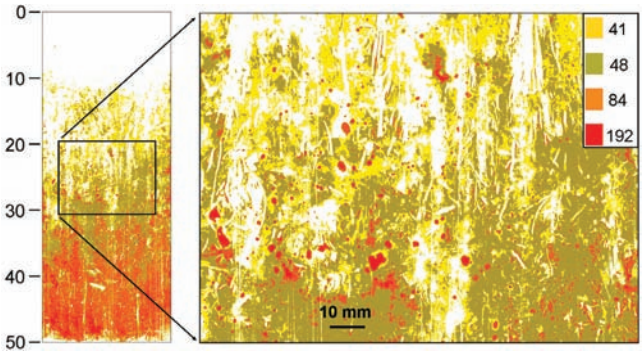


**Fig. 5. A digitally color enhanced image showing an enlarged portion of an IRIS panel inserted into the Schoenoplectus marsh for 60 min, illustrating the high degree of spatial variation in $S^{2-}$ concentration in the marsh and the ability of the Fe oxide coated panels to capture the variation visually. Colors show areas of different $S^{2-}$ concentrations (mg/L).**

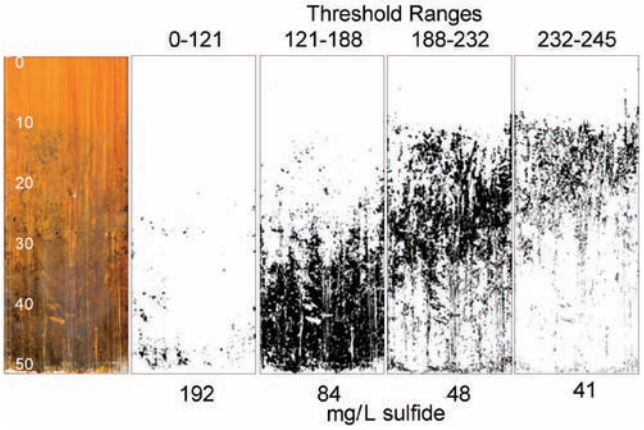


**Fig. 4. Example of a panel that was inserted into the Shoenoplectus marsh for 60 min and then scanned, processed, and analyzed using the four specified threshold values. Darker areas on the color panel represent zones with higher $S^{2-}$ concentration. Scale on left in centimeters.**

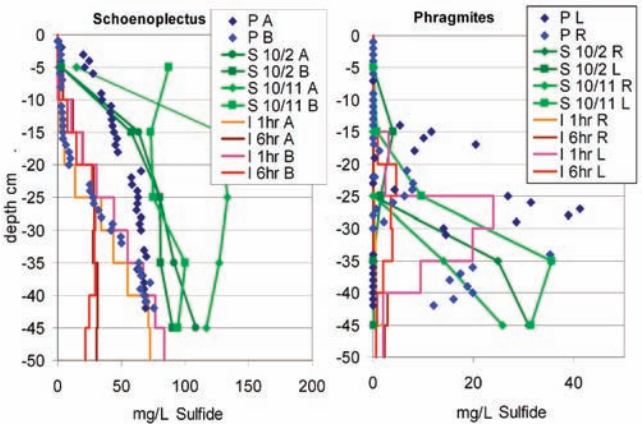


**Fig. 6. Sulfide pore water analyses using peepers (P), sippers (S), and IRIS panels (I); A and B represent duplicates; L and R indicate samples collected on the left and right sides of the Phragmites site.**

**Table 2. Statistical ranges in pore water $S^{2-}$ concentration among duplicate determinations using three methods when integrated across vertical distances of 5 or 10 cm. All measurements were made at the Schoenoplectus site during the period between 28 Sept. and 11 Oct. 2006. Sipper data were only integrated across 10 cm but were measured on two separate dates (2 and 11 Oct. 2006).**

| Method | Pore water $S^{2-}$ concentration | | | | | | |
|---|---|---|---|---|---|---|---|
| | IRIS panels | | Peepers | | Sippers (10 cm) | | |
| | 5 cm | 10 cm | 5 cm | 10 cm | Oct. 2 | Oct. 11 | Combined |
| | mg/L | | | | | | |
| Avg. range | 9.1 | 9.1 | 22.2 | 19.1 | 7.0 | 47.0 | 27.0 |
| Max. range | 17.1 | 13.5 | 38.8 | 38.3 | 18.3 | 72.7 | 72.7 |
| Min. range | 0.0 | 0.0 | 0.4 | 3.5 | 0.0 | 22.4 | 0.0 |

vertical resolution. In general, the IRIS panels replicated as well as or better than either the peepers or the sippers (Fig. 6).

Despite this variability, when the data were compared among the methods, a strong linear relationship was found between the IRIS panel data and the peeper data (integrated across 5-cm increments) (Fig. 7). The average difference between the IRIS panels and the peepers was 12.1 mg/L. A strong logarithmic (nonlinear) relationship was found between the IRIS panels and the sippers, which diverged dramatically from a 1:1 line. The average difference between the IRIS panels and the sippers was 46.2 mg/L, with the latter generally being higher. Because samples collected using sippers are extracted quickly from the soil using suction, the higher values associated with these data suggest that some of the easily extractable pore water held in large pores may be especially enriched with $S^{2-}$.

In measurements made at the Phragmites site, there was a great deal more variability. This is probably related to greater variations in the soil properties, especially the proportion of mineral sediment in the soils, with the north side of the site having a thicker Oa2 horizon with lower organic C content (Table 1). The soil heterogeneity around the Phragmites site makes the duplicate analyses less useful and interferes with making any meaningful comparisons between methods at that site. Nevertheless, it underscores that all methods suffer from some degree of variability that is related to the particular method.

## CONCLUSIONS

Polyvinyl chloride panels coated with an Fe oxide paint (IRIS panels or tubes) can be used to effectively and rapidly determine the levels of soluble $S^{2-}$ in marsh pore water. The reproducibility of IRIS panels appears to be as good as or better than other common methods (peepers and sippers). The average pore water $S^{2-}$ values collected using peepers are generally similar to data from IRIS panels, and $S^{2-}$ values from sippers are typically higher than IRIS data. In comparison to peepers, the time required to obtain data is far shorter (a couple of hours in comparison to a week or longer). Average pore water $S^{2-}$ values can be calculated from IRIS panels. In addition, the images of the IRIS panels provide a great deal of fine-resolution spatial information on the concentration of $S^{2-}$ within the marsh soil that is unavailable by other methods. In summary, the use of IRIS technology can provide fast and reliable assessment of $S^{2-}$ in marsh pore water that includes a high level of fine-scale resolution not available by other methods. This should be useful both to researchers interested in documenting $S^{2-}$ concentrations or distributions in marshes and to managers or practitioners interested in rapid assessment of soluble $S^{2-}$.

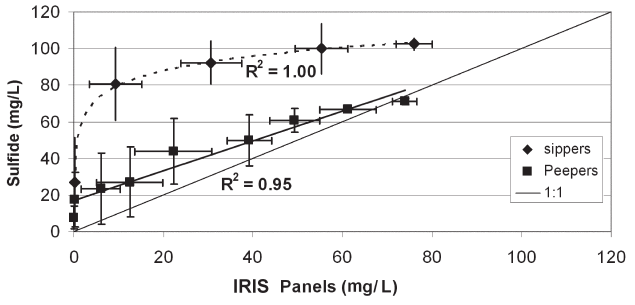


**Fig. 7. Comparison of pore water $S^{2-}$ determinations using IRIS panels to those made using peepers and sippers in the Schoenoplectus marsh. Plots show means and ranges of duplicate analyses.**

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