

**Additional Technical Guidance for Conducting
Redox and Sulphide Measurements in Marine Sediments**

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Background

For Cycle 2 of the Pulp and Paper EEM Program, mills discharging to marine waters were required to measure the oxidation-reduction potential (Redox or Eh) and sulphide content of the sediment samples collected for the invertebrate community survey. The Eh and sulphide values provide an indication of sediment quality related to organic enrichment. It has also been suggested that there is a correlation between Eh and sulphide values and impacts in the benthic invertebrate community (Hargrave et al, 1995; Wildish et al, 1999). Depressed Eh values or elevated sulphide concentrations are an indication of organic enrichment of the sediments, which could result in a shift in the benthic invertebrate community.

Instructions on how to conduct these measurements were provided in Section 7 of the Technical Guidance Document for Pulp and Paper Environmental Effects Monitoring (Environment Canada, 1998). A review of the Cycle 2 EEM interpretive reports for marine mills in the Atlantic Region indicated some discrepancies with the methods used for these measurements. This was particularly true for the sulphide measurements.

In order to be able to compare the Eh and sulphide results among mills and to evaluate the results against sediment quality ratings, it is important that the measurements be made using consistent methods to produce accurate and reliable results. This additional guidance is provided to address these concerns.

Measurements of Sediment Oxidation-Reduction Potential

The method cited in the 1998 technical guidance was Hargrave et al, 1995. This method calls for the direct measurement of Eh in the field with a specific ion meter and a suitable electrode. The probe is inserted directly into the sediment sample to make the measurement. Additional procedural guidance has since been published (Wildish et al 1999; Bugden et al 2001) which provide more specific details on conducting the measurements.

Calibration

To calibrate the dry platinum electrodes after storage, a 4 M KCl filling solution must be added 24 hours before use to activate them. (Note that use of a diluted filling solution, 0.2 M KCl, was incorrectly reported in Wildish et al. 1999 (Bugden et al. 2001)). Zobell's standard solutions are prepared following instructions provided in Wildish et al. (1999). The electrodes should then be standardized against Zobell's solutions as described in the Wildish report. The standards should always be kept at room temperature. Standardizing techniques will be specific to the type of electrode being

used. Refer to electrode manual for specific information. Between readings, the electrodes should be rinsed and stored in distilled water. During periods of analyses, calibration should be conducted at least once daily.

Making the measurements

Redox potential is to be measured while the sample is still in the core tube or the grab sampler. Water should be carefully drained from the sediment-water interface end of the sample before the calibrated probes are inserted into the sediment. This should be performed as soon as possible after the sample has been collected. The calibrated probe should be held in the top 2 cm of sediment for approximately 2-3 minutes or until an equilibrium has been reached. In sediments with a wide range of oxidation-reduction readings, the probe may need to be pushed in and out of the top 2 cm of sediment until a stable reading can be taken. If core samples cannot be analyzed within 3 hours of collection, it is recommended that the entire core be stored in the dark and on ice until Eh is measured and that measurement be made within 24 hours (Wildish et al. 1999).

Correcting readings

A source of confusion among Eh results from mills has been the question of whether or not the readings have been corrected as relative to the normal hydrogen electrode. For comparison with the definitions of sediment quality with respect to Eh levels as suggested by Wildish et al. (1999), it must be specified whether or not measurements are expressed as relative to the normal hydrogen electrode. The formula and table containing corresponding 'C' values for the calculation are provided in below, as well as in the report by Wildish et al.:

Formula 1 - To express mV readings as relative to the normal hydrogen electrode

$$E_{\text{NHE}} = E_0 + C$$

E_0 = mV of unknown

C = mV of reference relative to the NHE shown in Table 1

Table 1 - Reference electrode potential, mV, relative to NHE {C} at different temperatures and probe filling solution concentrations

<u>Temperature (celcius)</u>	<u>Orion #900001 1.5 M KCl</u>	<u>Orion #900011 Saturated 4 M KCl</u>
5	254	219
10	251	214
15	249	209
20	244	204
25	241	199
30	238	194
35	235	189

Reporting values

All Redox values should be reported in millivolts (mV) and as relative to the normal hydrogen electrode.

Measurements of Sediment Sulphides

The sulphide measurement method that was cited in the 1998 technical guidance was Tetra Tech (1996). Additional guidance is also provided in Wildish et al. 1999, and Hargrave et al. 1995 and Bugden et al. 2001.

Calibration

A 0.01-M solution of Na₂S can be prepared following instructions provided by Wildish et al. (1999). This solution will only be valid for 48 hours so it should be prepared shortly before measurements are conducted. A solution of SAOB (sulphide anti-oxidant buffer solution) should be purchased or prepared following instructions provided. To calibrate the electrode using a three point calibration, three concentrations of the Na₂S standard solution must be prepared (10, 100 and 1000 μM S²⁻) (Hargrave et al. 1995). A two point calibration procedure (10 and 1000 μM S²⁻) is described in Wildish et al. 1999. Electrodes are then calibrated to these solutions following given instructions and depending on the type of probe being used. A minimum of two points is needed to make a calibration curve. Calibration should be conducted before every sample analysis and logged.

Making the measurements

To take measurements, L-ascorbic acid is to be mixed with the SAOB solution shortly before analysis as the solution will only remain stable for 3 hours. A 5 cc sediment sample should be extracted from a 2 cm depth in the sediment while it is still in the corer or grab sampler. 5 mL of the prepared solution is then added to the 5 cc sediment sample and mixed thoroughly. Place electrodes in the sample so that all surfaces come in contact with the sediment. A stable reading should be achieved after approximately 1 minute. Once the SAOB solution is mixed with the sediment, the sulphide reading must be made immediately as the mixture is not stable and sulphide will be lost or reduced with time. Sediment samples for sulphide measurement can be stored for up to 24 hours as long as they are kept sealed from the air, in the dark and chilled on ice or refrigerated but not frozen.

Correcting and reporting readings

In Cycle 2 reports, some results were reported in μg/g from dry sediment samples. Others were reported as μg/g, mg/kg and μg/L without describing the methodology used during analysis. It is impossible to compare results reported in μg/g or mg/kg to results reported in μg/L or mg/L without a complete description of the sample preparation. It is

suggested that the sampling methods previously mentioned be used with reference to the cited documents. It is also suggested that all sediment sulphides be reported as $\mu\text{g/L}$ or $\mu\text{M/L}$ for comparison with the definitions of sediment quality as defined by Wildish et al. (1999). The final concentration reported must be within the range of calibration standards used to calibrate the sulphide electrode. That is, if sediments are expected to contain 500 to 5000 μM total sulphide, then a set of calibration standards spanning this expected range (100, 1000, 10000 μM) should be prepared. The measured concentrations of total sulphides should fall within the range of concentrations used to standardize the electrode.

Alternative method for sampling both Eh and sulphides

Another option for taking the Eh and sulphide measurements can also be used. An 5 ml aliquot of sediment is withdrawn from grab sampler or core tube into cut-off syringes. Once filled with sediment, the syringes are capped tightly to restrict exposure to oxygen. They are stored chilled (not frozen) until analysis within 24 h (maximum storage time). The extruded sediment sample is placed into a scintillation vial and then the Eh electrode is inserted. It is gently moved to ensure contact between the probe surface and sediment sample and then left undisturbed until a stable potential is read on the meter (usually 2-4 min). The Eh electrode is withdrawn and then the SAOB solution added (5 ml to 5 ml sediment). The sulfide is measured on the same sample. This procedure must be conducted as quickly as possible to minimize exposure to air. Standards are measured in a similar fashion. Any loss of sulfide in the time taken to make the measurements (usually < 5 min) on samples in the vials is considered to also occur in the standards used for calibration.

Interpretation of Results

Definitions of sediment quality with reference to Eh and sulphide measurements as defined by Poole et al. (1978), Pearson and Rosenberg (1978) and Wildish et al. (1999) are provided in Table 2.

Table 2 - Definitions of sediment quality with reference to Eh and sulphide readings

<u>Type of Measure</u>	<u>Group</u>				<u>Reference</u>
Microbial	Normal	Oxic	Hypoxic	Anoxic	Poole et al. (1978)
Macrofaunal	Normal	Transitory	Polluted	Grossly Polluted	Pearson and Rosenberg (1978)
Geochemical	Oxic a	Oxic b	Hypoxic	Anoxic	
Eh, mV(NHE)	>+100	0-100	-100-0	<-100	Wildish et al. (1999)
S, μ M	<300	1300-300	6000-1300	>6000	

(Wildish et al. 1999)

References

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