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**Savannah River National Laboratory**

# H-02 Wetland Treatment System Water Chemistry Sampling and Results Report

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# EXECUTIVE SUMMARY

The H-02 Wetland Treatment System is used to remove heavy metals (e.g., copper and zinc) from the H-Area process and storm water discharge. During initial operation, it was observed that the pH of the water leaving the equalization basin was elevated compared to the influent pH. Furthermore, this elevated pH carried through the wetland cells such that there was an average pH of 10 leaving the wetland cells during the day which exceeds the National Pollution Discharge Elimination System (NPDES) upper limit for pH of 8.5. The purpose of the current study was to evaluate two possible mechanisms behind the cause of the increase in pH within the equalization basin of the H-02 Wetland Treatment System. The two mechanisms evaluated were algal activity and inorganic chemistry interactions (e.g., interactions with the clay and/or bentonite liner).

The simultaneous rise and fall of both pH and dissolved oxygen (DO) measured throughout the day within the basin indicated that algae are influencing pH as the impact of algae on pH and DO will vary throughout the day due to the presence or absence of sunlight. While algal activity is clearly a factor in the pH of the basin it cannot explain the observed increase in the pH from the inlet to the outlet of the basin due to algae's inability to cause an overall increase in pH. Evaluation of inorganic ions within the treatment system demonstrated successful removal of heavy metals such as copper and lead but the data did not support interactions with the clay or bentonite liner as a cause for the observed increase in pH within the basin. This finding was supported by the absence of a trend of increasing pH with increasing depth in either the water column or the sediment column. A phosphate/carbonate mechanism, where these compounds act as bases and pH buffers, may explain the overall increase in pH within the basin and also the dampening of the pH oscillation caused by the algae.

Strategies for meeting the NPDES standard for pH from the H-02 Wetland Treatment System include allowing the H-02 wetland to mature so that it possesses a higher basic buffering capacity, removing phosphate/carbonate from the influent water, or acidifying the outlet water. To determine the most feasible choice, each method should be evaluated for ease of implementation and cost.

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## 1.0 INTRODUCTION

The H-02 Wetland Treatment System (Figure 1) is used to remove heavy metals (e.g., copper and zinc) from the H-Area process and storm water discharge. Routine flow enters an equalization basin by inlets on either the east (Location 1) or west end (Location 2). The west end influent constitutes 75% of the average flow into the basin which has an average residence time of approximately 3 days at low pool (i.e., 120 gal/min. through a volume of 0.5 million gallons). The water then exits via the basin outlet on the east end. Next, the water flows to a splitter box (Location 3) which evenly separates the flow between two wetland cells for a design flow of 60 gal/min. per wetland cell with a residence time in the cell of approximately 2 days. The wetland effluent is then combined (Location 4) and flows through a spillway before reaching the National Pollution Discharge Elimination System (NPDES) measurement point near Road 4. During initial operation, it was observed that the pH of the water leaving the equalization basin was elevated compared to the influent pH. Furthermore, the elevated pH remained through the wetland cells so that there was an average pH of 10 leaving the wetland cells during the daytime which exceeds the upper NPDES limit of 8.5.

The purpose of the current study was to evaluate the cause of the increase in pH within the equalization basin of the H-02 Wetland Treatment System. Possible mechanisms included algal activity and inorganic chemistry interactions (e.g., interactions with the clay and/or bentonite liner). Water quality parameters were evaluated throughout the H-02 Wetland Treatment system and over time in order to determine the cause of high pH values measured in the basin and wetland. Fluctuations in dissolved oxygen (DO) and accompanying changes in pH would be expected in systems where algae are an influencing factor. An unexpected increase or decrease in the concentration of inorganic substances may indicate operational changes or an inorganic chemistry influence on pH. In addition, alternative methods to alleviate or mitigate the pH increase were evaluated.

This study documents the results of sampling activities undertaken and conveys the analytical results along with suggestions for operation of the H-02 Wetland Treatment System. The water samples collected and the water quality data generated from this activity are for analytical purposes only, and as such, were not collected in support of compliance activities.

## 2.0 SAMPLING ACTIVITIES

The H-02 Wetland Treatment System Sampling Activities were developed to evaluate the water chemistry parameters in the treatment system. The Savannah River National Laboratory Environmental Sciences and BioTechnology Directorate (SRNL/ESBD) with support from the Defense Program Tritium Facility (DP/Tritium Facility) conducted the surface water grab sampling activities during two sampling events: 1. September 12, 2007; and 2. October 16-17, 2007 at the H-02 Wetland Treatment System.

The sampling locations at the H-02 Wetland Treatment System were:

1. East discharge pipe into the basin.
2. West discharge pipe into the basin.

3. Splitter-box discharge from the basin.
4. Discharge point from the wetland cells.

The sampling location layout at the H-02 Wetland Treatment System is depicted in Figure 1.

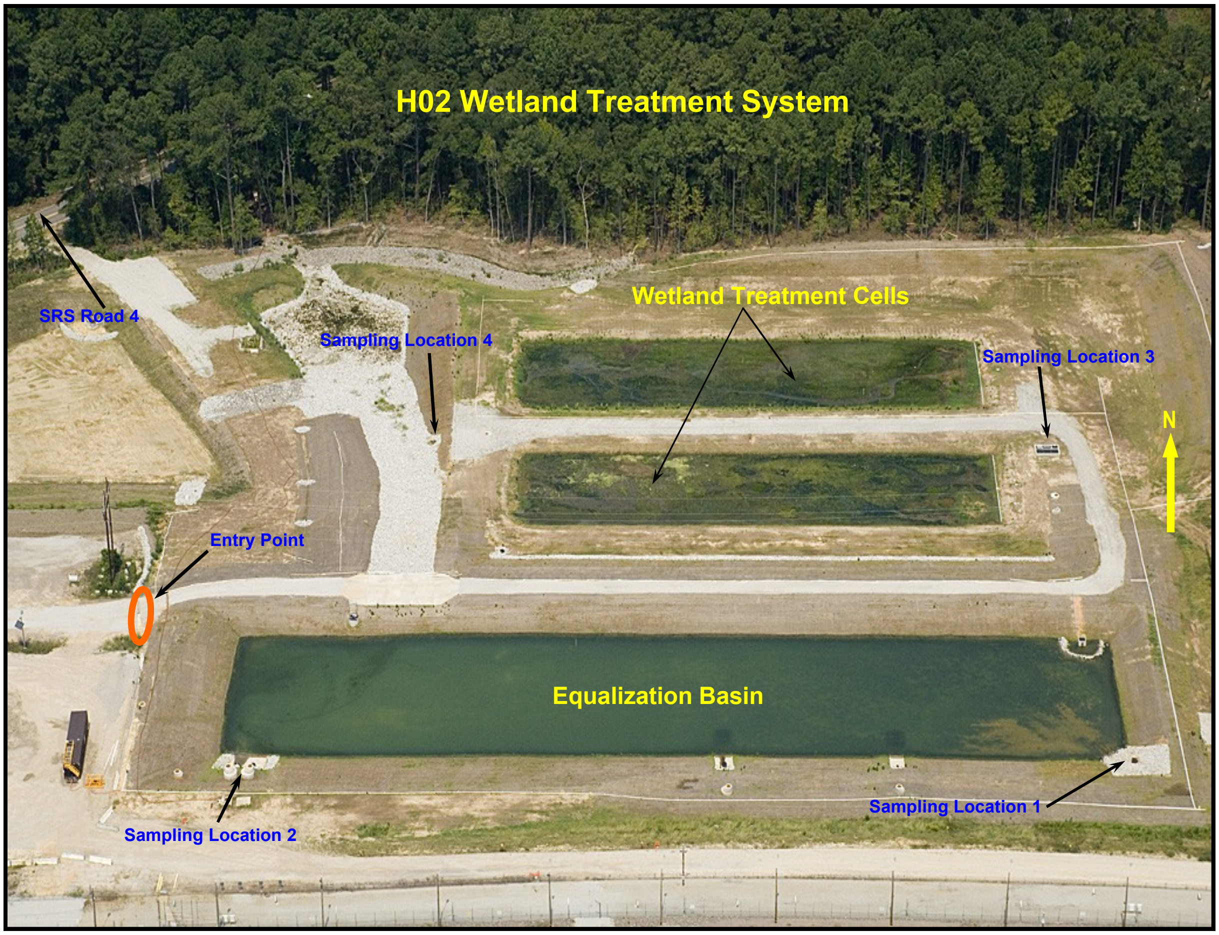

**Figure 1 – H-02 Sampling Location Layout**

The sampling frequency for these activities was four times per twenty-four hours over a two day period. The sampling periods for the different locations are:

1. Dawn (7-9 AM; Locations 1-4)
2. Midday (12-2 PM; Locations 1-4)
3. Dusk (6-8 PM; Locations 1-4)
4. Midnight (12-2 AM; Locations 3 & 4 only)

SRNL/ESBD personnel completed sampling periods 1-3 and DP/Tritium Facility personnel completed sampling period 4. Sampling period 4 was limited to sampling locations 3 & 4 only to mitigate additional safety risk during night operations. Sampling activities were conducted in accordance with the H-02 Wetland Treatment System Water Chemistry Sampling Instructions developed by SRNL/ESBD (see Attachment A). The September 12 sampling event was originally scheduled to extend into September 13, but inclement weather conditions required the suspension of the sampling activities.

The sampling protocol for both September 12 and October 16-17 was to collect the following water samples and water quality data:

- Three (3) grab samples of water at each sampling location (i.e., one cations, anions, and alkalinity)
- Water quality data collected using the YSI 6 Series Water Quality Logging System at each sampling location included:
    - pH
    - Temperature
    - Dissolved oxygen (DO)

Analytical testing of the grab water samples was conducted by WSRC Environmental Monitoring Section.

Horizontal and vertical pH profiles of the water in the basin were conducted on January 8, 2008. Two east-west transects at equal distances from the basin's east-west sides with five locations along each transect were measured (Figure 2). At each location, a calibrated YSI 6 Series Water Quality Logging System was used to measure pH, temperature, and DO content of the water at 6 in. increments from the surface of the pool to the sediment bottom. pH, temperature, and DO content were also recorded for water exiting the basin.

Figure 2 – Location of water column pH measurements

Cores were extracted from the sediment over the bentonite liner to assess the vertical pH profile of the sediment. Six cores were extracted from the east end of the basin using a plastic coring tube. Cores 1 and 2 were obtained at the location of water samples 1 and 10, respectively. Core 3 was located between cores 1 and 2. Cores 4 thru 6 were taken approximately 10 ft. west of samples 1 through 3. Cores were approximately 6 in. in length and were divided into thirds in the field. Core length was limited to 6 in. due to the difficulty of extracting samples from the dense clay material. The samples were then dried (48-hours at 40 °C) and soil pH determined using standard soil testing procedures.

## 3.0 RESULTS

### *Algae*

Preliminary measurements for pH throughout the H-02 Wetland Treatment System were collected from August 6th to October 29th, 2007 by DP/Tritium Facility and SRNL Personnel (Figure 3). Discrete water samples were taken for these measurements within 50 minutes of both 8 AM and 4 PM at the east and west inlets, the basin outlet, and the outlet to the spillway.

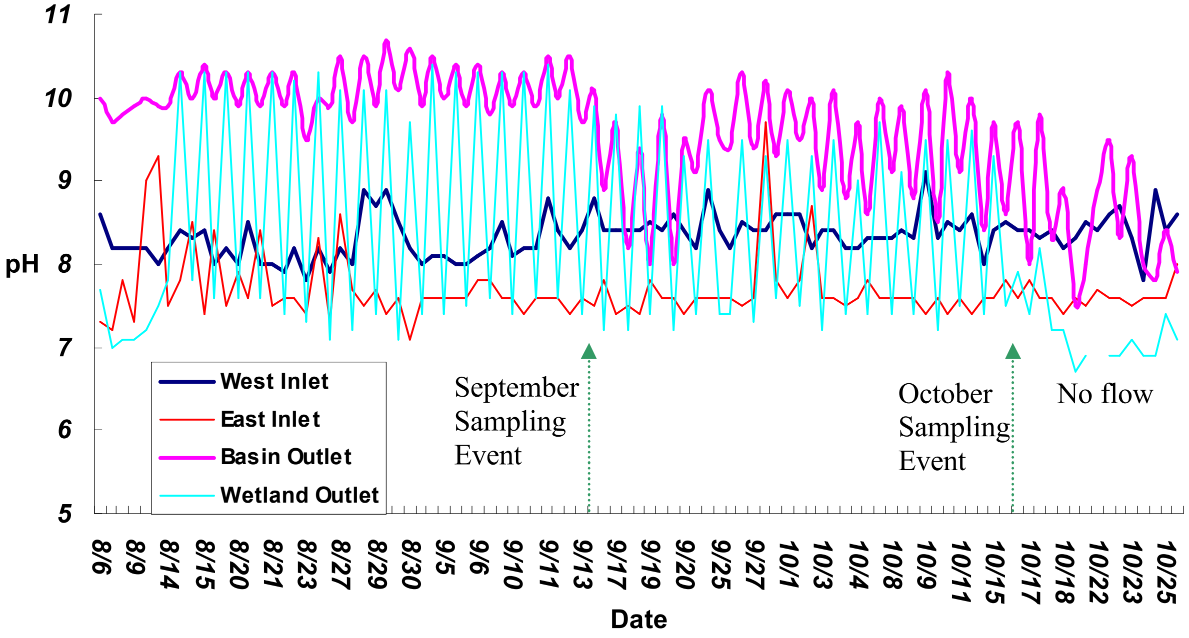

**Figure 3 – pH Measured in H-02 Wetland Treatment System from 8/6 to 10/25/2007**

The influent to the basin showed a relatively steady pH of 8.3 ± 0.3 (i.e., average pH ± one standard deviation) and 7.7 ± 0.4 for the west and east inlet, respectively. The outlet from the basin showed a slight oscillation around a pH of 9.6 ± 0.8. The higher standard deviation is due to both an overall depression in pH after 9/13/2007 and the slight oscillation in the pH from day to night as a result of algal activity (discussed below). The overall depression in the average pH after 9/13/2007 may relate to a rainfall event that occurred during the sampling week. At the wetland discharge, there is an average pH of 8.3 ± 1.3 and periodic exceedences of the NPDES upper limit for pH of 8.5.

Elevated pH from equalization basins compared to influent pH, as observed in the H-02 equalization basin, is not an uncommon occurrence as exemplified by experiences with the A-01 Wetland Treatment System. Data collected from the A-01 Wetland Treatment System in 2003 indicated that the pH in the effluent water from the equalization basin oscillated between 8.9 and 10.2 when it was distributed to the wetland cells from the splitter box. The system had been in operation for 3 years when this data was collected and the wetlands were fully vegetated and functional. The A-01 basin is similar in construction to the H-02 basin with a bentonite liner covered by clay fill material. After passage of the water through the first of the two wetland cells in the A-01 treatment system, water pH oscillated between 5.0 and 6.4. The pH cycling was not directly associated with the basin pH, most likely because of the equalization time of the wetland cell. The cell discharge spent approximately 18 hours at a constant pH of 6.4, with a slight reduction during the early morning and then returning to 6.4. Wetlands have tremendous buffering abilities due to the sediment/detrital biogeochemistry interactions that occur at the soil/water interface. Currently, the H-02 Wetland Treatment System does not possess a strong buffering capacity, as evidenced in Figure 3, because it has not reached maturation and is sparsely vegetated compared to the A-01 wetland. Once the H-02 wetland has matured it should possess a higher buffering capacity than the current new-growth system that is more readily influenced by the elevated pH from the equalization basin. The downward trend of the average pH in the wetland discharge over the period of study, which contributes to the higher standard deviation, may relate to the maturation of the wetland cells.

The rise and fall of pH throughout the day within the basin indicates that algae are influencing pH. During the day, algae utilize photosynthesis which consumes carbon dioxide and releases oxygen. At night or on heavily overcast days, "dark respiration" dominates which consumes oxygen and releases carbon dioxide. The carbon dioxide then reacts with water to form carbonic acid, which depresses pH overnight creating an oscillating pH from day to night (Zelitch, 1971). A more significant oscillation in pH is evident in the pH of the wetland discharge, possibly due to the presence of more algae in the wetland than in the equalization basin. This result is confirmed by an analysis of pH and DO throughout the H-02 Wetland Treatment System for approximately one day over 9/12/07 and 9/13/07 and over two days from 10/16/07 to 10/17/07 (Table 1 and Table 2).

**Table 1 - Water quality of the H-02 Wetland Treatment System, 9/12-9/13/07**

| **pH** | | | | |
|---|---|---|---|---|
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 7.3 | 8.1 | 9.4 | 7.3 |
| 12:30pm | 7.3 | 8.1 | 9.6 | 9.4 |
| 7:50pm | 8.1 | 8.4 | 9.9 | 8.4 |
| 12:55am | - | - | 10.0 | 7.7 |
| **DO (mg/L)** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 8.1 | 8.9 | 8.2 | 5.9 |
| 12:30pm | 8.2 | 7.6 | 10.6 | 12.0 |
| 7:50pm | 14.2 | 12.4 | 15.6 | 12.1 |
| 12:55am | - | - | 17.6 | 6.2 |
| **Temp (°C)** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 24.2 | 26.2 | 26.9 | 25.6 |
| 12:30pm | 24.4 | 28.0 | 28.3 | 29.8 |
| 7:50pm | 23.5 | 27.3 | 29.6 | 30.5 |
| 12:55am | - | - | 26.4 | 25.0 |

**Table 2 - Water quality of the H-02 Wetland Treatment System, 10/16-10/17/07**

| **pH** | | | | |
|---|---|---|---|---|
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 7.2 | 8.1 | 8.0 | 7.0 |
| 1:00pm | 7.2 | 8.2 | 9.0 | 8.0 |
| 7:00pm | 7.3 | 8.1 | 9.3 | 7.2 |
| 12:00am | - | - | 8.3 | 7.1 |
| 8:00am | 7.2 | 8.1 | 7.7 | 7.0 |
| 1:00pm | 7.3 | 8.5 | 9.0 | 7.7 |
| 7:00pm | 7.3 | 8.4 | 9.2 | 7.3 |
| 12:00am | - | - | 8.7 | 7.2 |
| **DO (mg/L)** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 9.2 | 8.2 | 7.8 | 5.9 |
| 1:00pm | 9.3 | 8.3 | 11.4 | 12.1 |
| 7:00pm | 9.4 | 8.8 | 12.9 | 6.7 |
| 12:00am | - | - | 9.1 | 6.2 |
| 8:00am | 9.7 | 9.9 | 7.6 | 5.1 |
| 1:00pm | 12.4 | 9.1 | 13.3 | 11.8 |
| 7:00pm | 9.7 | 9.3 | 12.2 | 7.4 |
| 12:00am | - | - | 9.9 | 6.5 |
| **Temp (°C)** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 21.0 | 24.8 | 20.4 | 18.0 |
| 1:00pm | 23.0 | 26.8 | 25.6 | 27.6 |
| 7:00pm | 22.9 | 26.8 | 24.6 | 24.8 |
| 12:00am | - | - | 23.2 | 21.8 |
| 8:00am | 21.9 | 25.6 | 22.1 | 21.1 |
| 1:00pm | 23.5 | 27.3 | 26.2 | 28.2 |
| 7:00pm | 23.1 | 26.8 | 25.9 | 25.9 |
| 12:00am | - | - | 23.7 | 21.9 |

The change in DO with time in the September measurement at the splitter box (Table 1) did not indicate a diurnal shift with pH (i.e., no shift in pH corresponding to a decrease in DO as the algae take in DO and release carbon dioxide). On the other hand, the 48hr measurement in October indicated a clear diurnal trend within the splitter box where both the pH and DO decreased overnight (Table 2), which is expected in a system where algae influence pH. Though the September sampling lacked a trend between pH and DO, possibly due to a rainfall event which occurred during the sampling, the October sampling supports the hypothesis that algae are influencing the pH within the basin based on corresponding fluctuations with DO. However, algae generally serve to alternate or decrease pH rather than cause an overall increase in pH as observed from the inlet to the outlet of the basin, which suggests that the algae mechanism alone is not responsible for the observed pH changes. In addition, algaecide added to the basin in November 2007 did not seem to alleviate the pH increase from the inlet to the outlet of the basin. Repeated trials with algaecide in the summer, when algae are active, may be necessary to confirm this finding. While the oscillation in the pH and DO leaving the basin indicates that algal activities within the basin are influencing the pH, the increase in the average pH of the water in the basin effluent compared to the inlet water points toward the possibility of an additional chemical reaction occurring within the basin.

### *Inorganic Chemistry*

### *Clay and bentonite liner*

Two possible chemical reactions that may occur within the basin to influence pH are reactions between the incoming water and either the bentonite liner or the clay top layer at the bottom of the basin. Anions, negatively charged ions, in water contacting the sodium bentonite liner ($Na(Al,Mg)_6SiO_{30}(OH)_6*(H_2O)_n$) can remove hydroxyl groups from the smectite portion of bentonite. While any anion may displace hydroxyl ions from the bentonite surface, it is the phosphate ion which is anticipated to react most strongly with the bentonite liner. Studies by Wanner (1987), Kaya and Ören (2005), and Nessa et al. (2007) indicate that contact with smectite can increase water pH to between 9 and 10. The same phenomenon may occur within the clays and minerals present in the soil layer above the bentonite liner.

As a significant change in the concentration of inorganics, particularly anions, from the inlet to the outlet of the basin would indicate the presence of chemical interactions within the basin that may be affecting pH, the concentrations of a range of cations (positively charged ions) and anions were measured throughout the treatment system. The anions chloride, nitrate, total phosphorous, sulfate, and total alkalinity as well as 23 cations were measured from the same water samples taken for DO measurements in September and October. For a complete list of the substances measured and their detection limits see Appendix B. Of the 23 cations evaluated, only aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), potassium (K), manganese (Mn), sodium (Na), lead (Pb), and zinc (Zn) were measured above the minimum detection limit in the September sampling (Table 3). In addition to those substances found in the September sampling, the October sampling measured recordable levels of magnesium (Mg) (Table 4). Both samplings showed reportable concentrations of all the anions evaluated namely chloride (Cl-), nitrate ($NO_3^-$), total phosphorous, sulfate ($SO_4^{2-}$), and total alkalinity. The concentrations of analytes measured above the detection limit for both the September and October sampling periods are presented in Table 3 and Table 4, respectively.

## Table 3 – Inorganics in mg/L for H-02 Wetland Treatment System, 9/12-9/13/07

| | | | | |
|---|---|---|---|---|
| **Anions** | | | | |
| **Alk (as $CaCO_3$)** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 46 | 55 | 68 | 75 |
| 12:30pm | 46 | 120 | 68 | 70 |
| 7:50pm | 40 | 69 | 69 | 68 |
| 12:55am | - | - | 45 | 50 |
| **$Cl^-$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 3.2 | 3.1 | 4.2 | 4.6 |
| 12:30pm | 2.8 | 8.8 | 4.4 | 4.4 |
| 7:50pm | 2.7 | 4.8 | 4.2 | 3.5 |
| 12:55am | - | - | 3.1 | 3.0 |
| **$NO_3^-$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.06 | 0.08 | 0.04 | 0.04 |
| 12:30pm | 0.04 | 0.33 | 0.04 | 0.04 |
| 7:50pm | 0.07 | 0.10 | 0.04 | 0.04 |
| 12:55am | - | - | 0.20 | 0.05 |
| **Total Phosphorous** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.37 | 0.47 | 0.49 | 0.36 |
| 12:30pm | 0.33 | 1.00 | 0.48 | 0.41 |
| 7:50pm | 0.32 | 0.60 | 0.51 | 0.48 |
| 12:55am | - | - | 0.48 | 0.34 |
| **$SO_4^{2-}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 3.1 | 1.2 | 1.4 | 1.1 |
| 12:30pm | 1.5 | 3.9 | 1.4 | 1.3 |
| 7:50pm | 1.6 | 2.3 | 1.6 | 2.1 |
| 12:55am | - | - | 2.8 | 2.8 |
| **Cations** | | | | |
| **$Al^{3+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.24 | <0.05 | 0.07 | 0.16 |
| 12:30pm | 0.10 | <0.05 | 0.05 | 0.39 |
| 7:50pm | <0.05 | <0.05 | 0.07 | 0.39 |
| 12:55am | - | - | 0.39 | 0.37 |
| **$Ca^{2+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 2.63 | 1.02 | 1.58 | 3.28 |
| 12:30pm | 1.72 | 2.54 | 1.47 | 4.81 |
| 7:50pm | 1.29 | 1.53 | 1.45 | 1.71 |
| 12:55am | - | - | 1.84 | 2.31 |

**Table 3 (cont.)– Inorganics in mg/L for H-02 Wetland Treatment System, 9/12-9/13/07**

| **Cations (cont.)** | | | | |
|---|---|---|---|---|
| **$Cu^{2+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.370 | 0.009 | 0.025 | 0.011 |
| 12:30pm | 0.410 | 0.022 | 0.020 | 0.017 |
| 7:50pm | 0.680 | 0.011 | 0.026 | 0.017 |
| 12:55am | - | - | 0.024 | 0.013 |
| **$Fe^{2+}/Fe^{3+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.23 | <0.02 | 0.14 | 0.98 |
| 12:30pm | 0.12 | <0.02 | 0.11 | 0.83 |
| 7:50pm | 0.05 | <0.02 | 0.11 | 0.70 |
| 12:55am | - | - | 0.31 | 0.63 |
| **$K^{+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.99 | 0.21 | 0.46 | 0.72 |
| 12:30pm | 0.32 | 0.52 | 0.38 | 0.61 |
| 7:50pm | 0.25 | 0.28 | 0.43 | 0.45 |
| 12:55am | - | - | 0.90 | 0.98 |
| **$Mn^{2+}/ Mn^{4+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | <0.01 | <0.01 | <0.01 | 0.06 |
| 12:30pm | <0.01 | <0.01 | <0.01 | 0.03 |
| 7:50pm | <0.01 | <0.01 | <0.01 | 0.03 |
| 12:55am | - | - | 0.02 | 0.04 |
| **$Na^{+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 22.0 | 27.1 | 31.9 | 32.8 |
| 12:30pm | 19.1 | 63.1 | 32.2 | 36.1 |
| 7:50pm | 19.8 | 33.1 | 32.2 | 32.1 |
| 12:55am | - | - | 21.3 | 22.4 |
| **$Pb^{2+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.033 | <0.002 | <0.002 | <0.002 |
| 12:30pm | 0.037 | <0.002 | <0.002 | <0.002 |
| 7:50pm | 0.047 | <0.002 | <0.002 | <0.002 |
| 12:55am | - | - | <0.002 | <0.002 |
| **$Zn^{2+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.04 | 0.03 | 0.02 | <0.01 |
| 12:30pm | 0.05 | 0.04 | 0.02 | 0.11 |
| 7:50pm | 0.03 | 0.03 | 0.02 | 0.01 |
| 12:55am | - | - | 0.07 | 0.01 |

## Table 4 - Inorganics in mg/L for the H-02 Wetland Treatment System, 10/16-10/17/07

| **Anions** | | | | |
|---|---|---|---|---|
| **Alk (as $CaCO_3$)** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 40 | 60 | 74 | 80 |
| 1:00pm | 47 | 58 | 65 | 74 |
| 7:00pm | * | * | 70 | 73 |
| 12:00am | - | - | 72 | 77 |
| 8:00am | * | * | * | * |
| 1:00pm | 43 | 120 | 70 | 74 |
| 7:00pm | 46 | 90 | 70 | 72 |
| 12:00am | - | - | * | * |
| **$Cl^-$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 2.7 | 4.3 | 5.1 | 5.4 |
| 1:00pm | 3.2 | 3.9 | 4.9 | 5 |
| 7:00pm | * | * | 5.2 | 4.9 |
| 12:00am | - | - | 5.1 | 5 |
| 8:00am | * | * | * | * |
| 1:00pm | 2.8 | 9.5 | 5 | 4.8 |
| 7:00pm | 2.9 | 6.1 | 5 | 4.6 |
| 12:00am | - | - | * | * |
| **$NO_3^-$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.07 | 0.14 | 0.02 | 0.00 |
| 1:00pm | 0.06 | 0.08 | 0.03 | 0.15 |
| 7:00pm | * | * | 0.18 | 0.15 |
| 12:00am | - | - | 0.08 | 0.08 |
| 8:00am | * | * | * | * |
| 1:00pm | 0.07 | 0.42 | 0.07 | 0.16 |
| 7:00pm | 0.06 | 0.26 | 0.20 | 0.17 |
| 12:00am | - | - | * | * |
| **Total Phosphorous** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.43 | 0.66 | 0.63 | 0.43 |
| 1:00pm | 0.49 | 0.50 | 0.61 | 0.40 |
| 7:00pm | 0.50 | 0.52 | 0.64 | 0.40 |
| 12:00am | - | - | 0.61 | 0.50 |
| 8:00am | 0.44 | 0.50 | 0.62 | 0.48 |
| 1:00pm | 0.46 | 1.40 | 0.67 | 0.44 |
| 7:00pm | 0.44 | 0.81 | 0.69 | 0.42 |
| 12:00am | - | - | 0.61 | 0.49 |

*Lab error, data missing

## Table 4(cont.) - Inorganics in mg/L for the H-02 Wetland Treatment System, 10/16-10/17/07

**Anions (cont.)**

**$SO_4^{2-}$**

| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
|---|---|---|---|---|
| 8:00am | 1.4 | 1.5 | 1.6 | 1.2 |
| 1:00pm | 1.4 | 1.4 | 1.6 | 1.5 |
| 7:00pm | * | * | 1.6 | 1.7 |
| 12:00am | - | - | 1.5 | 1.3 |
| 8:00am | * | * | * | * |
| 1:00pm | 1.4 | 3.2 | * | 1.5 |
| 7:00pm | 1.2 | 2.2 | 1.5 | 1.7 |
| 12:00am | - | - | * | * |

**Cations**

**$Al^{3+}$**

| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
|---|---|---|---|---|
| 8:00am | 0.11 | <0.05 | 0.19 | 0.28 |
| 1:00pm | 0.11 | <0.05 | 0.14 | 0.17 |
| 7:00pm | 0.16 | <0.05 | 0.14 | 0.21 |
| 12:00am | - | - | 0.12 | 0.15 |
| 8:00am | 0.09 | <0.05 | 0.11 | 0.09 |
| 1:00pm | 0.12 | <0.05 | 0.14 | 0.22 |
| 7:00pm | 0.06 | <0.05 | 0.16 | 0.30 |
| 12:00am | - | - | 0.22 | 0.24 |

**$Ca^{2+}$**

| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
|---|---|---|---|---|
| 8:00am | 1.46 | 1.40 | 2.00 | 3.98 |
| 1:00pm | 1.62 | 1.46 | 1.72 | 2.40 |
| 7:00pm | 1.66 | 1.47 | 1.76 | 2.37 |
| 12:00am | - | - | 2.03 | 3.39 |
| 8:00am | 1.38 | 1.05 | 2.08 | 4.00 |
| 1:00pm | 1.51 | 2.86 | 1.82 | 2.55 |
| 7:00pm | 1.48 | 2.26 | 1.73 | 2.23 |
| 12:00am | - | - | 1.96 | 3.29 |

**$Cu^{2+}$**

| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
|---|---|---|---|---|
| 8:00am | 0.350 | 0.020 | 0.026 | 0.011 |
| 1:00pm | 0.590 | 0.010 | 0.085 | 0.013 |
| 7:00pm | 0.340 | 0.010 | 0.030 | 0.020 |
| 12:00am | - | - | 0.036 | 0.018 |
| 8:00am | 0.410 | 0.010 | 0.068 | 0.013 |
| 1:00pm | 0.430 | 0.030 | 0.040 | 0.017 |
| 7:00pm | 0.340 | 0.010 | 0.038 | 0.019 |
| 12:00am | - | - | 0.028 | 0.022 |

*Lab error, data missing

### Table 4(cont.) - Inorganics in mg/L for the H-02 Wetland Treatment System, 10/16-10/17/07

| **Cations (cont.)** | | | | |
|---|---|---|---|---|
| **$Fe^{2+}/Fe^{3+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.09 | <0.02 | 0.24 | 0.98 |
| 1:00pm | 0.17 | <0.03 | 0.24 | 0.56 |
| 7:00pm | 0.11 | <0.04 | 0.22 | 0.52 |
| 12:00am | - | - | 0.23 | 0.78 |
| 8:00am | 0.1 | <0.05 | 0.24 | 1.01 |
| 1:00pm | 0.1 | <0.06 | 0.21 | 0.69 |
| 7:00pm | 0.08 | <0.07 | 0.22 | 0.64 |
| 12:00am | - | - | 0.24 | 0.95 |
| **$K^{+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.28 | 0.71 | 0.71 | 1.07 |
| 1:00pm | 0.33 | 0.40 | 0.62 | 0.66 |
| 7:00pm | 0.33 | 0.32 | 0.69 | 0.09 |
| 12:00am | - | - | 0.75 | 1.08 |
| 8:00am | 0.29 | 0.29 | 0.74 | 1.13 |
| 1:00pm | 0.29 | 2.39 | 0.71 | 0.66 |
| 7:00pm | 0.32 | 0.46 | 0.71 | 0.79 |
| 12:00am | - | - | 0.77 | 1.03 |
| **$Mg^{2+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.09 | 0.12 | 0.20 | 0.40 |
| 1:00pm | 0.10 | 0.12 | 0.17 | 0.23 |
| 7:00pm | 0.10 | 0.11 | 0.17 | 0.24 |
| 12:00am | - | - | 0.21 | 0.36 |
| 8:00am | 0.10 | 0.10 | 0.21 | 0.40 |
| 1:00pm | 0.09 | 0.24 | 0.18 | 0.25 |
| 7:00pm | 0.10 | 0.18 | 0.17 | 0.22 |
| 12:00am | - | - | 0.20 | 0.36 |
| **$Mn^{2+}/Mn^{4+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | <0.01 | <0.01 | 0.01 | 0.04 |
| 1:00pm | <0.01 | <0.01 | 0.01 | 0.01 |
| 7:00pm | <0.01 | <0.01 | <0.01 | 0.02 |
| 12:00am | - | - | 0.01 | 0.04 |
| 8:00am | <0.01 | <0.01 | 0.01 | 0.05 |
| 1:00pm | <0.01 | <0.01 | <0.01 | 0.01 |
| 7:00pm | <0.01 | <0.01 | <0.01 | 0.01 |
| 12:00am | - | - | 0.01 | 0.05 |

*Lab error, data missing

**Table 4(cont.) - Inorganics in mg/L for the H-02 Wetland Treatment System, 10/16-10/17/07**

| **Cations (cont.)** | | | | |
|---|---|---|---|---|
| **$Na^+$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 19.0 | 29.8 | 34.0 | 35.4 |
| 1:00pm | 22.1 | 28.3 | 31.3 | 34.9 |
| 7:00pm | 23.4 | 27.1 | 34.6 | 33.8 |
| 12:00am | - | - | 33.8 | 34.4 |
| 8:00am | 20.1 | 26.5 | 32.0 | 34.9 |
| 1:00pm | 19.8 | 58.4 | 33.7 | 34.0 |
| 7:00pm | 21.8 | 43.8 | 33.6 | 34.1 |
| 12:00am | - | - | 34.4 | 34.7 |
| **$Pb^{2+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.014 | <0.002 | <0.002 | <0.002 |
| 1:00pm | 0.031 | <0.002 | <0.002 | <0.002 |
| 7:00pm | 0.015 | <0.002 | <0.002 | <0.002 |
| 12:00am | - | - | <0.002 | <0.002 |
| 8:00am | 0.022 | <0.002 | <0.002 | <0.002 |
| 1:00pm | 0.026 | - | <0.002 | <0.002 |
| 7:00pm | 0.026 | <0.002 | <0.002 | <0.002 |
| 12:00am | - | - | <0.002 | <0.002 |
| **$Zn^{2+}$** | | | | |
| Time | *East* | *West* | *Splitter Box* | *Outlet to Spillway* |
| 8:00am | 0.03 | 0.04 | 0.02 | <0.01 |
| 1:00pm | 0.03 | 0.03 | 0.02 | <0.01 |
| 7:00pm | 0.03 | 0.03 | 0.02 | <0.01 |
| 12:00am | - | - | 0.02 | <0.01 |
| 8:00am | 0.03 | 0.03 | 0.02 | <0.01 |
| 1:00pm | 0.03 | 0.05 | 0.03 | <0.01 |
| 7:00pm | 0.03 | 0.03 | 0.02 | <0.01 |
| 12:00am | - | - | 0.02 | <0.01 |

*Lab error, data missing

If the anions present in the influent water are reacting with the clay or bentonite liner, serving to remove hydroxyl ions which increase the pH of the water, a portion of the anion concentrations should decrease from the inlet to the outlet of the basin. Furthermore, in order to create the one to two pH unit increase in water pH observed from the inlet to the outlet, the reduction in the anion concentration should be significant (i.e., an order of magnitude drop in concentration). However, no significant decrease in the concentration of any of the anions was observed. Alkalinity experienced an increase in concentration which is likely due to dissolution of carbonate minerals in the clay. The concentration of $NO_3^-$ dropped by approximately a half or a third during some measurements but this is not the order of magnitude decrease that would indicate reactions with the bentonite liner and may be accounted for by uptake of nitrate by aquatic plants (e.g., algae). The phosphate concentration, considered to the most likely anion to react with the liner, did not experience a drop in concentration. These results do not support a chemical reaction occurring wherein influent anions exchange with hydroxyl ions on the bentonite liner surface.

It is apparent that the H-Area process water composition is not uniform over time which can confound an analysis of the inorganic concentrations within the basin. For example, the west inlet influent experienced a spike in the concentration of Ca, K, Na, alkalinity, Cl, $NO_3^-$, and $SO_4^{2-}$ in the September 12:30 PM influent sample. In addition, the only measurable concentrations of lead were from the east inlet during both the September and October samplings, though at no time was lead measured in the outlet. Aside from these operational influences on the concentration of inorganic ions in the basin, there was also an increase in the concentration of Al, Ca, Fe, K, Na, Mg, and Mn from the inlet to the outlet of the basin in both samplings (Table 3 and Table 4). As the top layer clay contains natural organic matter as well as sediment, which can be sources of the above cations, an increase in the concentration of these cations following contact between the clay and the process water is not unexpected and likely not of concern. In addition, small amounts of sediment may have been picked up with the grab samples and the inorganic ion concentration of the elements within the sediments may have been inadvertently measured. While the changes in the concentration of inorganic ions within the treatment system indicated successful removal of heavy metals such as copper and lead, they did not support the hypothesis of significant interactions with the clay or bentonite liner as a cause for the observed increase in pH.

A vertical and horizontal pH profile within the equalization basin was performed to identify the source of the pH increase as in the top (i.e., an algal influence) or the bottom (i.e., a bentonite liner or clay influence) of the basin. A higher pH in the water closest to the bottom of the basin would indicate a clay and bentonite liner mechanism, while a higher pH closest to the surface would indicate an algal influence. The results of these analyses are presented in Table 5 and Table 6.

**Table 5 - pH, temperature, and DO values of water measured during vertical and horizontal profiles of the equalization basin, 1/8/08**

| Location | Depth (in.) | pH | Temp (°C) | DO (mg/L) |
|---|---|---|---|---|
| Basin outlet | Surface | 8.44 | 14.68 | 13.11 |

| Location | Depth (in.) | pH | Temp (°C) | DO (mg/L) |
|---|---|---|---|---|
| 1 | Surface | 8.34 | 13.35 | 12.77 |
| 1 | 6 | 8.35 | 13.40 | 13.13 |
| | | | | |
| 2 | Surface | 8.84 | 13.36 | 14.01 |
| 2 | 6 | 8.86 | 13.35 | 13.97 |
| 2 | 12 | 8.89 | 13.33 | 13.98 |
| 2 | 15 | 8.89 | 13.33 | 14.00 |
| | | | | |
| 3 | Surface | 8.92 | 13.93 | 14.04 |
| 3 | 6 | 8.91 | 13.78 | 14.12 |
| 3 | 12 | 8.93 | 13.66 | 14.16 |
| 3 | 18 | 8.95 | 13.67 | 14.17 |
| 3 | 22 | 8.92 | 13.61 | 14.17 |
| | | | | |
| 4 | Surface | 8.88 | 14.50 | 13.87 |
| 4 | 6 | 8.93 | 13.89 | 14.07 |
| 4 | 12 | 8.93 | 13.89 | 13.96 |
| 4 | 18 | 8.92 | 13.85 | 14.06 |
| 4 | 24 | 8.91 | 13.87 | 14.09 |
| 4 | 27 | 8.89 | 13.83 | 14.11 |
| | | | | |
| 5 | Surface | 8.84 | 14.74 | 13.61 |
| 5 | 6 | 8.85 | 14.58 | 13.66 |
| 5 | 12 | 8.86 | 14.41 | 13.74 |
| 5 | 18 | 8.90 | 14.18 | 13.75 |
| 5 | 24 | 8.93 | 13.85 | 13.85 |
| 5 | 30 | 8.96 | 13.74 | 13.94 |

| Location | Depth (in.) | pH | Temp (°C) | DO (mg/L) |
|---|---|---|---|---|
| 10 | Surface | 8.62 | 13.73 | 13.68 |
| 10 | 6 | 8.61 | 13.73 | 13.52 |
| | | | | |
| 9 | Surface | 8.92 | 13.67 | 14.06 |
| 9 | 6 | 8.93 | 13.66 | 14.09 |
| 9 | 12 | 8.95 | 13.55 | 14.10 |
| 9 | 15 | 8.96 | 13.54 | 14.05 |
| | | | | |
| 8 | Surface | 8.91 | 13.83 | 13.96 |
| 8 | 6 | 8.91 | 13.91 | 13.95 |
| 8 | 12 | 8.93 | 13.86 | 13.94 |
| 8 | 18 | 8.95 | 13.82 | 13.99 |
| 8 | 21 | 8.96 | 13.76 | 14.00 |
| | | | | |
| 7 | Surface | 8.94 | 14.05 | 14.31 |
| 7 | 6 | 8.95 | 13.85 | 14.34 |
| 7 | 12 | 8.96 | 13.82 | 14.34 |
| 7 | 18 | 8.97 | 13.79 | 14.35 |
| 7 | 24 | 8.99 | 13.78 | 14.36 |
| 7 | 27 | 9.01 | 13.75 | 14.47 |
| | | | | |
| 6 | Surface | 8.88 | 14.65 | 13.69 |
| 6 | 6 | 8.90 | 14.07 | 13.85 |
| 6 | 12 | 8.94 | 13.89 | 13.88 |
| 6 | 18 | 8.95 | 13.80 | 13.93 |
| 6 | 24 | 8.95 | 13.81 | 13.95 |
| 6 | 30 | 8.99 | 13.75 | 14.00 |

**Table 6 - pH of equalization basin sediment at different depths, 1/8/08**

| Location | Depth (in.) | pH | Location | Depth (in.) | pH | Location | Depth (in.) | pH |
|---|---|---|---|---|---|---|---|---|
| 1 | Upper | 6.05 | 2 | Upper | 5.737 | 3 | Upper | 5.499 |
| 1 | Middle | 5.33 | 2 | Middle | 5.464 | 3 | Middle | 5.423 |
| 1 | Lower | 5.22 | 2 | Lower | 5.158 | 3 | Lower | 5.110 |
| | | | | | | | | |
| 4 | Upper | 5.77 | 5 | Upper | 5.499 | 6 | Upper | 5.522 |
| 4 | Middle | 5.24 | 5 | Middle | 5.426 | 6 | Middle | 5.299 |
| 4 | Lower | 5.29 | 5 | Lower | 5.517 | 6 | Lower | 5.141 |

The water column and the sediment depth pH profiles did not support the hypothesis of interactions of the water with either the clay or the liner as a substantial contributor to the pH increase in the equalization basin. The water pH was lower at the shallow end of the basin than in the deeper (west) end by approximately 0.3-0.6 pH units and increased about 0.05 pH units as the water depth increased (Table 5). Considering that error for pH measurements is generally ± 0.1 pH units, the difference in water pH with depth is negligible. During this sampling period, the algae in the basin were fairly inactive due to low temperatures and application of an algaecide to the basin in November 2007. Water column pH may be reevaluated during the summer, when temperature and algae activity are higher, to confirm the results of this sample period. The sediment pH samples showed a pH decrease with depth of the sediment sample which is the reverse of the trend expected if the bentonite liner, located at the bottom of the sediments, is a factor influencing the increase of the basin pH (Table 6). In addition, as there is no identifiable hydrological force other than diffusion through the dense clay material, it is unlikely that the liner has any influence on the water pH.

### *Phosphate and carbonate ions*

The high quantity of sodium present in the H-02 treatment water measured in Table 3 and Table 4 and knowledge of typical additives to cooling tower water suggest that phosphate as trisodium phosphate ($Na_3PO_4$) and/or carbonate as sodium carbonate ($Na_2CO_3$) may have been added to the H-02 process water. Therefore, an alternative inorganic chemistry mechanism can be explored that deals with the buffering capacity of the phosphate ($PO_4^{3-}$) and/or carbonate ($CO_3^{2-}$) ions.

Given the strength of these anions as bases (e.g., the ability of $PO_4^{3-}$ to remove hydrogen ions to form phosphoric acid ($H_3PO_4$)), they can increase the pH of water and serve as a pH buffer. These properties can be used to explain the observed pH trends within the equalization basin. Acting as a base, the anions produce a pH of approximately 8 within the influent water to the basin. When the algae consumes carbon dioxide during photosynthesis there is a decrease in the concentration of carbonic acid within the basin. The removal of carbonic acid may then cause the pH to rise above the NPDES standard. Furthermore, Figure 3 indicated a small oscillation in the equalization basin pH compared to the approximately 2 unit pH oscillations in the wetland cells. This event could be explained by a smaller quantity of algae or a higher concentration of phosphate and/or carbonate ions in the equalization basin than in the wetland cells. When carbon dioxide is released during the respiration process of the algae, there is the potential for the subsequent formation of carbonic acid ($H_2CO_3$). However, the presence of the pH buffers may serve to limit the influence of the dissolved carbon dioxide leading to a less significant pH decrease in the basin compared to the wetland cells where the concentration of these anions is lower. In this way, the phosphate/carbonate ion mechanism incorporates the impact of algae within the basin, which is evident in the oscillation of the pH over time, while also explaining why there is an overall pH increase from the inlet to the outlet of the basin.

## 4.0 RECOMMENDED STUDIES

Strategies for meeting the NPDES standard for pH from the H-02 Wetland Treatment System include allowing the H-02 wetland to mature so that it possesses the buffering capacity evidenced in the similar A-01 wetland, removing phosphate/carbonate from the influent water, or acidifying the outlet water. While the first option will occur over time, the remaining two options concern the cost effectiveness of treating the inlet or the outlet of the basin. Removal of the phosphate/carbonate ion influence can entail either eliminating these ions from the process water by utilizing a sufficient replacement compound or by treating phosphate in the influent to the basin. The acidification process requires determining the type and quantity of acid to use to lower the pH before the NPDES measurement point.

### *Removal of Phosphates/Carbonate Ions*

Firstly, it should be established whether trisodium phosphate and/or sodium carbonate are being added to the H-02 process water and for what purpose. Once the purpose is known, a suitable alternative compound that does not possess the buffering capacities of the phosphate and carbonate ions can be determined.

If there is no suitable alternative to the use of the basic anions, a precipitation method may be employed to remove these ions from the inlet water containing the highest concentration of these ions (the west inlet according to Table 3 and Table 4). Calcium, aluminum, and iron are three common multivalent cations used to precipitate phosphates through formation of a low solubility compound. Aluminum and iron precipitation of phosphate is generally favorable under low pH conditions (below 7.5) and therefore may not be suitable for the relatively high pH of the basin influent. Calcium will form precipitates with both phosphates and carbonates and, therefore, enough calcium must be added to react with the inlet water's alkalinity (the majority of which is composed of carbonates) before precipitation of phosphate will occur. As such, the dosage of calcium needs to be about 1.5 times the concentration of the alkalinity (Metcalf and Eddy, 2002). In addition to the increased chemical demand, the most common source of calcium for precipitation is lime ($Ca(OH)_2$) which will lead to an increase in pH. High pH favors the precipitation of phosphates but defeats the overall purpose of lowering pH so an alternative calcium source would need to be determined, perhaps calcium sulfate. The small amount of precipitate sludge that would be formed would be expected to settle out of the relatively still water of the equalization basin and should not impact the wetland cells.

### *Acidification of the Basin Outlet*

Common acids utilized for pH control include hydrochloric acid, phosphoric acid, nitric acid, and sulfuric acid. Given that chloride can be toxic to aquatic life depending on the dose, hydrochloric acid is not a suitable candidate for pH control for water to a wetland. For natural systems, the addition of phosphoric acid, nitric acid, and sulfuric acid may be beneficial as these acids would adjust pH as well as contribute nutrients to the wetland. Natural mineral sources of phosphate and projected sulfate conditions within the wetland leave nitrogen as the limiting nutrient for the wetland; therefore, addition of nitric acid may be preferred. Consideration of the cost, with phosphoric acid being the most expensive and sulfuric acid and nitric acid being comparable, further supports the use of nitric acid for pH control. However, nitric acid is considered highly corrosive and, while sulfuric acid is slightly less hazardous than nitric acid, there are relatively lower risks associated with the use of phosphoric acid. Given the considerations of nutrient addition, cost, and safety, nitric acid is the preferred pH control additive as it would address the pH issue and add essential nutrients to the wetland. The risk association with the use of nitric acid can be mitigated with appropriate safety procedures. If the risk is deemed too high, sulfuric acid may be an acceptable alternative.

The quantity of 67% nitric acid to be added can be determined by titration until the pH is steady at the desired near neutral pH (i.e., approximately 7-8). The process should be repeated at least three times in order to determine the quantity of nitric acid required to reach the desired pH level with a measure of certainty.

Once the volume of nitric acid ($V_n$) needed to neutralize a known volume of the basin water ($V_w$) is determined, the required rate of nitric acid addition ($r_n$) can be calculated from the flow of water to the basin by the following equation.

$$R = \text{Ratio of volume of acid required per volume of water} = \frac{V_n}{V_w} \text{ (mL nitric/mL water)}$$

$$Q = \text{Basin effluent flow} = 120 \text{ gal/min} = 454{,}250 \text{ mL/min.}$$

$$r_n \text{ (mL nitric /min.)} = Q * R$$

The storage vessel for the nitric acid must be glass or a plastic container approved for acid storage. The volume of this storage basin would depend on the anticipated duration of acid addition and on the availability of staff to refill the basin. The volume of the basin may then be calculated by multiplying the expected duration of use by $r_n$. A delivery port would extend from the basin to the desired addition point. A suitable location for acid addition would be on top of the splitter box at the point where the water is divided between the two wetland cells. In addition to providing a degree of mixing between the nitric acid and the water, this location places the apparatus above the water line unlike a placement at the basin outlet where the apparatus may be adversely affected by high flow in the basin. A flow meter would regulate the $r_n$.

## 5.0 CONCLUSION

During initial operation of the H-02 Wetland Treatment System, it was observed that the pH of the water leaving the equalization basin was elevated compared to the influent pH and this elevated pH exceeded the upper NPDES limit of 8.5. In order to determine the cause of this elevated pH with the goal to address the cause so that the wetland system is operating in NPDES compliance, two possible mechanisms were evaluated. The first mechanism evaluated was that of algal activity. Diurnal fluctuations in pH and DO measured within the basin and wetland cells (i.e., a rise in pH and DO during the day and a drop in pH and DO at night) indicated that algae are an influencing factor for pH. Though algae are clearly a factor influencing pH within the basin, algae generally do not cause an overall increase in pH, as observed from the inlet to the outlet of the basin. As algal activity alone cannot be responsible for the observed basin outlet pH values, chemical reaction mechanisms that can result in an overall increase in pH were also evaluated. While the concentration of inorganic ions within the treatment system indicated successful removal of heavy metals such as copper and lead, it did not support interactions with the clay or bentonite liner as a cause for the observed increase in pH. This finding was supported by the absence of a trend of increasing pH with increasing depth in either the water column or the sediment column. The high concentration of sodium in the influent water to the basin suggested the presence of associated phosphates (as $Na_3PO_4$) and/or carbonates (as $Na_2CO_3$). These compounds may act as bases and pH buffers which would explain the overall increase in pH within the basin and also the dampening of the pH oscillation caused by the algae.

Strategies for meeting the NPDES standard for pH from the H-02 Wetland Treatment System include allowing the H-02 wetland to mature so that it possesses a higher buffering capacity, removing phosphate from the influent water, or acidifying the outlet water. To determine the most feasible choice, each method should be evaluated for ease of implementation and cost.

## 6.0 REFERENCES

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# APPENDIX A

## H-02 Wetland Treatment System Water Chemistry Sampling Instructions

## H-02 Wetland Treatment System Water Chemistry Sampling Instructions

## 1.0 PURPOSE & SCOPE

This document establishes work instructions for collecting surface water grab samples and water quality data from the H-02 Wetland Treatment System. The subject samples and data are for analytical purposes only, and as such, are not to be collected in support of compliance activities. This document is applicable to all SRNL/ESBD and DP/Tritium Facility personnel who collect these samples and data associated with this effort.

## 2.0 PERFORMANCE

### 2.1 Sampling Locations

The sampling locations to be used in support of this effort are as follows:

(1) East Discharge Pipe into Basin
(2) West Discharge Pipe into Basin
(3) Splitter-box Discharge from Basin
(4) Discharge from Wetland Cells

Figure 1 - H-02 sampling locations layout is attached.

### 2.2 Sampling Frequency

The sampling frequency for this effort will be four times per day over a period of two days. The sampling periods for the different locations are as follows:

(1) Dawn (7 – 8 AM: Locations 1-4)
(2) Midday (12 - 2 P.M.: Locations 1-4)
(3) Dusk (7 – 8 PM: Locations 1-4)
(4) Approx Midnight (12 - 2 A.M.: Locations 3 and 4 only)

SRNL/ESBD sampling personnel will complete sampling periods (1) – (3) and DP/Tritium Facility personnel will complete sampling period (4).

### 2.3 Sampling Protocol per Location

The sampling kits will be provided by WSRC-Environmental Monitoring (EMS). These kits will consist of sampling bottle, ice coolers/chests, and blue ice (commercial chemical ice packs). SRNL/ESTB will collect and distribute sampling kits. The sampling protocol for this effort is to collect the following from each location per the aforementioned frequency:

- Three (3) grab samples of water (i.e., one for cations, one for anions, and one for alkalinity)
- Water quality data to include:
  - pH
  - Temperature
  - Dissolved oxygen
  - Redox potential (Eh)

The grab samples are to be collected per SRS 3Q1-3 Procedure 3030, *Grab Sampling of Surface Water*. Each bottle is labeled and entries for sample collection date and time, and sampler's initials need to be filled in on the label. Completed grab samples will be placed upright in the provided cooler with the blue ice pack surrounding the sample bottles. Sampling at Sample Location 3 (splitter-box discharge from basin) requires the use of a sampling pole extension located adjacent to the splitter-box. Grab samples will be collected using the sampling pole extension and the sample bottles filled from the water collector on the end of the sampling pole at the surface. **Caution:** No physical entry into the interior of the splitter-box is required and care needs to be exercised during execution of sampling activities with sampling pole extension.

The water quality data are to be collected using a YSI 6 Series Water Quality Logging System. YSI operational steps are:

1. Ensure YSI probe and 650 MDS controller are assembled correctly.
2. Push the green button on the 650 MDS controller to energize the system.
3. The "Sonde Run" text should be highlighted on the controller and push the enter arrow button to begin analysis.
4. Analysis will take approximately 5 minutes.
5. Data readings will appear on the 650 MDS controller and record data on the data sheets provided.
6. Turn off system by pushing the green button on the 650 MDS controller.

Stream water safety protocol should be adhered to during sampling activities per SRS 3Q1-3 Procedure 3020, *Stream Water Safety.* Copies of the noted procedures are attached to this work instruction.

### 2.4 Sample Disposition

The grab samples in the collection bottles are to be placed in an ice chest and chilled using blue ice. The SRNL/ESTB sampling personnel will deliver the completed grab samples EMS Sample Receiving at 735-B. The DP/Tritium

Facility sampling personnel will place the ice chest and the YSI 6 unit at entry point to the H-02 site adjacent to the concrete barriers.

## 3.0 REFERENCES

SRS 3Q1-3 Procedure 3030, *Grab Sampling of Surface Water*.
SRS 3Q1-3 Procedure 3020, *Stream Water Safety*.

## 4.0 ATTACHMENTS

H-02 Sampling Location Layout
SRS 3Q1-3 Procedure 3030, *Grab Sampling of Surface Water*.
SRS 3Q1-3 Procedure 3020, *Stream Water Safety*.

## Attachments

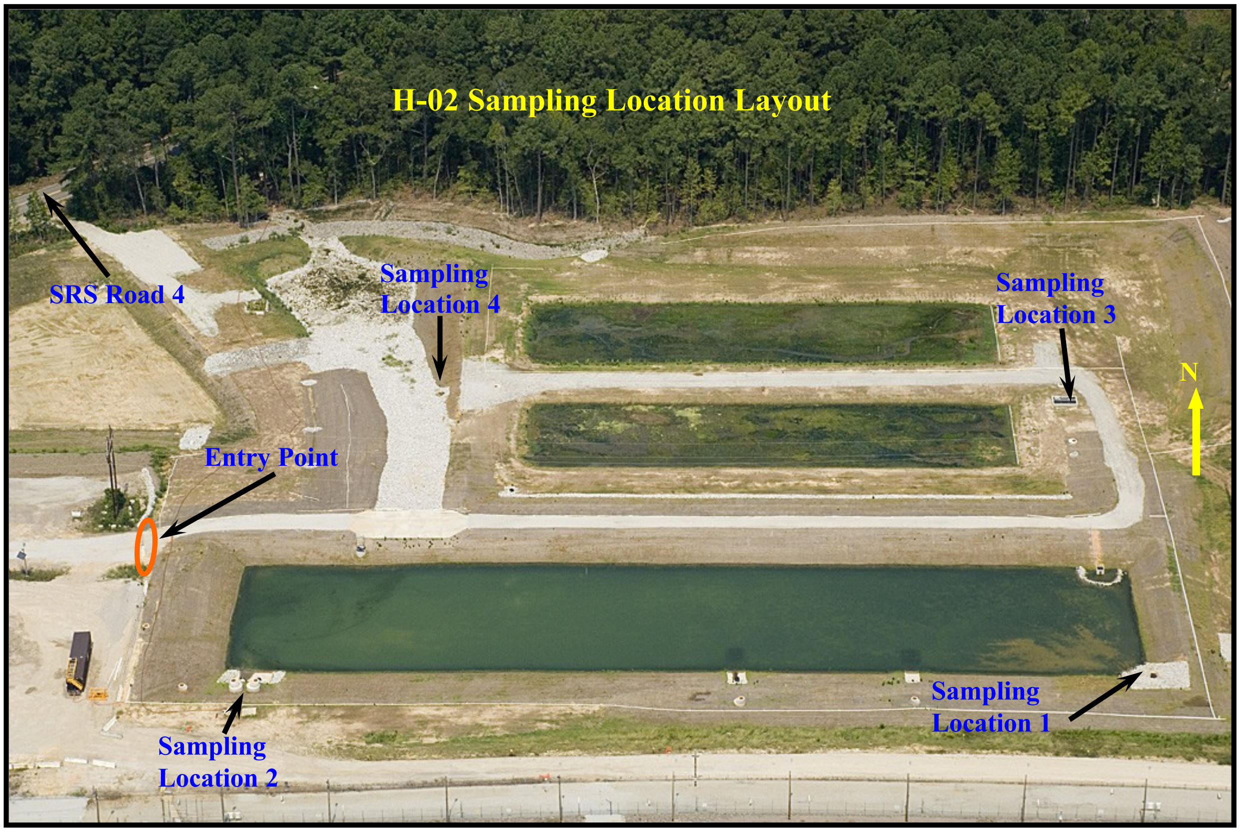
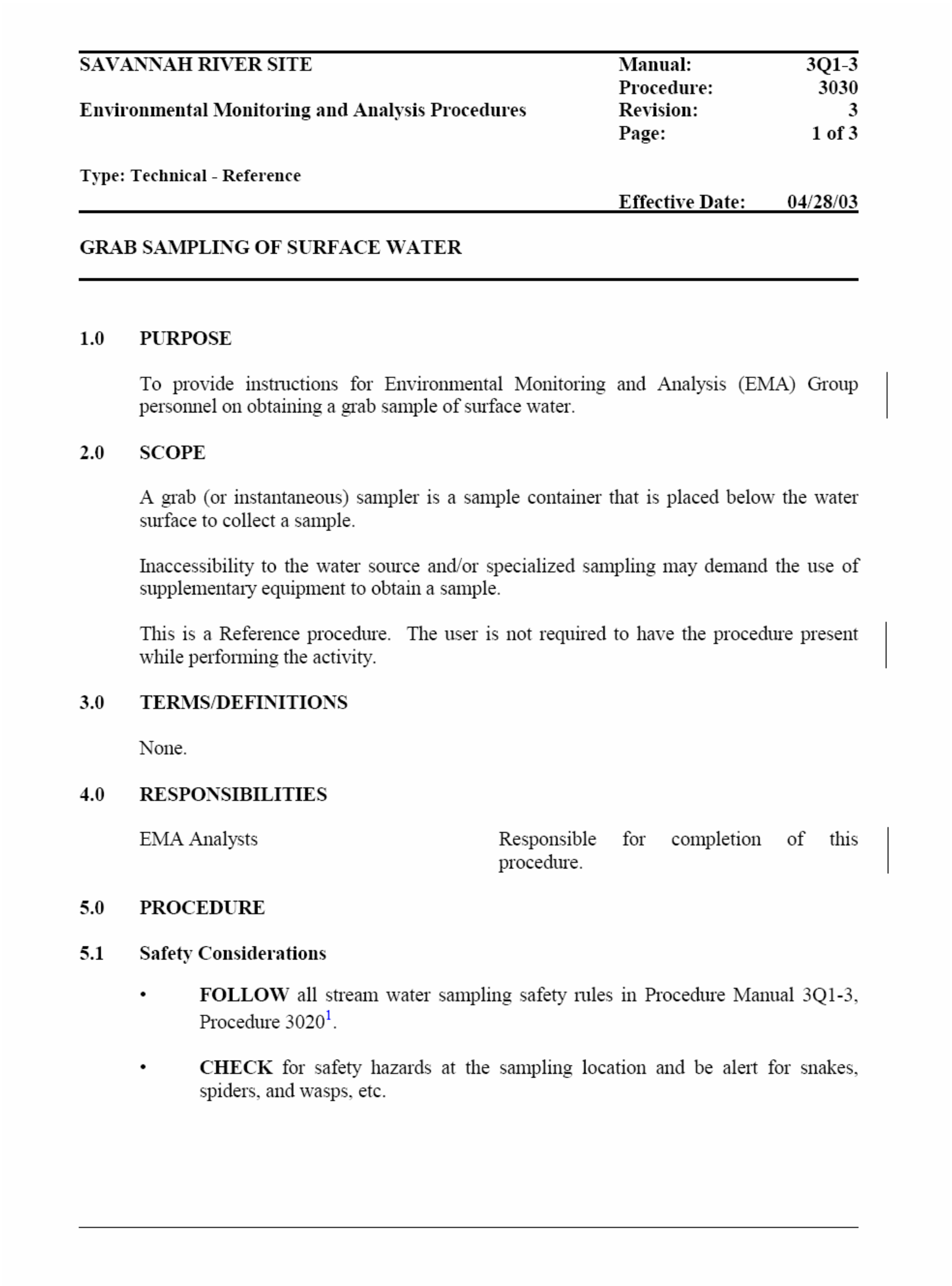


Figure 1 - H-02 Sampling Locations Layout



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| **SAVANNAH RIVER SITE** | **Manual:** | **3Q1-3** |
| | **Procedure:** | **3030** |
| **Environmental Monitoring and Analysis Procedures** | **Revision:** | **3** |
| | **Page:** | **1 of 3** |
| **Type: Technical - Reference** | | |
| | **Effective Date:** | **04/28/03** |

## GRAB SAMPLING OF SURFACE WATER

### 1.0 PURPOSE

To provide instructions for Environmental Monitoring and Analysis (EMA) Group personnel on obtaining a grab sample of surface water.

### 2.0 SCOPE

A grab (or instantaneous) sampler is a sample container that is placed below the water surface to collect a sample.

Inaccessibility to the water source and/or specialized sampling may demand the use of supplementary equipment to obtain a sample.

This is a Reference procedure. The user is not required to have the procedure present while performing the activity.

### 3.0 TERMS/DEFINITIONS

None.

### 4.0 RESPONSIBILITIES

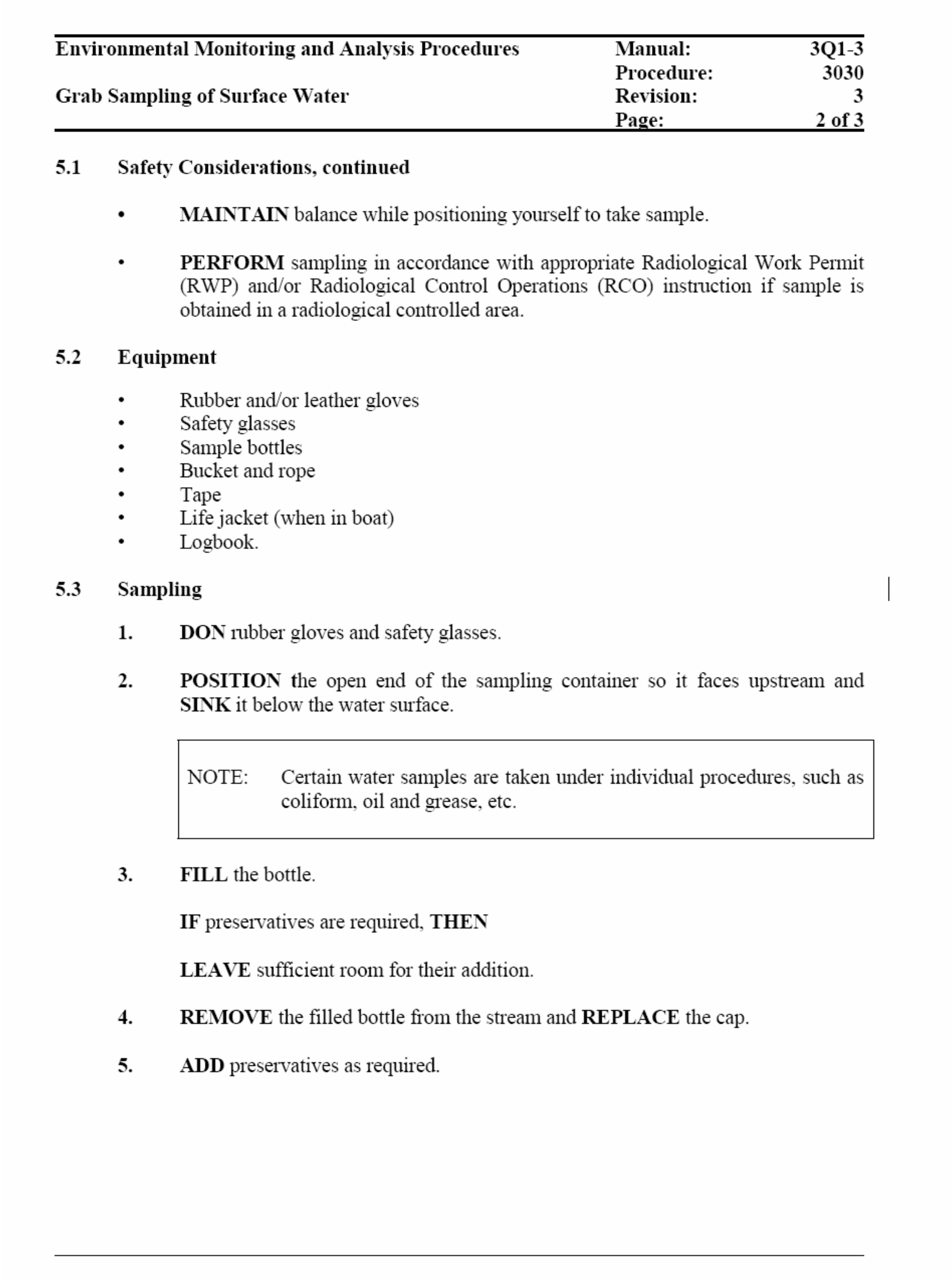
| | |
|---|---|
| EMA Analysts | Responsible for completion of this procedure. |

### 5.0 PROCEDURE

### 5.1 Safety Considerations

- **FOLLOW** all stream water sampling safety rules in Procedure Manual 3Q1-3, Procedure 3020[1].

- **CHECK** for safety hazards at the sampling location and be alert for snakes, spiders, and wasps, etc.



**Environmental Monitoring and Analysis Procedures**

**Grab Sampling of Surface Water**

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### 5.1 Safety Considerations, continued

- **MAINTAIN** balance while positioning yourself to take sample.
- **PERFORM** sampling in accordance with appropriate Radiological Work Permit (RWP) and/or Radiological Control Operations (RCO) instruction if sample is obtained in a radiological controlled area.

### 5.2 Equipment

- Rubber and/or leather gloves
- Safety glasses
- Sample bottles
- Bucket and rope
- Tape
- Life jacket (when in boat)
- Logbook.

### 5.3 Sampling

1. **DON** rubber gloves and safety glasses.
2. **POSITION** the open end of the sampling container so it faces upstream and **SINK** it below the water surface.

> NOTE: Certain water samples are taken under individual procedures, such as coliform, oil and grease, etc.

3. **FILL** the bottle.

   **IF** preservatives are required, **THEN**

   **LEAVE** sufficient room for their addition.
4. **REMOVE** the filled bottle from the stream and **REPLACE** the cap.
5. **ADD** preservatives as required.

## 5.3 Sampling, continued

6. **FILL** out label with location, date and time of sample, sampler's name, analyses to be performed, and preservations added to sample or **ATTACH** pre-printed Environmental Monitoring Computer Automation Project (EMCAP) label completed as required. **INDICATE** that the sample is a grab sample on the sample label.

7. **COMPLETE** all required entries in the sampling logbook.

8. AFTER SAMPLING:

   a. **PERFORM** housekeeping, as necessary to ensure that site is clean.

   b. **DELIVER** sample(s) to the appropriate laboratory or lab courier.

   c. **ADVISE** management of any unusual conditions.

   d. **RETURN** equipment to storage.

## 6.0 RECORDS

Records generated as a result of performance of this procedure are maintained in accordance with Procedure Manual 1B, Procedure 3.31[2], Records Management.

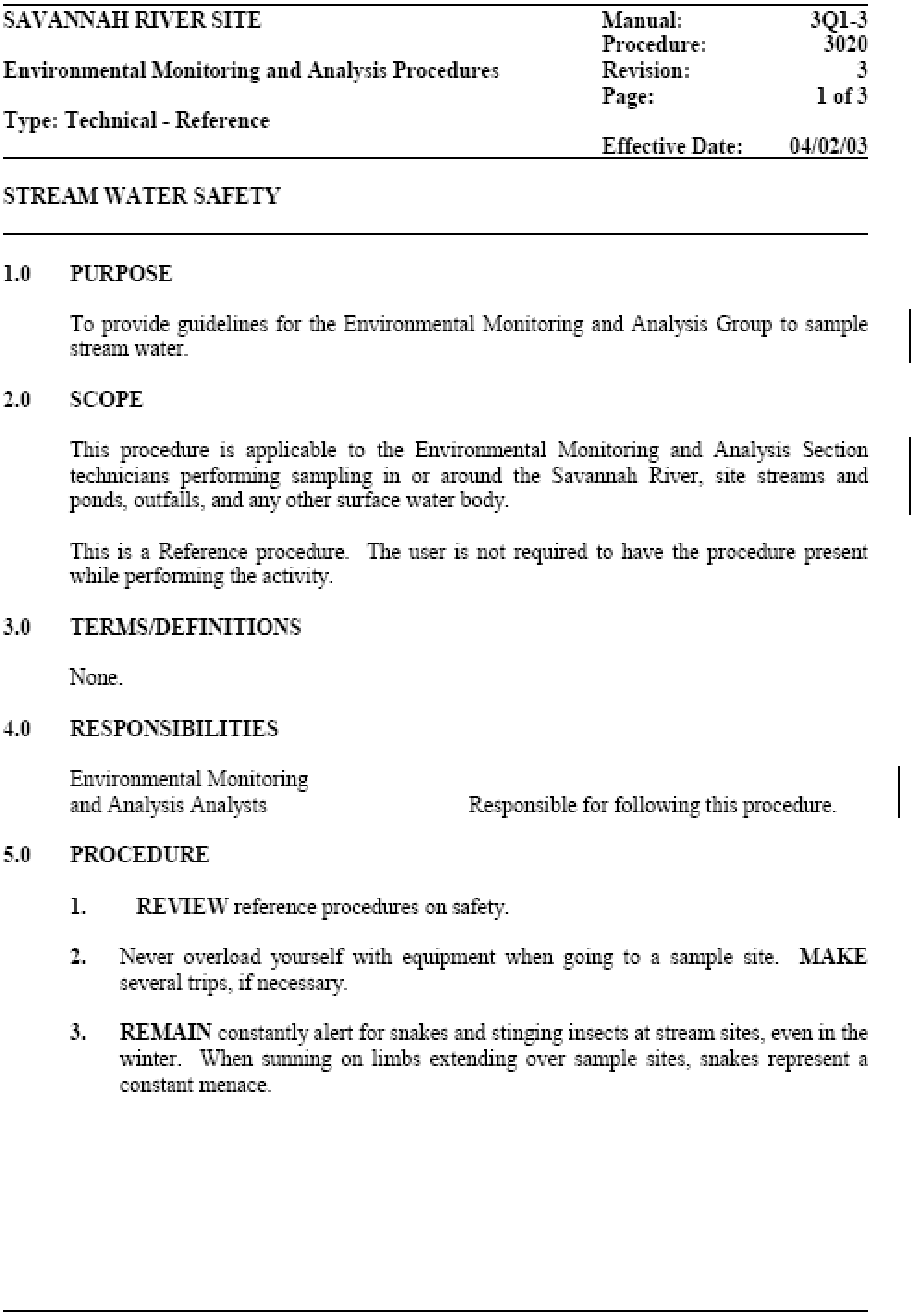
logbook

## 7.0 REFERENCES

[1] Procedure Manual 3Q1-3, Procedure 3020, Stream Water Safety
[2] Procedure Manual 1B, Procedure 3.31, Records Management

## 8.0 ATTACHMENTS

None.



**SAVANNAH RIVER SITE**

**Environmental Monitoring and Analysis Procedures**

**Type: Technical - Reference**

| | |
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| **Procedure:** | 3020 |
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STREAM WATER SAFETY

## 1.0 PURPOSE

To provide guidelines for the Environmental Monitoring and Analysis Group to sample stream water.

## 2.0 SCOPE

This procedure is applicable to the Environmental Monitoring and Analysis Section technicians performing sampling in or around the Savannah River, site streams and ponds, outfalls, and any other surface water body.

This is a Reference procedure. The user is not required to have the procedure present while performing the activity.

## 3.0 TERMS/DEFINITIONS

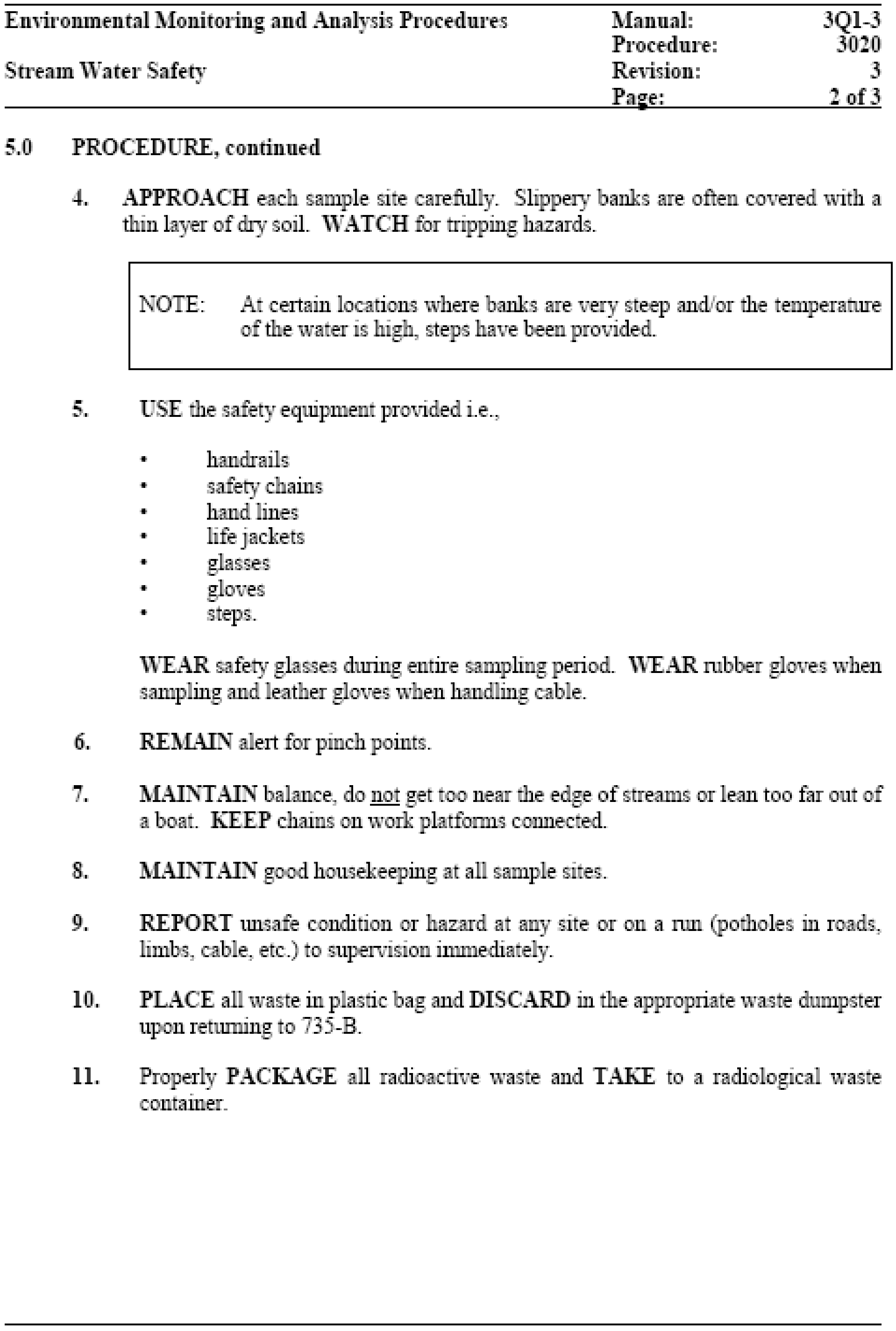
None.

## 4.0 RESPONSIBILITIES

| | |
|---|---|
| Environmental Monitoring and Analysis Analysts | Responsible for following this procedure. |

## 5.0 PROCEDURE

1. **REVIEW** reference procedures on safety.
2. Never overload yourself with equipment when going to a sample site. **MAKE** several trips, if necessary.
3. **REMAIN** constantly alert for snakes and stinging insects at stream sites, even in the winter. When sunning on limbs extending over sample sites, snakes represent a constant menace.



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|---|---|---|
| **Environmental Monitoring and Analysis Procedures** | **Manual:** | **3Q1-3** |
| | **Procedure:** | **3020** |
| **Stream Water Safety** | **Revision:** | **3** |
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## 5.0 PROCEDURE, continued

4. **APPROACH** each sample site carefully. Slippery banks are often covered with a thin layer of dry soil. **WATCH** for tripping hazards.

> NOTE: At certain locations where banks are very steep and/or the temperature of the water is high, steps have been provided.

5. **USE** the safety equipment provided i.e.,

   - handrails
   - safety chains
   - hand lines
   - life jackets
   - glasses
   - gloves
   - steps.

   **WEAR** safety glasses during entire sampling period. **WEAR** rubber gloves when sampling and leather gloves when handling cable.

6. **REMAIN** alert for pinch points.

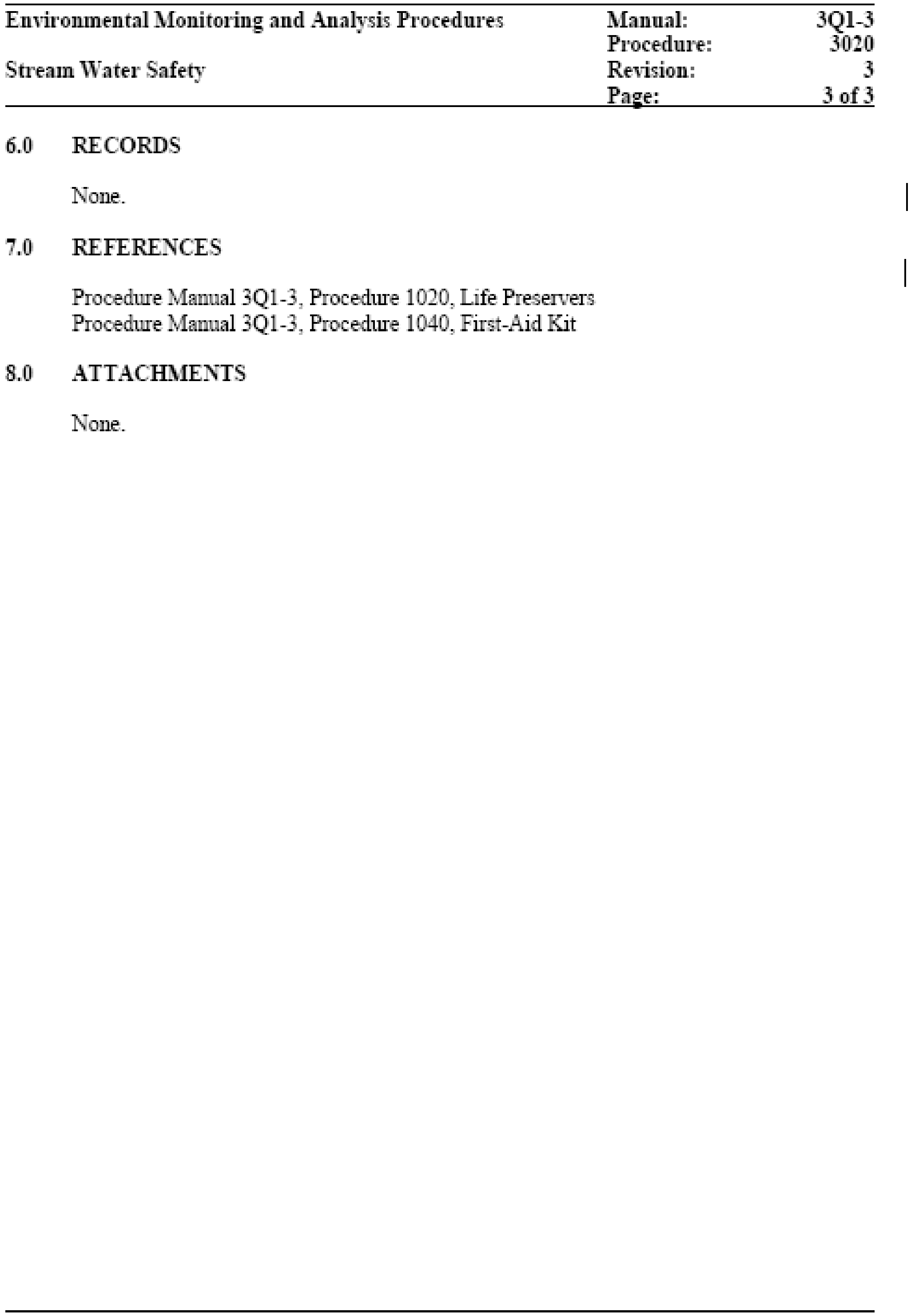
7. **MAINTAIN** balance, do not get too near the edge of streams or lean too far out of a boat. **KEEP** chains on work platforms connected.

8. **MAINTAIN** good housekeeping at all sample sites.

9. **REPORT** unsafe condition or hazard at any site or on a run (potholes in roads, limbs, cable, etc.) to supervision immediately.

10. **PLACE** all waste in plastic bag and **DISCARD** in the appropriate waste dumpster upon returning to 735-B.

11. Properly **PACKAGE** all radioactive waste and **TAKE** to a radiological waste container.



| Environmental Monitoring and Analysis Procedures | Manual: | 3Q1-3 |
|---|---|---|
| | Procedure: | 3020 |
| Stream Water Safety | Revision: | 3 |
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## 6.0 RECORDS

None.

## 7.0 REFERENCES

Procedure Manual 3Q1-3, Procedure 1020, Life Preservers
Procedure Manual 3Q1-3, Procedure 1040, First-Aid Kit

## 8.0 ATTACHMENTS

None.

## APPENDIX B

## H-02 Wetland Treatment System Inorganics Measured

| Analyte | Symbol | PQL* | Units |
|---|---|---|---|
| Silver | Ag | 0.005 | mg/L |
| Aluminum | Al | 0.05 | mg/L |
| Arsenic | As | 0.005 | mg/L |
| Barium | Ba | 0.05 | mg/L |
| Beryllium | Be | 0.001 | mg/L |
| Boron | B | 0.05 | mg/L |
| Calcium | Ca | 0.05 | mg/L |
| Cobalt | Co | 0.02 | mg/L |
| Chromium | Cr | 0.005 | mg/L |
| Copper | Cu | 0.005 | mg/L |
| Iron | Fe | 0.02 | mg/L |
| Potassium | K | 0.006 | mg/L |
| Manganese | Mn | 0.01 | mg/L |
| Molybdenum | Mo | 0.01 | mg/L |
| Sodium | Na | 0.03 | mg/L |
| Nickel | Ni | 0.01 | mg/L |
| Lead | Pb | 0.002 | mg/L |
| Antimony | Sb | 0.005 | mg/L |
| Selenium | Se | 0.005 | mg/L |
| Tin | Sn | 0.01 | mg/L |
| Titanium | Ti | 0.05 | mg/L |
| Vandaium | V | 0.01 | mg/L |
| Zinc | Zn | 0.01 | mg/L |
| Alkalinity | as $CaCO_3$ | 10 | mg/L |
| Chloride | Cl | 1 | mg/L |
| Nitrate | $NO_3^-$ | 0.02 | mg/L |
| Phosphorus | P | 0.01 | mg/L |
| Sulfate | $SO_4^{2-}$ | 1 | mg/L |

*Practical quantification limit (PQL): practical and routinely achievable detection limit with a relatively good certainty that any reported value is reliable