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Evaluation of Subsurface Flow Wetlands vs. Free-water Surface Wetlands Treating NPR-3 Produced Water – Year No. 2

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L.M. Jackson and J. E. Myers

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY/ROCKY MOUNTAIN OILFIELD TESTING CENTER

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ABSTRACT

Treatment wetlands, when designed properly, are emerging as a reliable technology for the tertiary treatment of produced water, storm water and other wastewater. The Department of Energy (DOE) Rocky Mountain Oilfield Testing Center (RMOTC) site located north of Casper, Wyoming, uses a constructed wetland to treat water produced from oil production. Upgrades to this treatment facility will be based on data collected from this three-year pilot study. The first year focused on design and construction of pilot units, acclimation and basic data collection. The units are set up outdoors to test climatic influences on treatment such as evapotranspiration rates and plant growth rates. In the second year of the project, we saw maturation of the microorganism and plant populations. Second year data collection includes first year study parameters plus an expanded data set including microbial activity, REDOX profiles, water balances, organic compounds, salts, and tracer studies.

Introduction

At RMOTC, the Naval Petroleum Reserve No. 3 (NPR-3) produces an average of 40,000 barrels of produced water each day. The constituents of concern in the produced water are primarily petroleum hydrocarbons and salts. The current constructed wetland system may be undersized when operating near its maximum capacity. A system upgrade is being designed to increase capacity and enhance treatment performance. Pilot wetland units were set up in 2001 to unrestrict the produced water treatment system. Data gathered from the pilot units are being used in the design of the facility upgrade.

Wetlands can treat petroleum industry wastewater and provide wildlife benefits. Treatment wetland facilities can be viable, healthy ecosystems. At RMOTC the wetland treated water meets discharge standards and keeps a normally dry creek wet year-round providing riparian habitat for many species. Using a low-energy treatment wetland is less expensive to operate than the traditional high-energy injection well.

Scope

The second year pilot wetland test parameters included pH, electrical conductivity (EC), total dissolved solids (TDS), chemical oxygen demand (COD), flow rates, hydraulic retention time (HRT), water temperature, plant growth, solids deposition, evapotranspiration (ET), and oxidation-reduction potential (REDOX). Water balances and tracers studies were conducted. Selected background sites were tested to compare plant growth (stem density and plant height). Microbial activity was also tested to determine the rate of maturation of wetland as the microbial and plant communities expanded.

Background

Wetlands are complex biological systems and home to many interconnected nutrient cycles and biotic associations. Essential elements involved in the ability of a wetland to process wastewater include the hydroperiod, pH, temperature, nutrient loading, soil type, and water quality, as well as the bacterial and plant activity.

Wetlands are composed of hydrophytes, hydrosoils, and hydroperiods. Hydrophytes are plants which are adapted to soils which can be either partially or fully anoxic (with low or nonexistent levels of oxygen). A hydrosoil is a saturated growth medium which typically has, but does not always have, a low carrying capacity for oxygen due to this water saturation. A hydroperiod is the cycle of flooded and dry conditions that a wetland experiences.

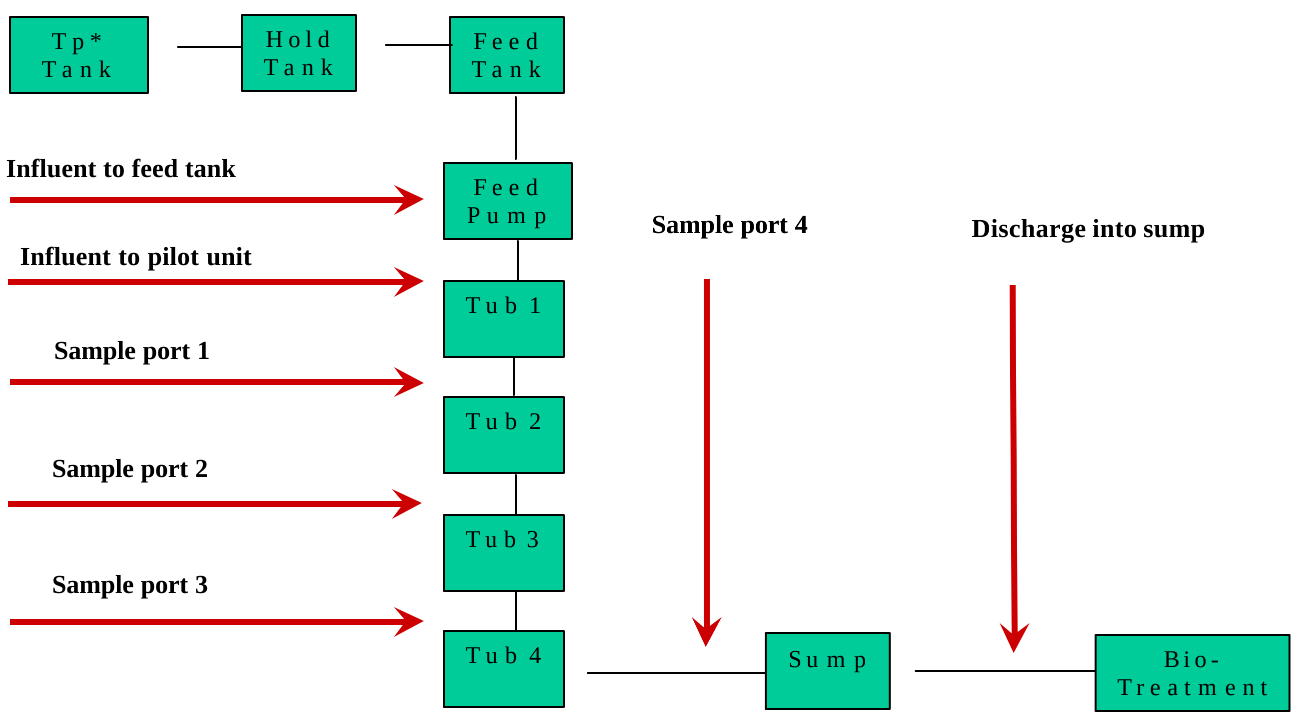
The RMOTC wetland pilot units were set up outdoors to test climatic influences on treatment. The free-water surface (FWS) and subsurface flow (SSF) wetland microcosm systems were filled with local soils, gravel, sharp sand and planted with native wetland plants (cattail, bulrush). Wetland plants are typically annuals and/or perennials with 1-2 year life cycles depending on the climate. Most of the wetland microbes are found in the root zone. When the plants fully populate the wetland, the microbial population acclimates and expands completely to fill all ecological niches. In Wyoming this process is expected to take about 3 years.

EXPERIMENTAL METHODS

For our pilot wetlands at NPR-3, we measured pH, EC, TDS, COD, temperature and dissolved oxygen (DO) with off-the-shelf meters and commercially available HACH test kits. Most of parameters were sampled daily to monitor pilot wetland performance and to adjust treatment based on the characteristics of the NPR-3 produced water. Soil samples were also collected and tested for pH and nitrate-nitrogen, phosphorus, and potassium levels. Biological Activity Reaction Tests (BARTs) were carried out on the soil and water column for each tub to determine the activity of certain types of bacteria. The activity is related to the absence, presence and/or population of microbes.

Process Flow Diagram

Each system is comprised of a feed stream, four 100-gal tubs, four sampling ports and a common discharge sump. Below is a process flow diagram of the Free Water Surface (FWS) and Subsurface Flow (SSF) pilot wetlands.



*Tp is an acronym for the Tensleep formation.

Figure 1.

Test Schedule

Most of the samples were collected from the pilot wetlands according to a pre-determined schedule by summer interns over an 8 week period. RMOTC personnel set up the wetlands prior to the interns' arrival and operated the wetlands after the interns had left. Sampling frequency and some of the test parameters are shown in the table below.

Table 1.

Parameter	**Daily**	**Weekly**
Flow rates	X	
Water Temperature	X	
Water pH	X	
Total Dissolved Solids	X	
REDOX	X	
Dissolved Oxygen	X	
Electrical Conductivity	X	
Chemical Oxygen Demand		X
Plant Density		X
Soil Tests		X

RESULTS AND DISCUSSION

Data for this project was collected from June 1, 2002, through September 15, 2002. Common analytical tests were selected to evaluate treatment performance of each system (Table 1). Natural wetland systems were monitored as well; however, for the purposes of this paper only data from the FWS and SSF Systems are presented and discussed.

HYDRAULIC RETENTION TIME (HRT)

HRT refers to the average length of time water is retained in the pilot wetland. It is a measure of contact time for treatment. Mathematically, HRT is the liquid volume of the pilot wetland divided by the flowrate. The pilot wetlands were operated with a target HRT of about 24 hours. Actual HRTs varied due to the drift on the calibration of the pumps, evapotranspiration, and wildlife drinking from the tubs.

HYDROPERIOD

A wetland hydroperiod is influenced by evapotranspiration and the HRT. Evapotranspiration is the net water loss due to the combined forces of evaporation and transpiration. The HRT relates to the time period in which the water remains in a wetland, and therefore, the extent that the wetland system is able to influence the character of the water. Other variables affecting HRT are soil porosity (hydraulic conductivity), water depth, and plant density. When relating wetland treatment performance to the hydroperiod, one should also specify the HRT, water depth, soil chrematistics and plant density.

For the pilot wetlands, flowrates were collected daily from the influent port to each tub with a graduated cylinder and a watch. The void volume of the each wetland was measured as a part of the wetland start-up process. HRT was calculated.

During June and July, the HRT for FWS wetland Tub No. 1 averaged 1.2 days. For FWS Tub No. 2 the HRT was 2.2 days. For FWS Tub No. 3 the HRT was 3 days. For FWS Tub No. 4 the HRT was 5.5 days. The fluctuation in HRT from FWS Tub No. 1 to FWS Tub No. 4 was attributed to the settling of the palettes on which the tubs rest and to wildlife drinking from Tub No.s 3 and 4. Some of the test parameters did not make much sense until the HRT data was reviewed.

TEMPERATURE

Water temperature is important because of its influence on water chemistry and biological activity. Test parameters such as DO, pH, TDS and EC are affected by temperature. Warm water holds less dissolved oxygen than cool water. Plant and microbial growth are strongly influenced by temperature. Typically, warm water has more dissolved salts (EC, TDS) than cool water does. Microbes and plants exist over a wide temperature range. Optimal temperatures for microbial activity and plant growth range from 68-77°F.

Effects of Temperature on Total Dissolved Solids and Electrical Conductivity

The EC and TDS of the influent produced water to the pilot wetlands were compared to the water temperature data. For the RMOTC produced water, relationships were observed among the water temperature, EC and TDS. The warm water held more ions in solution than the cool water. The EC and TDS were proportional. Just as Wyoming hot spring water is typically mineral rich so is RMOTC's produced water.

Temperatures for both FWS and SSF wetlands averaged 69-71°F. The warm temperatures supported good plant growth in each wetland. There was evidence of slight increases in EC and TDS concentrations in the wetlands through mid-June and July. Seasonal ambient temperature increases contributed to increased evapotranspiration rates. As the water evaporated, the concentration of ions increased. This resulted in increased TDS and EC concentrations. When the ambient temperatures decreased in the fall, the evapotranspiration rates decreased and so did the EC and TDS concentrations.

DISSOLVED OXYGEN (DO)

DO measures the amount of free oxygen available in the water. Sufficient DO is essential for good water quality, and to support plant, aquatic and microbial life. Too low or high concentrations of DO can be harmful to aquatic life. Several environmental factors influence DO concentrations in bodies of water. These factors include:

- Volume and velocity of water flowing in the water body.
- Climate/Season.
- The type and number of organisms in the water body.
- Altitude.
- Dissolved or suspended solids.
- Amount of nutrients in the water.
- Organic Compounds.

DO is an important parameter to take into consideration when working with a wetland since the amount of dissolved oxygen in the water is directly related to the population size and community of aerobic bacteria the system can sustain. If more food (organic compounds) is available for the bacteria, then more bacteria will grow and use oxygen; and the DO concentration will drop.

Low DO concentrations can also contribute to the nutrient levels in the water. Since algae and bacteria use nutrients as energy sources, water with high amounts of nutrients can produce algae and bacteria in large quantities. When these algae and bacteria die other microbes decompose them and use up oxygen. This process is called eutrophication. However, nutrients can also lead to increased plant growth. This can lead to high DO concentrations during the day as photosynthesis occurs, and low DO concentrations during the night when photosynthesis stops and plants and animals use the oxygen during respiration. During acclimation of pilot wetlands, it is important to remain consistent in the time of day that DO readings are taken to ensure appropriate comparisons can be made.

The DO levels for both FWS and SSF pilot wetlands ranged between 1.2 to 7.2 mg/L. Ideal DO levels generally range from 3.0 to 5.0 mg/L depending upon the aquatic habitat. The DO levels in the FWS wetlands fell within the optimal range for supporting wetland plants and microbial activity, thereby providing a suitable environment for oxidizing water soluble organic compounds (WSO) in the water column of the pilot wetlands. The SSF wetlands had lower DO levels than the FWS wetlands. The lowest readings were taken from Tub No. 2 with an average of 1.6 mg/L of DO and average water temperature of 79°F. At about 1.0 mg/L of DO oxygen becomes the limiting factor in aerobic treatment.

Overloading the pilot wetlands with nutrients (fertilizer) may have contributed to the low DO concentrations. The fertilizer helped to promote plant growth, but it may also have increased the microbial community's demand for DO.

pH

The measurement of a solution's acidity or alkalinity is called pH. A pH of 7 is considered neutral, anything less than 7 is acidic and anything greater than 7 is alkaline. pH is the –log of the concentration of hydrogen cations present in solution. Wetland soil pH strongly influences microbial activity, plant grow and the thermodynamics of organic and inorganic cycles. The bacteria commonly used to oxidize hydrocarbons require a pH in the 6.5 and 8.5 range.

Factors affecting the pH of RMOTC produced water include:

- Geology and soils of the watershed.
- Concentration of carbon dioxide in the water.

Acidic and alkaline compounds can be released into water from different types of rock and soil. When calcite ($CaCO_3$) is present, carbonates (HCO_3, CO_3^{-2}) can be released, increasing the alkalinity of the water which raises the pH. Indirectly soil pH is related to the EC of the water flowing over the soil. For RMOTC produced water, soil pH correlated to EC of the produced water. The elevated soil pH was attributed to the alkaline or sodic soil conditions.

Carbon dioxide (CO_2) can enter a water body from a variety of sources, including the atmosphere, runoff from land, release from bacteria in the water, and respiration by aquatic organisms. Dissolved CO_2 forms a weak acid. Natural, unpolluted rainwater can be as acidic as pH 5.6 (or lower), because it absorbs CO_2 as it falls through the air. Because plants take in CO_2 during the day and release it during the night, pH levels in water can change from day to night, hence, DO levels are indirectly related to pH levels as well. DO concentration changes are reduced as a wetland matures.

Both FWS and SSF wetlands were well buffered with pH levels ranging from 6.5 to 8.5. Increases in pH were proportional to temperatures, ET, EC and TDS, and inversely proportional to DO and CO_2. The wetland soil and water pH levels supported microbial activity and plant growth.

CHEMICAL OXYGEN DEMAND (COD)

COD is the amount of oxygen required to oxidize organic (and some inorganic) compounds. For this project COD was measured using the dichromate COD method and a spectrophometer.

The COD levels decreased in the SSF wetlands and met the 100 mg/L target discharge. The COD levels increased in the FWS wetland system due to over fertilization and high ET (wildlife drinking from pilot wetlands). The target COD was not met.

Table 2.

Month	Average FWS COD (mg/L)	Average SSF COD (mg/L)
June	86	32
July	166	44
August	56	
September	56	
Comments	Tub No. 3 had an upset (nutrient overland) due to over fertilization. SRB flourished.	No further monitoring after August 1

Monitoring of biochemical oxygen demand (BOD) along with COD would help to determine how much of the COD is readily biodegradable. Flushing with clean water or adding additional topsoil may help stabilize the organic overload in FWS wetland Tub No.s 3 and 4. If the nutrient overload remains persistent water flushing and soil addition will be done in the third year of this project.

ELECTRICAL CONDUCTIVITY (EC)

EC measures a solution's ability to carry an electrical current. Typically, this measurement quantifies the amount of dissolved salts in a solution. EC is useful in determining the variation or change in the salt content of natural and produced waters.

The RMOTC produced water is brackish water. Summer seasonal increases in ambient temperature lead to increased ET and increases in EC in both the FWS and SSF pilot wetlands. To minimize the increases in EC and ET, the HRTs might be shortened. Alternatively the water might be further cooled to drop out additional solids and some salts.

TOTAL DISSOLVED SOLIDS (TDS)

TDS is similar to EC. It is a measure of dissolved solids. Many of those solids contribute to EC. To meet water quality standards for drinking and domestic use, water must not exceed 500 mg/L of TDS. High TDS levels may cause water to be corrosive, salty or have a brackish taste.

Factors influencing TDS include:

- Geology and soil in the watershed.
- Decaying plants and animals.
- Fertilizer runoff.

Some rock and soil release ions very easily when water flows over them. If acidic water flows over rocks containing calcite ($CaCO_3$), such as calcareous shales, calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions will dissolve into the water causing TDS to increase. However, some rocks such as quartz-rich granite, are very resistant to dissolution and don't dissolve easily when water flows over them. As plants and animals decay, dissolved organic particles are released and can contribute to the TDS concentration. Fertilizer can dissolve in water and contribute to TDS.

The FWS wetland treated water is of moderate quality. It is not suitable for human drinking purposes but it can grow native Wyoming plants and is used by wildlife. The SSF wetland treated water is also of moderate quality. The concentration of TDS in the SSF wetland is lower than the FWS wetland water because evaporation is minimized with the subsurface flow. This is no water exposed to air. The removal of the TDS is attributed to solids and ion deposition onto the pea-gravel in the wetland.

MICROBIAL ACTIVITY

In the pilot wetlands the bacteria consume the water soluble organic compounds (WSO) such as hydrocarbons and COD. Bacteria contain unique enzymes which allow for the metabolism of the WSO. Degradation of WSO by aerobic bacteria produces metabolites which are incorporated into cell mass, used as energy, and/or are converted to nontoxic biological wastes. WSO is used as an energy or carbon source by other bacteria, fungi, and hydrophytes.

The Biological Activity Reaction Test (BART) work was done using the manufacturer's instructions and previous experience with such testing. These are rapid tests that semi-quantitatively determine the relative presence or absence of microbial populations. Disappearance of differential media (food) within the BART tube indicates the presence or absence of that population of microorganisms in the sample. The time required for the indicator to confirm the presence is proportional to the number of microorganisms present in the sample. The advantages of BARTs are that they are cost effective, require only limited amounts of training and are simple to interpret. However, the method is not as rigorous as a full microbiological screen.

Water and sediment column samples were collected and evaluated for microbial activity. The results of the BART evaluation indicated that there were significant populations of microorganisms capable of metabolizing organic and inorganic compounds throughout the FWS pilot wetland system.

Table 3.

Month	**FWS Soil**	**FWS Water**
SRB		
August	1,000 CFU/mL	10,000 CFU/mL
September	1,000 CFU/mL	10,000 CFU/mL
Comments	Aggressive	Aggressive
	FWS Soil	**FWS Water**
HAB		
August	100 CFU/mL	1000 CFU/mL
September	1000 CFU/mL	1000 CFU/mL
Comments	Not aggressive	Not aggressive.

BARTs provide a "snapshot" of the microbial flora in the water and sediment columns. The pilot wetland systems supported at least two types major of groups of microorganisms: heterotrophic bacteria and sulfur reducing bacteria. The concentration and location of specific populations were consistent with what was seen with the water chemistry.

Heterotrophic Bacteria

Heterotrophic bacteria (HAB) were present in both the soil and water columns. Heterotrophs metabolize BOD_5 and hydrocarbons under aerobic conditions. The presence of HABs indicated that sufficient energy is available for aerobic degradation of organic compounds in the both wetland soils and water. Comparatively, the HAB population was not as active as the sulfur utilizing organisms discussed in the following section.

Sulfate Reducing Bacteria

Sulfate reducing bacteria (SRB) were present throughout the FWS pilot wetland soils and waters. The water chemistry suggested that conditions were well suited for these organisms to thrive in all parts of the wetlands. However, the highest SRB activity was found in FWS pilot wetland Tub No. 3. The SRB BARTs for Tub No. 3 developed a positive response within two days. The indication was a black slime ring growth in the BART tube. The high concentration of sulfate in the produced water ensured that there was a ready supply of substrate for the SRBs.

REDOX (OXIDATION-REDUCTION POTENTIAL)

REDOX is the oxidation-reduction potential. REDOX determines if a wetland can oxidize or reduce a compound. The combination of pH and REDOX is a predictor, if it is thermodynamically possible to degrade (oxidize or reduce) a compound. In general, a positive REDOX oxidizes, while a negative REDOX reduces.

In late June and early July visual observations suggested the presence of SRB in FWS wetland Tub No. 3 and 4. The water became opaque and had a sewer-like odor. REDOX data confirmed that the conditions were suitable for SRBs to be present. When the REDOX is between –100 and –400 mV and a carbon is present, SRB can convert sulfate into hydrogen sulfide.

Table 4.

Month	**Average FWS REDOX (mV)**	**Average SSF REDOX (mV)**
June	-23	103
July	-131	98
August	-124	31
September	-132	71
Comments	Sulfate Reduction	Oxidation

Based on BART and REDOX data, the FWS pilot wetlands had HAB and SRB present in wetland water and soils. Both oxidation and reduction were occurring. The SRB showed greater activity than the HAB. The over application of fertilizer and the decaying plant materials from the first year of the pilot work supplied the SRB with an abundance of sulfate and carbon.

SOIL NUTRIENTS

Nutrient levels are critical in biological treatment systems such as wetlands. The levels of essential nutrients control how well the plants (and microbes) grow. For optimum growth, plants require a certain ratio of specific nutrients. Typically a ratio of C:N:P of 100:5:1 is suitable for most biological treatment systems. If this nutrient ratio becomes unbalanced plant growth becomes adversely affected.

Nutrient levels are also important to the microbial population of the system. An unbalanced ratio can adversely affect the growth rate of preferred microbes for waste treatment. An unbalanced ratio can change the composition of the microbial population and generate undesirable and smelly metabolites from anaerobic pathways with sulfur and nitrogen containing compounds.

Some of the factors influencing nutrient availability are:

- Soil pH.
- REDOX.
- Presence in relation to other nutrients.
- Ion exchange.
- Organic matter.

Nitrogen deficiency symptoms in plants are initially characterized by a general yellowing (chlorosis) of older leaves. Frequently the yellow leaves turn brown (necrosis) and die. Young leaves tend to be green and yellow as they mature. Leaf veins stay green while the rest of the leaf turns yellow.

Soil analysis determined that the FWS system was nitrate limited and overloaded with potassium. This unbalanced nutrient ratio was most noticeable in FWS wetland Tub No. 3. This wetland tub had the highest number of all the wetland tubs of salt-marsh bulrush with an abnormal yellow-green color. This was attributed to the elevated concentration of potassium. This nutrient imbalance, along with the elevated pH, contributed to reduced numbers of softstem bulrush and to the lower overall height of the plants.

PLANT DENSITY AND GROWTH RATES

Hydrophytes (wetland plants) serve as storage sites for carbon and nutrients and play a role in the movement of gasses to and from the hydrosoil (wetland soils). Oxygen is transported from the air through the plant into the rhizome (root zone). This ensures that aerobic respiration can be maintained by the non-photosynthetic portion of the hydrophyte's tissues that are buried in the anoxic hydrosoil. Some of this oxygen becomes available to the microbes associated with the rhizome. This oxygen tends to counteract the toxic to aerobes end-products of anaerobic bacterial respiration such as hydrogen sulfide.

NPR-3 contains two distinctive types of natural wetlands. These are riparian zone wetlands that are fed by surface waters and playa lake wetlands that are fed by snow melt, rain runoff and evaporation cycles. The free-water surface (FWS) pilot wetlands simulate the riparian zone wetlands. The riparian zone and playa lake wetlands contain emergent hydrophytes: softstem bulrush (*Scirpus validus*), dwarf spikerush (*Scirpus americanus)*, broadleaf cattail (*Typha latifolia L*.) and the salt-marsh bulrush (*Scirpus robustus*). The plants are adapted to saturated soils and are characterized by extensive underground rhizome or bulbous anatomy. The playa lake wetlands have higher concentrations of the salt-tolerant plants than do the riparian zone wetlands.

The FWS and SSF pilot wetland plants are native to the site and received the same water source. They were harvested onsite in the previous year and transplanted into pilot wetlands. After two years, the plant communities appear to be well acclimated. Plant stem density has increased twofold. Plant growth began in the pilot units when the soil temperature reached 50-55°F. Plants begin to suffer heat stress when ambient temperatures reached around 100°F. We did observe some signs of chlorosis and necrosis in some of the pilot wetlands. The signs were attributed to limited nitrogen in the soil and potassium overload attributed to a fertilizer addition in May.

SUMMARY

Treatment wetland performance is influenced by the climate much as natural wetlands are influenced. For this Wyoming wetland study, the main influence was temperature. The temperature regulated plant growth, microbial activity and the amount of dissolved solids and salts (TDS and EC). Some nutrient ratios were unbalanced. Corrective measures will be attempted in the third year of this project to improve wetland performance.

Both FWS and SSF wetlands can treat the RMOTC produced water and meet NPR-3 discharge limits. The wetland treated water provides riparian wetland habitat for wildlife. In the dry climate of Wyoming, water reuse is highly beneficial.

As a result of the wetland treatment of the RMOTC produced water, we found that:

- Overall water quality was improved.
- pH was within target range for microbial activity and plant growth.
- DO was appropriate for aerobic activity and plant growth.
- TDS was similar to background water quality.
- Good plant growth was observed in all pilot wetlands as plant density increased twofold in the second year as compared to the first year.
- FWS wetland biological functions were similar to the natural riparian zone wetlands.
- TDS and EC were similar for the RMOTC produced water.
- Deposition of salts (TDS, EC) onto the wetland soil created alkaline environment and elevated pH levels.

IMPROVEMENTS

Future Work

The third year of the wetland pilot will collect kinetic data for upgrade of the NRP-3 treatment wetland. Simulated upsets are planned to test wetland recovery strategies.

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