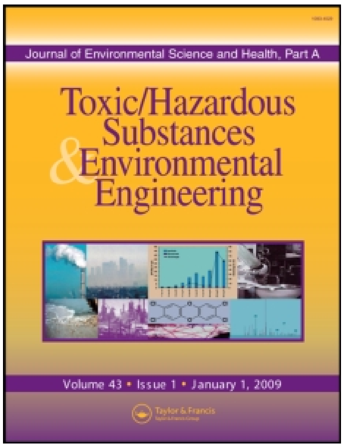

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Preliminary water quality assessment of Spunky Bottoms restored wetland

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The approximately 1200-acre "Spunky Bottoms" wetland in Southern Illinois has been undergoing restoration to conditions prior to levying of the Illinois River and draining of adjacent floodplain for intensive agriculture (*circa* 1900). As part of a long-term water quality impact assessment of this restoration project, baseline water quality monitoring was conducted soon after restoration began. During this baseline/preliminary assessment, water samples were taken every 2–4 weeks from 10 sampling wells and seven surface water sites throughout the wetlands area for a period of 18 months. Measured parameters include nutrients (nitrate (NO_3^-) and phosphate (PO_4^{3-}), cations and anions (SO_4^{2-}, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}) commonly found in surface and well water, trace metals (Al, Cd, Cu, Fe, Mn, Ni, Pb, Se, Zn), total dissolved solids (TDS), pH, and trace organics (triazine herbicides and their metabolites). In general, highest concentrations of ions were found in the southwest and northeast perimeter of the wetland area for both surface and ground water samples. Primarily low concentrations of heavy metals and organic compounds were found throughout the wetland sampling area. Distribution of NO_3^--N suggests that this restored wetland, even at its infant age, may still contribute to biogeochemical (particularly N) element cycling. Continued monitoring and further research is necessary to determine long-term specific contribution of restored wetland to biogeochemical cycles.

Keywords: Restored wetland, nutrients, cations and anions, trace metals, trace organics.

Introduction

Preservation of aquatic wetland ecosystems is vital to protect wildlife habitats, protect water quality, and provide for aesthetically pleasing environmental sanctuaries for recreational purposes. Aquatic wetland ecosystems are being lost or degraded at a dramatic rate throughout the world. Wetland area loss in the United States since European settlement is roughly estimated near 50%.[1,2] Installation of drain tiles and river levying to facilitate agricultural land use practices has been a primary contributor to wetland loss in many U.S. states, including Illinois since *circa* 1900.[1–3] Illinois has shown a significant loss of aquatic wetlands to agriculture and residential land use since *circa* 1800. Approximately 3–4% (500,000 acres) of the state of Illinois was designated as wetland in 1990.

Surface and groundwater quality is important both nationally[4,5] and in Illinois.[6] Aquatic wetlands protect water quality by serving as a buffer system to slow water runoff from storm events and allow infiltration into soils, percolation into soil-groundwater systems, and allow time for water purification through natural physical, chemical, and biological process.[7–11] Due to heavy agriculture land use, stormwater runoff in Illinois tends to have high nutrients such as nitrate and phosphorus loading,[6] this not only leads to eutrophication, depletion of aquatic dissolved oxygen and fish kills, but also present public health concerns when nitrate level in the drinking water supplies (particularly from surface water source) exceeds safe level and leads to "methemoglobinemia" or "blue baby syndrome"—a potential fetal condition caused by lack of oxygen supply in blood among babies when nitrate metabolites interacts with hemoglobin.[12] Many studies have shown wetlands particularly constructed wetlands (human-made, engineered wetland areas) are especially efficient in the removal, and beneficial reuse, of nitrogen (N) and phosphorous (P) compounds with N removal of 55%–93%[13–16] and P removal of 42%–97%.[17–21]

In addition, natural aquatic systems including ponds and constructed wetland have been shown to be able to remove and detoxify some heavy metals very successfully.[22–24] Wetland plants as well as microbial consortium incorporate such toxic metals as cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), mercury (Hg), arsenic (As) and etc, into their tissues.[25–27]

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A majority of water purification experimental studies have focused on engineered wetland systems while relatively little research has been published on water quality enhancement, particularly long-term enhancement for restored wetlands with few exceptions, except for the on-going Florida Everglade restoration project.[28,29] In addition, there has been some criticism of the ability of restored wetlands to mimic natural wetlands, including failure to attract targeted endangered waterfowl species.[30]

Much of the flood plain adjacent to the Illinois River was levied and drained for intensive agricultural use by pumping water collected in the wetland into the Illinois River (*circa* 1900). The rich alluvial soils allowed highly productive agriculture due to the accumulation of nutrients during thousands of years of natural flood cycles and resulting silt deposition. Spunky Bottoms wetland in Southern Illinois was purchased by The Nature Conservancy in 1998 with a goal of restoration to more natural conditions prior to intensive agricultural use. This approximately 2,000-acre site (containing approximately 1200-acres of wetland) in Southern Illinois has been undergoing restoration in cooperation with The Wetlands Initiative, funded by a grant from The National Fish and Wildlife Foundation.

Restoration efforts included increasing the level of water in the area by reducing the amount of water being pumped out, more than 7,500 hardwood trees and hundreds of pounds of prairie seed have been planted, prairie cordgrass and sedges have been transplanted and efforts have been made to control non-native, invasive species. Water flow through Spunky Bottoms wetland is primarily from northwest to southeast, entering the wetland through runoff from the upland topography to the west (Fig. 1). Water then flows through drainage ditches (North Market, Main Road, and South Cox) to the pump house. Excess water collected is then pumped over the levy into the Illinois River to facilitate agricultural land use. Sources of water contaminants are primarily non-point sources due to adjacent agricultural land use.

To assess the long-term water quality impact of this restoration project, baseline water quality monitoring started soon after restoration began for a period of 18 months. Water quality parameters monitored included nutrients (NO_3^- and PO_4^{3-}), anions and cations (sulfate (SO_4^{2-}), chloride (Cl^-), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+})) commonly found in surface and ground water, trace metals (aluminum (Al), Cd, Cu, iron (Fe), manganese (Mn), Ni, Pb, selenium (Se),

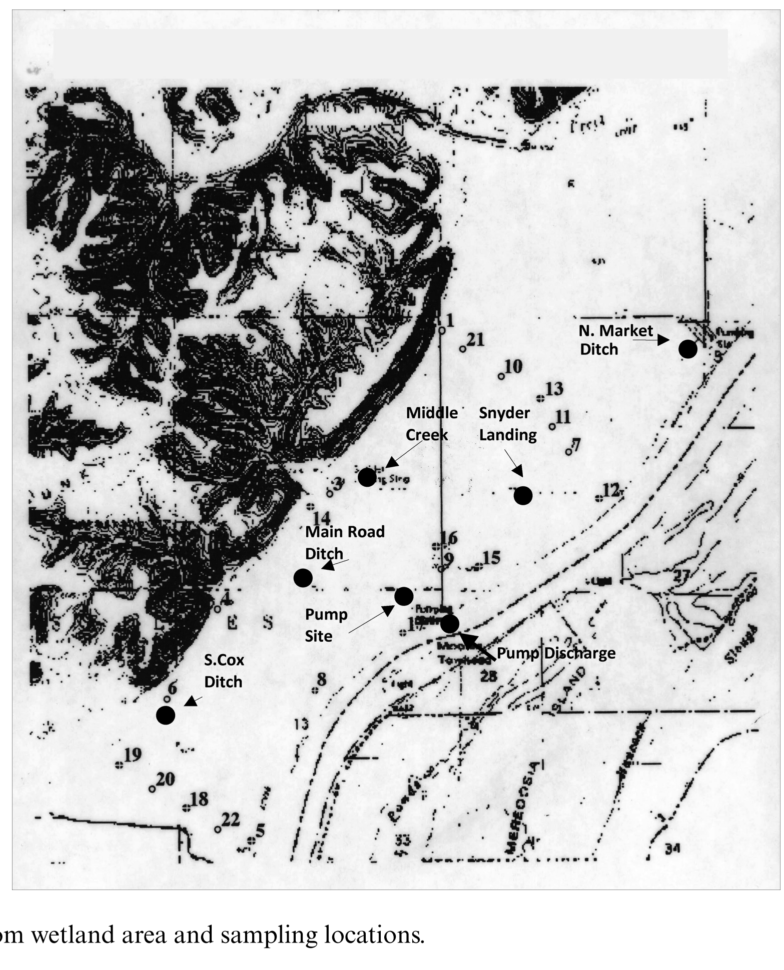

Fig. 1. Map of Spunky Bottom wetland area and sampling locations.

Zn), total dissolved solids (TDS), pH, and trace organics. The results of this baseline water quality monitoring are presented in this paper. Distribution of nutrients and other pollutants concentrations and implication of these in terms of water quality enhancement in a restored wetland at its very early stage are discussed.

Materials and methods

Collection of water samples

Water samples were collected every 2–4 weeks from ten sampling wells and seven surface water sites throughout the wetlands area. The surface sites included four drainage ditches, a tributary (Middle Creek), the collection pond where the water was pumped into the river, and the discharge site. Four surface sites were deep enough to collect top and bottom samples (when the water depth was greater than three feet). A map of the area with sampling locations is shown in Figure 1.

Water quality analysis

Several instrumental techniques were employed for the analyses including ion chromatography (anions and cations), inductively coupled plasma (ICP) atomic emission spectroscopy (trace metals), spectrophotometry (phosphate), potentiometry using an ion selective electrode (nitrate), and gas chromatography/mass spectrometry (trace organics). Specific parameters and methods are listed in Table 1.

Samples were received within 24 hours of collection. The samples were filtered through a 43 micrometer (μm) filter then stored at 4°C until analysis. Total dissolved solids, nitrates by ion selective electrode, and phosphate by spectrophotometry were analyzed by methods described in Standard Methods for the Examination of Water and Wastewater.[31] Since nitrates were analyzed by two different methods (ion chromatography and ion selective electrode) in many samples, the average of the two methods was reported when two values were available.

Table 1. Summary of water quality parameters monitored and the methods employed.

Parameters	*Methods*
NO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}	Ion chromatography
Al, Cd, Cu, Fe, Mn, Ni, Pb, Se, Zn	ICP
PO_4^{3-}	Spectrophotometry
NO_3^-	Ion selective electrode
pH	pH electrode
Total dissolved solids (TDS)	Gravimetric
Trace organics (triazine and their metabolites)	GC/MS

Anion and cation analysis

Anions and cations were measured by a Dionex DX500 ion chromatographic system (Dionex Corporation, Sunnyvale, CA) containing a GP40 gradient pump and an ED40 electrochemical detector. Anions were separated on an Ion Pac AS14 column (4 mm × 250 mm) and measured by suppressed conductivity using an ASRS-Ultra (4 mm) suppression column. The mobile phase consisted of 3.5 mM Na_2CO_3/1 mM $NaHCO_3$ at 1.0 mL/min. Cations were separated on an Ion Pac CS12A column (4 mm × 250 mm) and measured by suppressed conductivity using a CSRS-Ultra (4 mm) suppression column. The mobile phase consisted of 22 mM H_2SO_4 at 1.0 mL/min. Data collected were analyzed using PeakNet chromatography software.

Trace metal analysis

Trace metals were analyzed on a Thermo Jarrell Ash IRIS inductively coupled plasma (ICP) atomic emission spectrometer (Thermo Fisher Scientific, Waltham, MA). Specific metals and wavelengths are listed in Table 2. When two wavelengths were used, the average was reported.

Trace organic analysis

For organic compounds analysis, this study focused on commonly used herbicides in Illinois—triazine herbicides and their metabolites. Water samples were analyzed for trace organics using a combination of solid phase microextraction (SPME) and gas chromatography/mass spectrometry (GC/MS). The SPME microfiber (polydimethylsiloxane/divinylbenzene) was first immersed in 5 mL of the water sample for 10– 30 minutes to allow adsorption of the organic compounds in the water on to the fiber. The organic compounds were desorbed from the fiber by inserting the fiber assembly into the injection port of a model 1800B GCD Hewlett-Packard GC/MS (Agilent Corporation, Santa Clara, CA) for 2 minutes at 250°C. After desorption, the organics were separated on a Hewlett Packard HP5

Table 2. Metals analyzed and wavelengths used for ICP analysis.

Metal	*Wavelengths, nm*
Aluminum	309.3, 396.2
Cadmium	214.4, 228.8
Copper	227.3
Iron	238.2, 259.9
Lead	220.3, 261.4
Manganese	259.3, 260.5
Nickel	221.6, 231.6
Tin	189.9
Zinc	213.9

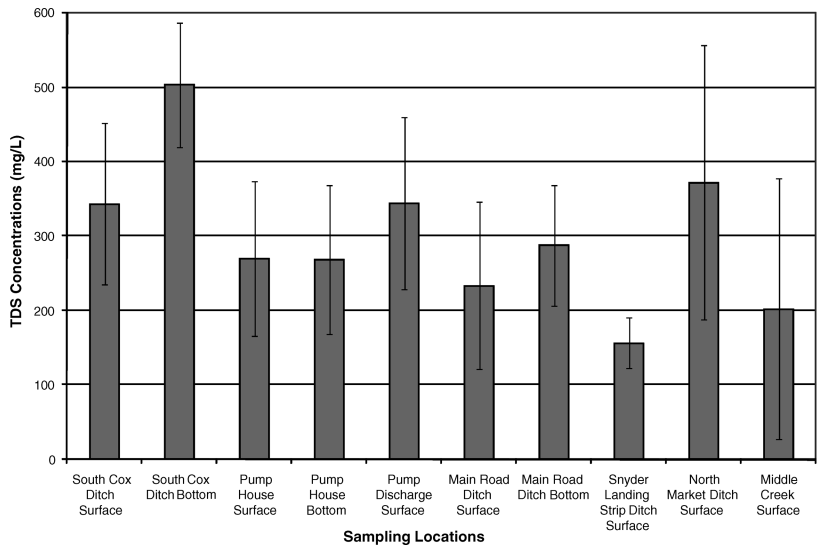

Fig. 2. Average TDS concentrations in surface water sites (error bars represent one standard deviation).

cross-linked 5% phenylmethylsiloxane capillary column (30 meters × 0.15 mm id × 0.25 micron film thickness) at an initial temperature of 60°C for two minutes then a temperature program from 60°C to 200°C at 60°C/minute, isothermal at 200°C for 1 minute, 200°C to 280°C at 10°C/minute, and isothermal at 280°C for 3 minutes.

Statistical data analysis

Water quality data were subjected to one-way analysis of variance (ANOVA) with Statistical Packet for Social Science (SPSS) software version 14.1. Significance was determined and probability (p) levels reported for ANOVA results. Sampling location was identified as independent variables. Water quality parameters were identified as dependent variables.

Results and discussions

Distribution of TDS, Ca^{2+}, Mg^{2+} and other ions

Surface water samples. Distribution of TDS, Ca^{2+} and Mg^{2+} in the surface water of the sampling area is presented in Figures 2, 3 and 4. As described in the introduction, water flow through Spunky Bottoms wetland is primarily from northwest to southeast, entering the wetland through runoff from the upland topography to

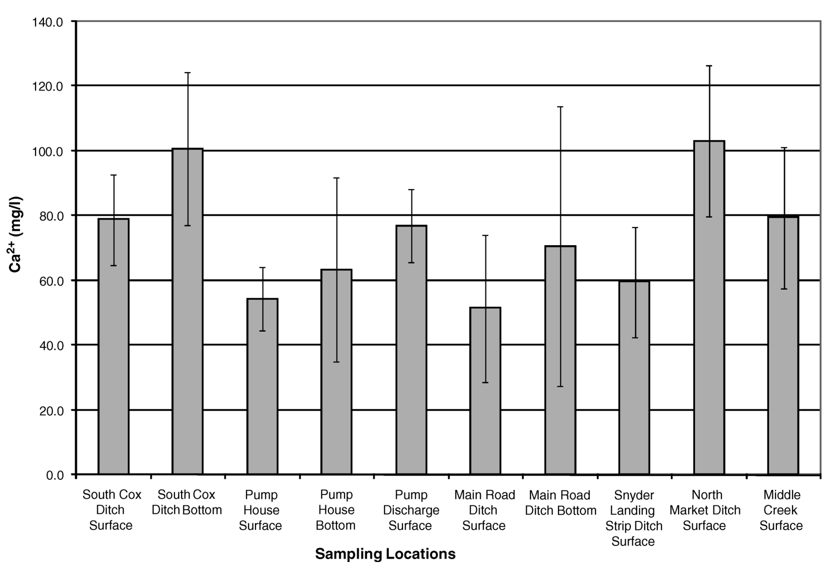

Fig. 3. Average Ca^{2+} concentrations in surface water Sites (error bars represent one standard deviation).

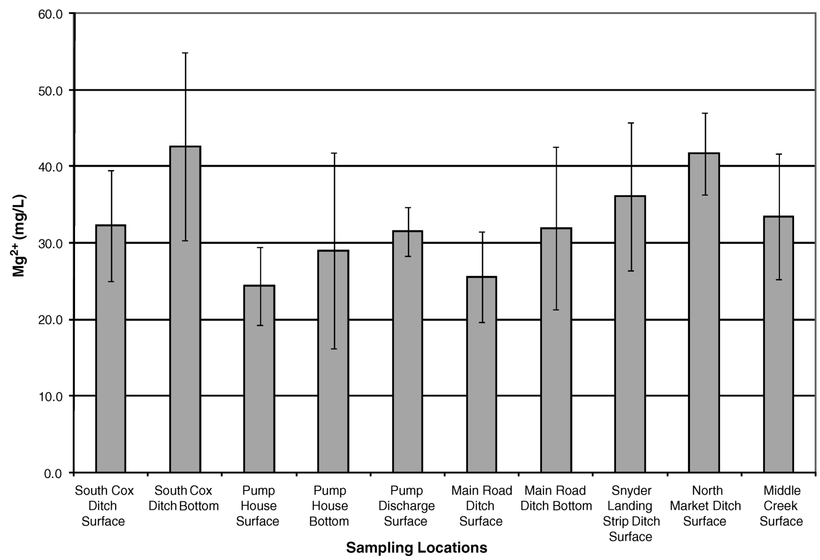

Fig. 4. Average Mg^{2+} concentrations in surface water sites (error bars represent one standard deviation).

the northwest. Water then flows through drainage ditches (North Market, Main Road, and South Cox) to the pump house site. Excess water collected is then pumped over the levy into the Illinois River to facilitate agricultural land use (Fig. 1). Considering this flow pattern, it is not surprising to observe highest concentrations of TDS, Ca^{2+} and Mg^{2+} found in the southwest (South Cox Ditch) and northeast (N. Market Ditch) perimeter of the wetland area where water samples collected may have been stagnant at the sites for extend period of time so Ca^{2+}, Mg^{2+} and other minerals from the soil were dissolved in water.

On the other hand, water samples collected from the central areas had lower mineral contents since water had been actively flowing through these areas resulting less contact time with soil. It also worth noting that Ca^{2+}, Mg^{2+} and TDS level of water sample collected at pump discharge site (into the Illinois River) were higher than that of pump site. One would expect the water quality at the pump discharge site should be about the same as that of pump site; the observed difference may be due to accumulation of ions from evaporation. Water was pumped into the discharge site only when the water level at the pump site was sufficiently high. During restoration, water levels were allowed to slowly rise after planting with native vegetation.

For most sites where both top and bottom samples were available, significantly higher concentrations of Ca^{2+}, Mg^{2+} and TDS were observed among bottom samples. This is probably due to the fact that bottom water is in close proximity to soil which is rich in minerals.

Statistical analysis using one-way ANOVA indicated the observed spatial differences in TDS and Mg^{2+}were statistically significant at a significance level of 0.05 (P-values = 0.039 and 0.0054, respectively, for TDS and Mg^{2+}). Differences in Ca^{2+} level among different sampling locations were not found to be statistically significant at this level, but worth noting (P-value = 0.067).

Distribution of other ions (Na^+, K^+, Cl^-, SO_4^{2-}, etc) in the surface water samples along with results of one-way ANOVA tests are presented in Table 3. It is interesting to note that highest concentrations of K^+, Na^+, $SO_4^{2-}$and Cl^-concentrations were found at the pump discharge site, further supporting the hypothesis that evaporative loss of water may have occurred primarily at the pump discharge site.

Groundwater samples. Distribution of TDS and all ions analyzed in groundwater samples along with results of one-way ANOVA tests are presented in Table 4. As indicated by P-values, most ions except K^+ (P-value = 0.398) varied significantly among various locations in the wetland. In general, higher concentrations of ions were found in the northeast and southwest perimeter of the wetland (well locations GW-5, GW-13 and GW-18).

Distribution of nutrients (N and P)

Figures 5 and 6 present the distribution of NO_3^--N in the surface and groundwater samples of the wetland area. As indicated in Figure 5, higher concentrations of NO_3^--N in surface water were observed at the perimeter of the wetland (particularly at South Cox ditch). It is also very interesting to note that NO_3^--N concentrations (top and bottom) at the pump house site were the second lowest concentrations. Results from the ANOVA test indicated the differences between pump house site and other sites were statistically significant (P-value = 0.0043). Considering the water flow pattern, the above observations were evidence supporting that reduction of nitrate occurred as water passed through the

Table 3. Distribution of chloride, sulfate, sodium and potassium concentrations in the surface water samples of Spunky Bottoms wetland.

Sample locations	$Cl^{-}\ \mu g/L$ (Avg. ± std dev)	$SO_4^{2-}\ \mu g/L$ (Avg. ± std dev)	$Na^{+}\ \mu g/L$ (Avg. ± std dev)	$K^{+}\ \mu g/L$ (Avg. ± std dev)
South Cox Ditch surface	17.10 ± 8.0	33.0 ± 9.7	10.9 ± 5.2	6.5 ± 7.2
South Cox Ditch bottom	18.28 ± 7.8	43.4 ± 16.9	10.8 ± 4.1	4.5 ± 3.2
Pump House surface	14.23 ± 4.6	25.1 ± 8.5	10.0 ± 3.5	4.8 ± 2.3
Pump House bottom	15.92 ± 9.7	29.0 ± 14.0	12.5 ± 7.0	4.8 ± 2.4
Pump Discharge surface	41.81 ± 10.3	58.0 ± 10.1	42.2 ± 22.2	29.4 ± 54.9
Main Road Ditch surface	23.53 ± 26.0	26.3 ± 9.0	10.5 ± 4.2	4.3 ± 1.2
Main Road Ditch bottom	17.40 ± 15.9	38.2 ± 15.1	11.3 ± 8.0	5.6 ± 3.7
Snyder Landing Strip Ditch surface	17.27 ± 17.0	23.9 ± 9.4	13.5 ± 11.6	4.5 ± 3.0
North Market Ditch surface	11.97 ± 0.9	23.5 ± 11.0	7.9 ± 1.3	4.4 ± 1.6
Middle Creek surface	5.51 ± 1.0	27.9 ± 2.1	11.7 ± 2.5	2.7 ± 1.3
P-value (ANOVA test)	0.0014	0.013	0.719	0.117

Table 4. Distribution of TDS, calcium, magnesium, chloride, sulfate, sodium and potassium concentrations in the ground water samples of Spunky Bottoms wetland.

	mg/L (Avg. ± Std. Dev)						
Sample locations	*TDS*	Ca^{2+}	Mg^{2+}	Cl^{-}	SO_4^{2-}	Na^{+}	K^{+}
GW-5	501.8 ± 243.9	55.3 ± 14.9	21.2 ± 8.6	31.2 ± 15.4	65.1 ± 23.2	25.7 ± 5.3	3.3 ± 2.5
GW-8	270.0 ± 28.3	58.9 ± 8.9	21.7 ± 5.5	16.2 ± 0.7	37.8 ± 5.0	16.5 ± 4.2	2.3 ± 2.4
GW-12	174.0 ± 66.3	103.4 ± 7.0	32.9 ± 2.8	26.0 ± 6.8	36.3 ± 7.0	17.5 ± 1.2	3.6 ± 2.4
GW-13	264.9 ± 144.1	64.1 ± 13.1	24.7 ± 6.4	42.5 ± 21.1	49.4 ± 9.0	14.7 ± 7.0	3.0 ± 2.3
GW-15	281.0 ± 193.7	67.7 ± 44.0	21.0 ± 15.6	12.6 ± 5.4	24.2 ± 9.4	18.3 ± 8.7	2.9 ± 1.9
GW-16	160.7 ± 66.6	36.2 ± 8.0	15.3 ± 4.0	15.0 ± 4.7	26.4 ± 2.4	10.8 ± 0.9	3.5 ± 2.3
GW-18	383.3 ± 146.7	112.3 ± 20.8	35.8 ± 7.2	16.1 ± 4.2	42.9 ± 8.3	10.9 ± 2.5	0.7 ± 1.0
GW-19	164.0 ± 82.0	82.1 ± 12.7	29.6 ± 4.3	10.6 ± 2.4	24.0 ± 5.2	9.1 ± 3.0	1.3 ± 1.0
P-value (ANOVA)	0.055	0.000043	0.0052	0.00024	0.000098	0.00001	0.398

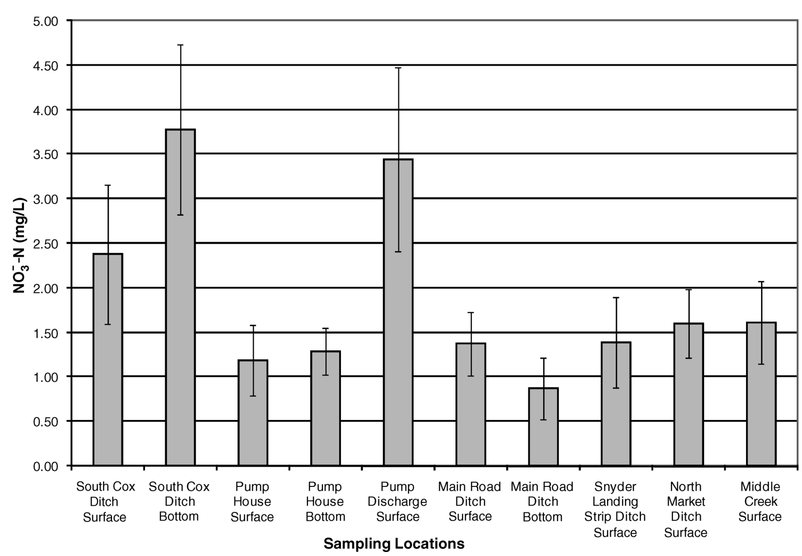

Fig. 5. Average NO_3^--N concentrations in surface water sites (error bars represent one standard deviation).

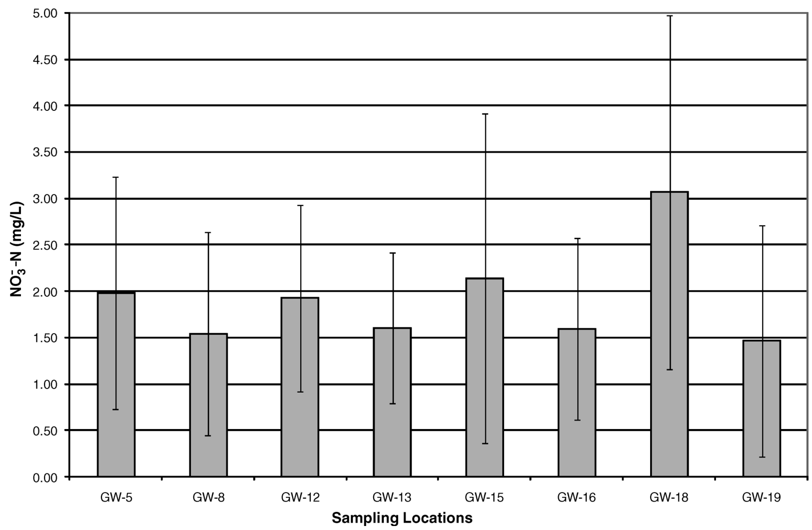

Fig. 6. Average NO_3^--N concentrations in Spunky Bottom well water Sites (error bars represent one standard deviation).

restored wetland. The highest concentrations of NO_3^--N were observed at the pump discharge site into the Illinois River. This may be due to accumulation of nitrates from evaporation since water was pumped into the discharge site only when the water level at the pump site was sufficiently high. This was also observed with other ions (Na^+, K^+, Cl^-, SO_4^{2-}) as discussed in the previous section.

As presented in Figure 6, NO_3^--N concentrations in the groundwater samples varied significantly over time. The highest concentration was observed at well site GW-18 (southwest corner of the wetland) while concentrations at other sites are very close to each other. One-way ANOVA test indicated that observed differences from various sites are not statistically significant (P-value = 0.455). It is not anticipated that restored wetland in its early stages would have any impact on groundwater nitrate removal.

Phosphate was analyzed by both ion chromatography and spectrophotometry; however, in most samples, concentrations were at or below the minimum detection limit (MDL) of 100 μg/L for both methods. Thus, no further attempt was made to analyze these data.

Distribution of heavy metals

Table 5 contains data from trace elements obtained by ICP. Only those elements with measured concentrations above

Table 5. Detectable heavy metal distribution in Spunky Bottom wetland sampling area.

	mg/L (Avg. ± Std. Dev)			
Sample locations	*Al*	*Fe*	*Ni*	*Pb*
GW-5	0.122 ± 0.014	0.009 ± 0.002	0.122 ± 0.048	0.021 ± 0.007
GW-8	0.121, NA	0.010, NA	0.133, NA	NA
GW-12	0.140 ± 0.003	0.010 ± 0	0.173 ± 0.016	0.028 ± 0.010
GW-13	0.142 ± 0.007	0.088 ± 0.131	0.168 ± 0.035	0.013 ± 0.008
GW-15	0.315 ± 0.205	0.058 ± 0.068	0.119 ± 0.043	0.022 ± 0.016
GW-16	0.113 ± 0.037	0.028 ± 0.02	0.111 ± 0.053	0.010 ± 0
GW-18	0.261 ± 0.086	0.042 ± 0.044	0.172 ± 0.026	0.023 ± 0.009
GW-19	1.490 ± 0.180	0.553 ± 0.125	0.0147 ± 0.024	0.01 ± 0
South Cox Ditch surface	0.192 ± 0.136	0.041 ± 0.059	0.059 ± 0.041	0.014 ± 0.007
South Cox Ditch bottom	0.585 ± 0.424	0.158 ± 0.155	0.106 ± 0.073	0.011 ± 0.001
Pump House surface	0.355 ± 0.389	0.165 ± 0.246	0.065 ± 0.027	0.018 ± 0.012
Pump House bottom	0.727 ± 0.741	0.424 ± 0.471	0.117 ± 0.037	0.007 ± 0.005
Pump Discharge surface	0.140, NA	0.016, NA	0.136, NA	0.01, NA
Main Road Ditch surface	0.234 ± 0.060	0.064 ± 0.070	0.134 ± 0.111	0.025 ± 0.022
Main Road Ditch bottom	0.267 ± 0.104	0.084 ± 0.074	0.084 ± 0.026	0.011 ± 0.002
North Market Ditch surface	0.136 ± 0.049	0.015 ± 0.009	0.050 ± 0.014	0.016, NA
North Market Ditch bottom	0.132 ± 0.058	0.018 ± 0.005	0.111 ± 0.078	0.012, NA

NA–only one sample was collected, therefore standard deviation was not available.

the MDL of approximately 10 μg/L are listed. Cd, Cu, Mn, Se, Zn were not found in any of the samples above the MDL. The highest concentrations of Al and Fe were found in well GW-19 located in the southwest corner of the sampling area. No trends were apparent with Ni or Pb. Lead concentration varied from the MDL of approximately 10 μg/L to about 40 μg/L.

Organic compounds

This study focused on analyses of samples for triazine herbicides commonly used in Illinois and their metabolites. Several samples taken from well and surface sites throughout the area were analyzed and only ubiquitous phthalates were found in some samples. Triazine herbicides and their metabolites were below the MDL of 10 μg/L.

Curent status of Spunky Bottom wetlands

In the relatively few years since restoration began, this land now is a thriving wetland landscape that gets richer in plant and animal life every year. The replanted hardwood trees and upland prairie species are thriving, as are other wetland plant species that have re-emerged from a seedbank that survived during the decades the preserve was farmed. Every summer thousands of American lotus bloom on the restored wetlands. Waterfowl are returning to the preserve in impressive numbers—peaks of more than 16,000 ducks and geese.[32] The restoration has also attracted several uncommon species rarely seen in the local area, including river otters, and American and least bitterns.

Conclusions

Spunky Bottoms wetland in Southern Illinois has been undergoing restoration to more natural conditions prior to intensive agricultural use. Restoration efforts included increasing the level of water in the area by reducing the amount of water being pumped out, planting of hardwood trees and prairie grass and controlling non-native, invasive species. Water flow through Spunky Bottoms wetland is primarily from northwest to southeast, entering the wetland through runoff from the upland topography to the northwest. Water then flows through drainage ditches to the pump house site. Excess water collected is then pumped over the levy into the Illinois River to facilitate agricultural land use. In general, highest concentrations of ions were found in the southwest and northeast perimeter of the wetland area for both surface and groundwater samples. Lower concentrations of heavy metals and organic compounds were found throughout the wetland sampling area.

Higher concentrations of NO_3^--N in surface water were also observed at the perimeter of the wetland particularly at the southwest corner. It is also interesting to note that NO_3^--N concentrations in surface water samples at the pump house site were the second lowest concentrations observed. Considering the water flow pattern, the above observations are evidence supporting that reduction of nitrate occurred as surface water flow through the restored wetland even at its early stage. No significant nitrate reduction was observed in groundwater samples. This is somewhat anticipated since groundwater nitrate removal probably will not occur until extended period of time following restoration.

Phosphate concentrations in most samples were at or below the MDL of 100 μg/L. These results suggest that restored wetland, even at its infant age, may still contribute to biogeochemical (particularly N) element cycling. This is also supported by the diverse microbial communities and population identified in this wetland using phospholipid fatty acid and 16S ribosomal DNA polymerase chain reaction amplification-denaturing gradient gel electrophoresis (PLFA/DGGE) techniques.[33] Continued monitoring and further research is necessary to determine long-term specific contribution of restored wetland to biogeochemical cycles.

Acknowledgments

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