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Assessing hydrogeochemical heterogeneity in natural and constructed wetlands *

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Abstract. While “water quality function” is cited as an important wetland function to design for and preserve, we demonstrate that the scale at which hydrochemical samples are collected can significantly influence interpretations of biogeochemical processes in wetlands. Subsurface, chemical profiles for both nutrients and major ions were determined at a site in southwestern Wisconsin that contained areas of both natural and constructed wetlands. Sampling was conducted on three different scales: (1) a large scale (3 m between sampling points), (2) an intermediate scale (0.15 m between sampling points), and (3) a small scale (1.5 cm between sampling points). In most cases, significant vertical heterogeneity was observed at the 0.15 m scale, which was much larger than previously reported for freshwater wetlands and not detected by sampling water table wells screened over the same interval. However, profiles of ammonia and total phosphorus showed tenfold changes in the upper 0.2 meters of the saturated zone when sampled at the small (1.5 cm) scale, that was not depicted by sampling at the intermediate scale. At the intermediate scale of observation, one constructed wetland site differed geochemically from the natural wetlands and the other constructed wetland site due to application of off-site salvaged marsh surface and downward infiltration of rain. While important differences in dissolved inorganic phosphorus and dissolved inorganic carbon concentrations existed between the constructed wetland and the natural wetlands, we also observed substantial differences between the natural wetland sites for these constituents. A median-polishing analysis of our data showed that temporal variations in constituent concentrations within profiles, although extensively recognized in the literature, were not as important as spatial variability.

Introduction

Wetlands, once perceived as “worthless” land, are now recognized as a necessary component of a vital landscape. However, due to draining, filling, and construction practices, less than half of the pre-settlement wetland acreage

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remain in the coterminous United States. Wetland destruction also has had undesirable effects on other parts of the landscape, such as erosion, flooding, and deterioration of water quality (Novitski 1982; Kusler & Kentula 1989). The so called “water quality function” of wetlands is generally synonymous with the ability to retain and transform nutrients and metals, and is often the target function for constructed wetlands (e.g., Kadlec & Knight 1995). Our understanding of the controlling geochemical processes in wetlands, however, is not sufficient to reliably predict when desired water-quality functions will result, or to assess the effectiveness of replacement wetlands.

Evaluation of wetland water quality function is confounded by several factors. The term “wetland” remains broadly-defined, and encompasses a gradient of ecosystems that span shallow lake settings to occasionally saturated upland areas (Cowardin et al. 1979). The biogeochemically active zone of a wetland is near the surface, and as such is susceptible to variations in temperature, precipitation, infiltration, and nutrient loading. Wetland biota also undergo significant changes during the growing season, which exert considerable influence on the shallow hydrogeochemical system both in space and time (Hite & Cheng 1996). As a result of all of these factors, assessments of wetland water quality function remain difficult. Moreover, before any quantitative assessment of a *site-specific* water quality function can be performed, the hydrogeochemical system (and associated variations inherent therein) must first be characterized.

Assessments of a wetland’s water-quality function have been historically confounded by field methods designed for data collection at much larger scales. Generally, uncontaminated groundwater systems are relatively homogeneous and stable environments, especially when compared to surface water and atmospheric systems. Using groundwater systems as examples, hydrologic monitoring points are often installed without considering potential small-scale variations in chemistry (e.g., Siegel 1988; Marble 1990; PERL 1990). Variations in groundwater chemistry on scales less than one meter have been identified in contaminated mineral aquifers (e.g., Ronen et al. 1987; Smith et al. 1991) and at groundwater-lake interfaces (e.g., Krabbenhoft 1988; Krabbenhoft 1992). Investigations of wetland chemical heterogeneity have been generally restricted to wetlands that are flooded by surface water (e.g., Patrick & Delaune 1972; Gambrell & Patrick 1978; Klopatek 1978; Mohanty & Dash 1982; Howes et al. 1985). The majority of this research has been conducted in periodically flooded coastal wetlands, and has commonly focused on chloride and sulfate ions (e.g., Lord & Church, 1983; Casey & Lasaga, 1987; Harvey & Nuttle 1995) and, to a lesser extent, nutrients (e.g., Callender & Hammond 1982; Chambers & Odum 1990). This type of research has not been extensively performed in freshwater wetlands, and, to our knowledge, has not been applied to a paired natural and constructed wetland system. The purpose of this paper is twofold: to describe the methods used to reveal previously undetected chemical profiles in soil porewater in freshwater wetlands, and to document the complex nature of chemical heterogeneity (spatial and temporal) in natural and constructed wetlands. In addition, we describe potential mechanisms that explain the observed chemical heterogeneity.

Site Description

The Wilton wetland complex is located along the Kickapoo River in Monroe County, in the unglaciated region of southwestern Wisconsin (Figure 1). Hughes et al. (1981) describe the Kickapoo River basin as having steep slopes (30 to 40 percent), rounded ridges, and steep, narrow valleys. Geology of the site consists of thin (< 5 m) fluvial/lacustrine sediments overlying sandstone bedrock of Cambrian age. Adjacent bluffs are comprised of Cambrian sandstone capped by Ordovician carbonates. Natural wetlands within the flood plain have a thin accumulation of peat (ranging from 0.1 to 1 m) overlying fluvial deposits. The peat contains varying amounts of silt due to sediment transport from adjacent agricultural highlands.

High topographic relief (on the order of hundreds of meters) results in groundwater flow paths that are generally short and extend from the highlands to the river bottoms. Localized discharge promotes the formation of river-bottom wetlands that receive significant groundwater inflow (Hunt et al. 1996).

The natural wetland consists of about 1 hectare of natural shrub-carr/sedge meadow wetland dominated by *Carex ssp.* and *Alnus rugosa* and 7.5 hectares of riparian wetland dominated by *Alnus rugosa*, *Ulmus americana*, and *Fraxinus nigra*. During the summer of 1991, 3.8 hectares of an adjoining upland agricultural field were excavated for wetland construction purposes to mitigate a wetland loss associated with an adjacent road project. The field was excavated to depths that were specified based on pre-construction water levels from 72 piezometers in the field and in the natural wetland. Fifteen centimeters of salvaged marsh surface (SMS) from the destroyed wetland was applied over the constructed wetland. Additional SMS was obtained from an off-site wetland to complete the project because the area of the destroyed wetland (0.4 hectare) was smaller than the constructed wetland (Figure 1). During the growing season, the water table is generally 15 to 30 cm and 15 to 45 cm below ground surface in the natural wetland and the constructed wetland, respectively. As a result of their landscape setting, surface water inflow and outflow are not important to the water budgets of the natural or constructed wetlands.

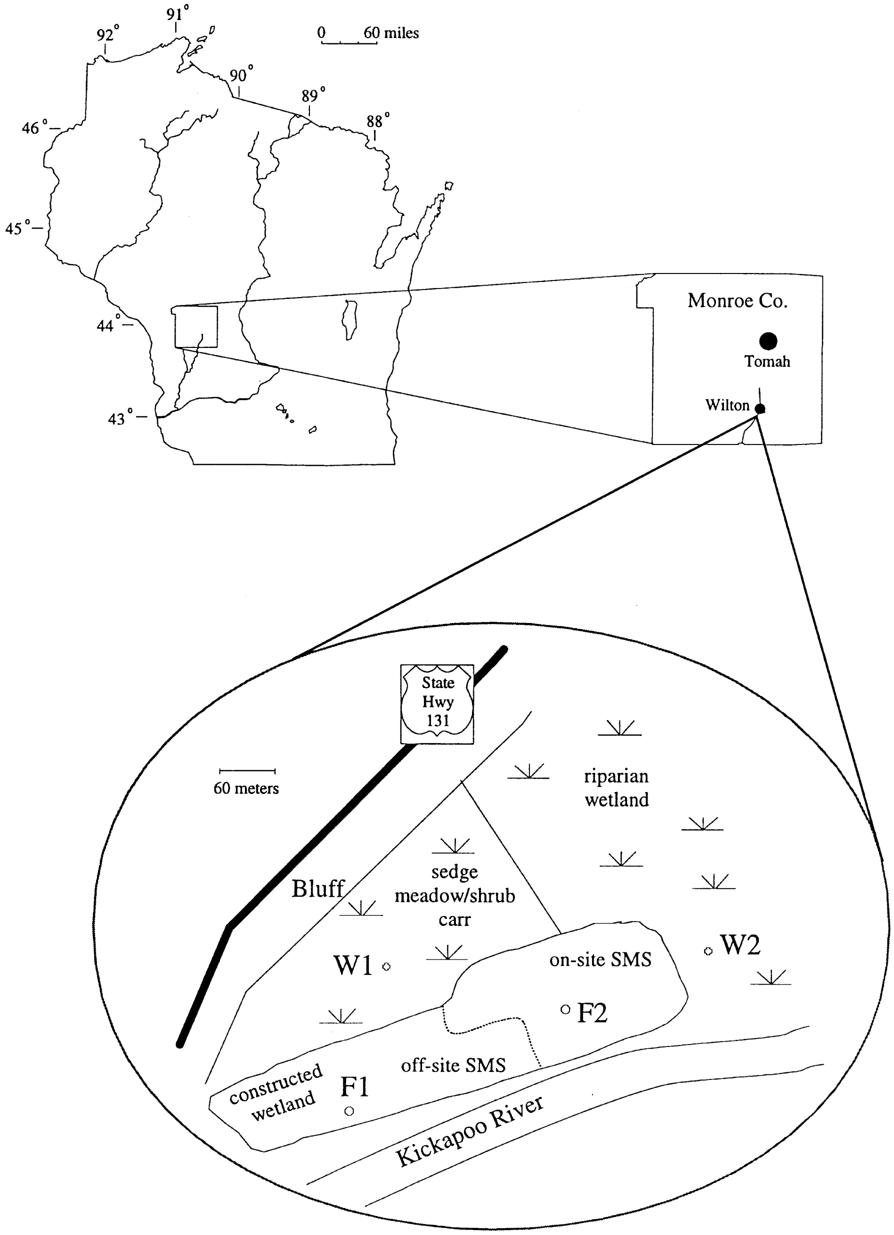

Figure 1. Location of the study site in the headwaters of the Kickapoo River basin in southwestern Wisconsin. Site map marks the locations of natural and constructed wetland sampling sites and delineates areas where on-site versus off-site salvaged marsh surface was applied during construction.

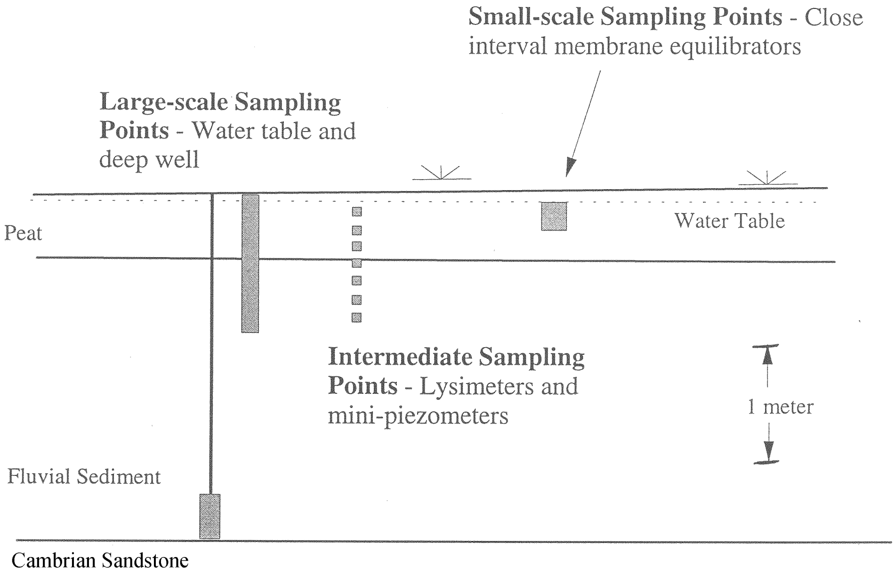

Figure 2. Schematic depiction of field instrumentation for large-scale, intermediate-scale, and small-scale vertical profile sampling.

Methods

Two sites in both the natural and the constructed wetland areas (Figure 1) were instrumented with vertically oriented sampling equipment (Figure 2). The sites were not along a physical or hydrochemical gradient. Rather, the two natural wetland sites (W1 and W2) were selected to typify the two dominant wetland vegetation communities (shrub carr/sedge meadow and a riparian systems); the two sites in the constructed area (F1 and F2) were selected to include areas of both on-site and off-site SMS. At each site, one meter deep soil cores were obtained within one meter of the vertical sampling profiles to characterize site stratigraphy.

During the 1992 growing season, investigations were conducted on three scales within the shallow groundwater system (Figure 2). “Large-scale sampling”, which is the sampling scale generally used in groundwater studies of wetlands, included samples from a water table well (1 m screened interval) and a deeper well located 3 to 7 meters below the water table (0.3 m screened interval). “Intermediate-scale sampling” employed seven equally-spaced points (suction lysimeters and mini-piezometers) positioned to envelop the interval spanned by the water table well (0.15 to 1.07 meters below land surface). “Small-scale sampling” was conducted at 0.015 meter intervals, and spanned the interval sampled by the upper most intermediate sampling point (0.03 to 0.25 meters below land surface).

Large-scale sampling – Water table wells were constructed of 3.8- or 5.1-cm diameter by 1-meter long PVC screen and riser. With the exception of site F2, deep piezometers were installed at a depth near the bedrock surface using the “mini-piezometer” methods of Lee and Cherry (1978). At site F2, the deep well consisted of a 3.8-cm diameter PVC screen installed using mud rotary methods. The 0.7-meter long screen was placed in the upper Cambrian sandstone bedrock.

The water table wells were completely evacuated or pumped to remove at least three well volumes with a peristaltic pump before sampling. Unfiltered samples were used for field measurements of conductivity, temperature and Eh, and laboratory measurements of pH and alkalinity. Filtered samples (0.45 μm cellulose nitrate filter) were collected for determination of dissolved inorganic carbon (DIC), nitrate + nitrite (NO_3 + NO_2), and dissolved inorganic phosphorus (DIP) analyses. Samples were collected at the beginning and end of the 1992 growing season (May and October).

Intermediate-scale sampling – Sampling equipment for the intermediate-scale sampling consisted of 1.4-cm diameter mini-piezometers with 2.5 cm long screens when the interval yielded sufficient water for sampling, and porous, ceramic-cup lysimeters when suction was necessary to withdraw samples in a reasonable period of time. The mini-piezometers were completely evacuated using a peristaltic pump and allowed to recover prior to sampling. The suction lysimeters were completely evacuated, put under negative pressure, then sampled the following day to allow time for recovery. The whole water and filtered water protocol used in the large-scale sampling was also followed for the intermediate sampling. Initially, suction lysimeter samples were filtered. On inspection, however, no non-filterable residue was detected and no significant differences were evident when filtered and unfiltered sample splits were analyzed for DIC. Subsequent lysimeter samples were considered filtered by way of their entrance through the porous, ceramic cup. Both mini-piezometer and lysimeter samples were collected monthly during the growing season and were analyzed for pH, DIC, DOC, alkalinity, NO_3 + NO_2, ammonia (NH_4), and dissolved inorganic phosphorus (DIP).

Concentrations of carbon dioxide (CO_2) and methane (CH_4) in porewater were obtained using headspace equilibration in the field (Cole et al. 1994). Equal volumes of aqueous sample and ambient air were vigorously shaken in a 60 ml syringe for three minutes. Samples of the ambient air used in the head-space equilibration were also collected. After equilibration, 20 ml of gas was withdrawn into a glass syringe for analysis by gas chromatography with a flame-ionization detector using an in-line methanizer.

Small-scale sampling – Small-scale samples were collected using close-interval membrane equilibrators (CIME) or "peepers" (Hesslein 1976). The samplers consisted of 5-ml horizontal chambers arranged vertically in a wedge-shaped acrylic body. The chambers were filled with degassed deionized water, covered with 0.45 micron cellulose nitrate filters, and secured with an acrylic face plate that contained openings aligned with the chambers in the sampler. The sampler was installed vertically into the wetland surface and remained in place for approximately three weeks to allow for chemical equilibration between water in the sampler and the adjacent porewaters. After this period of time, the sampler was removed, and the chambers evacuated with a syringe.

All samples collected at different scales were analyzed by similar methods. Nitrate + nitrite, NH_3, and DIP were analyzed colorimetrically with a Technicon Auto Analyzer II. Dissolved inorganic carbon was analyzed using an OI Model 700 TOC Analyzer. Metals (Fe and total P) were analyzed using inductively coupled plasma (ICP) emission spectrometry. Due to the small sample volumes obtainable for a given sampling site, only one duplicate sample was collected during each sampling.

Results and discussion

Spatial Heterogeneity – A striking observation is made by comparing NO_3 + NO_2, DIC, and DIP results for samples from water table wells against discrete samples taken over the same interval (Table 1). Samples taken from water table wells do not accurately depict the actual variability for any of these constituents, and do not represent the average or median profile concentrations properly. In most cases, the water table wells underestimated the average concentration in most chemical profiles at our study sites. An extreme example occurs at F1 where the samples from the water table well yielded NO_3 + NO_2 concentrations of about 220 ug/L, but all the discrete intervals had higher concentrations, with one sampling interval two orders of magnitude higher (Figure 3a). This anomalous measurement is likely due to heterogeneity in the flow rate of water into the well screen over the 1-meter sampling interval. High flow rates from discrete zones can result from high hydraulic conductivity and/or increased hydraulic gradients. These factors cause an "over sampling" of the high-flow zones with disproportionately lower contributions from low flow zones. Small-scale variations in conductivity in wetland peats and in a seemingly homogenous sand aquifer have been noted in the literature (e.g.,

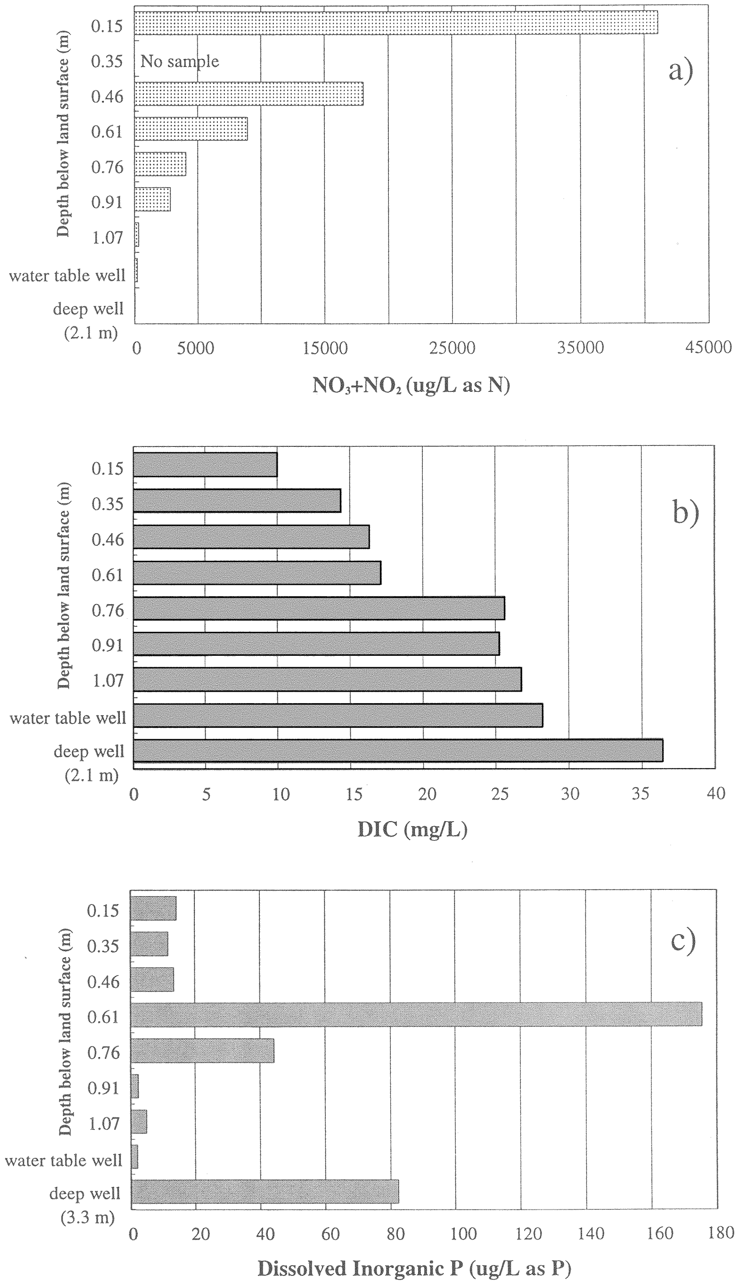

Figure 3. Comparison of water table well sampling (large scale) versus discrete-interval (intermediate scale) sampling from May 1992. Panels show profiles of NO_3 + NO_2 at constructed wetland site F1 (3a), DIC at constructed wetland site F1 (3b), and DIP at natural wetland site W1 (3c).

Table 1. Comparison of may 1992 samples from water table wells to samples obtained from intermediate-scale samplers

Nitrate + Nitrite (ug/L as N)

	Site F1	Site F2	Site W1	Site W2
Water Table Well	222	6	52	51
Profile Average	12560	45	45	22
Profile Median	6510	47	25	19
Profile Maximum	41080	80	97	47

DIC (mg/L)

	Site F1	Site F2	Site W1	Site W2
Water Table Well	31	41	81	49
Profile Average	12	49	82	51
Profile Median	13	43	87	51
Profile Maximum	22	83	100	62

Dissolved Inorganic P (ug/L as P)

	Site F1	site F2	Site W2	Site W2
Water Table Well	1	6	ND	ND
Profile Average	8	31	44	9
Profile Median	6	9	14	4
Profile Maximum	23	118	200	23

ND = not detected

Rycroft 1975; Sudicky 1986). During soil coring, a coarse gravel layer was encountered at a depth of 1-meter at site F1 (Table 2). The intermediate scale sample taken at 1.07 m and the deep well sample had low NO_3 + NO_2 concentrations. Thus, high flow contributions from low N groundwater likely accounts for the low NO_3 + NO_2 concentrations observed in the water table well at site F1. Regardless of the mechanistic reason, it is obvious that water table wells are not good sampling tools for establishing true constituent concentrations in wetlands, especially when the intent is to determine limiting nutrients, such as nitrate.

Intermediate-scale profiles of NO_3 + NO_2, DIC, and DIP showed substantial variability in both the natural and constructed wetlands (Figure 3a–c). The variability exemplified by the three profiles in Figure 3 were the norm for the monthly sampling rather than the exception. A Kruskal-Wallis test for significance (the nonparametric equivalent to the one-way analysis of variance) used the groups of NO_3 + NO_2, DIP, and DIC concentrations from the intermediate-scale sampling to determine whether the median concentrations for seven depths within the profile were statistically similar, or whether at

Table 2. Results of carbon system intermediate-scale sampling

Site	Depth (m)	soil texture	pH*	DOC* (mg/L)	DIC* (mg/L)	Alkalinity* (meq/L)	CO_2^{**} (umol/L)	CH_4^{**} (umol/L)
F1	0.15	black peat	6.2	9	7	0.2		
	0.30	brown sand, silt	6.2	7	7	0.3	298	ND
	0.46	brown sand, silt	6.6	3	12	0.5	580	ND
	0.61	brown sand, silt	6.8	4	16	0.9	599	ND
	0.76	brown sand, silt	6.9	2	28	1.7	501	ND
	0.91	gray sand, silt	7.0	8	23	1.6	614	ND
	1.07	sand, coarse gravel	7.0	4	23	1.6	359	7
F2	0.15	brown peat	6.9	16	105	5.9		
	0.30	brown sand	7.3	1	70	4.5	581	ND
	0.46	brown sand	7.3	2	53	3.8	841	ND
	0.61	brown sand	7.5	1	46	3.5	399	ND
	0.76	gray sand, silt	7.4	1	44	3.4	370	ND
	0.91	gray sand, silt	7.5	1	44	3.3	272	16
	1.07	gray sand, silt	7.3	2	42	3.2	272	22
W1	0.15	brown fibrous peat	7.1	19	106	8.5	490	ND
	0.30	brown fibrous peat	7.1	13	87	6.2	892	83
	0.46	black fibrous peat	7.0	8	99	6.2	113	100
	0.61	black fibrous peat	6.9	5	94	6.0	915	122
	0.76	black peat	7.1	4	96	6.5	1042	228
	0.91	gray brown sand, silt	7.3	1	78	5.8	803	188
	1.07	gray brown sand, silt	7.3	4	71	5.9	738	27
W2	0.15	black fibrous peat	7.0	8	68	3.9		
	0.30	black figrous peat	7.0	4	79	4.7	527	204
	0.46	gray sand, silt	7.3	3	58	4.2	265	ND
	0.61	brown sand, silt	7.3	2	54	4.0	298	26
	0.76	black peat/brown sand	7.3	1	49	3.6	234	15
	0.91	brown sand	7.3	1	47	3.7	269	ND
	1.07	brown coarse sand	7.4	2	47	3.6	282	2

ND = not detected
*Average of 1992 growing season measurements
**From single sampling October 3, 1994

least one sampling depth was statistically different. This test showed that 9 of the 12 intra-site profile samples had at least one significantly different ($p < 0.05$) median concentration; the three exceptions were $NO_3 + NO_2$ concentrations that were uniformly low throughout the profiles at F2, W1, and W2.

The profiles of $NO_3 + NO_2$ and DIC shown in Figures 3a and 3b are explained by the soil chemistry and downward hydraulic gradients at F1. Hunt (1993) used strontium isotopes and Sr : Ca ratios to show that the off-site SMS has a distinctly different chemistry than the on-site SMS and the intact peat of the natural wetland, and is coincidentally in a location where downward hydraulic gradients predominate. The fact that $NO_3 + NO_2$ concentrations near the top of the F1 profiles are about 2–3 orders of magnitude greater (Table 1) than the other sites, further supports these observations. Compared to the other sites where groundwater is the dominant water source, porewater at site F1 is nearly 100 percent rain-derived water (Hunt et al. 1996). The three order of magnitude change in $NO_3 + NO_2$ for this profile is likely controlled by a simple two-component mixing model, with end members consisting of high $NO_3 + NO_2$ porewaters leached from the off-site SMS and $NO_3 + NO_2$-poor groundwater. Corroborating evidence for this model is derived from the DIC profile (Figure 3b) where the two end members are DIC poor rain-derived water and DIC rich groundwater.

The sampling results for DIP from the natural wetland site W1 are especially intriguing (Figure 3c). The DIP profile shows a mid-profile maxima concentration, with lower concentrations at both shallower and deeper depths. Although profiles of DIP vary among the four sites, we generally observed mid-profile maximums, and the profiles at each site were reproducible. The fact that the DIP maximum occurs mid-profile suggests that the phosphorus source is *in situ* and likely the result of recycling mechanisms, such as mineralization of organic matter and/or dissolution of ferric hydroxide. More importantly, however, it should be noted that DIP concentrations observed by discrete sampling can be high in wetland soils where it may otherwise be interpreted (based on samples from water table wells) that phosphorus is the limiting nutrient.

Although the variability within and among the profiles was substantial, generally the same profile shape was observed for $NO_3 + NO_2$, DIP, and DIC regardless of the date sampled. For example, during any one sampling, $NO_3 + NO_2$ concentration profiles at constructed site F1 consistently spanned three orders of magnitude, yet the same general profile shape was maintained (Figure 4). This demonstrates that spatial heterogeneity can be important throughout the growing season and is not restricted to any one period of the year.

Efflux of greenhouse gases to the atmosphere is of interest in light of global climate change scenarios, and wetlands are an obvious source of gaseous-carbon production. The discrete interval sampling scheme used in the intermediate-scale sampling reveals profiles in chemical species important for carbon cycling, that would otherwise be undetected if larger sampling

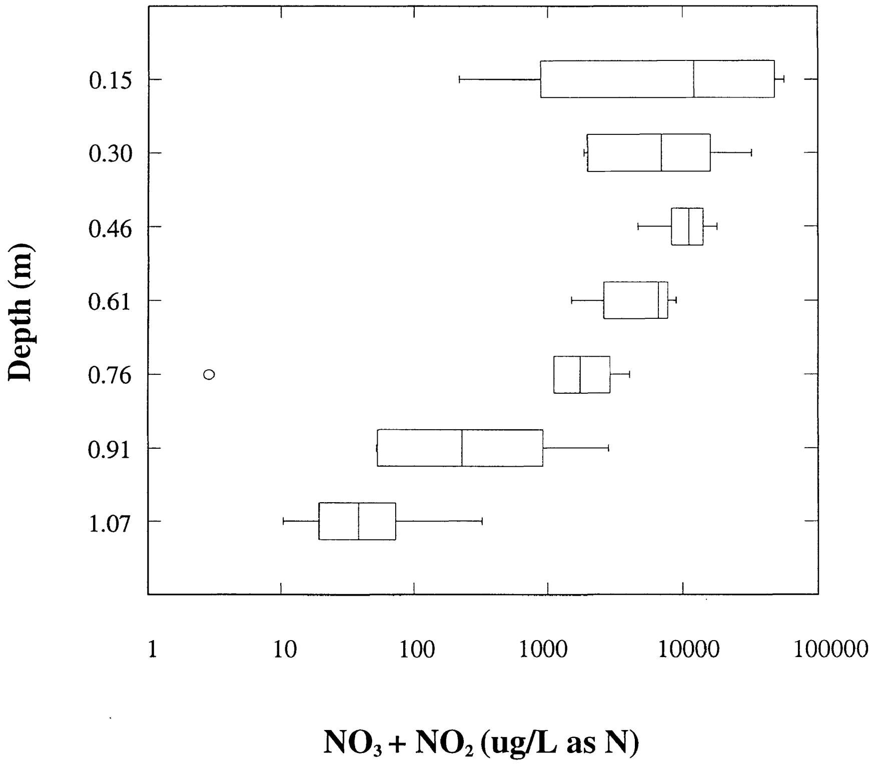

Figure 4. Box plots of NO_3 + NO_2 concentrations at depths of 0.15 to 1.07 m below ground surface at constructed wetland site F1, sampled six times over the 1992 growing season.

scales were employed (Table 2). The overall levels of DIC, alkalinity, CO_2, and CH_4 are quite high, but as before, substantial inter-site variability occurs. With the exception of DOC and shallow peat, there is no obvious relationship between soil texture and the carbon system constituents. We propose the observed trends in these constituents are controlled by water source, contact with carbonate minerals at depths greater than 1 meter, and density and depth of rooting zones (and attendant respiration).

Site F1 is notably different from the other sites (Table 2). Lower levels of DIC, alkalinity, and pH at site F1 are reflective of a rainfall water source, and the carbonate-poor, off-site SMS at this site. Profiles of DIC and alkalinity are similar for constructed wetland site F2 and the two natural wetland sites. Elevated levels of DIC and alkalinity at these sites are a result of upward discharge of groundwater, which has been in contact with carbonate minerals, and high root density giving rise to CO_2 production via respiration. Near surface pH depressions limited to the top 0.15–0.30 m at sites F1, F2, and

Table 3. Comparison of October 1992 intermediate-scale samples to small-scale average, median and maximum concentrations

Site W1	$NO_3 + NO_2$ (ug/L)	NH_4 (ug/L)
0.15 m lysimieter	14	28
Profile Average	14	457
Profile Median	11	440
Profile Maximum	42	1095

Site F2	$NO_3 + NO_2$ (ug/L)	NH_4 (ug/L)
0.15 m lysimieter	19	71
Profile Average	27	178
Profile Median	13	170
Profile Maximum	168	578

W2 are likely the result of the shallow root effects, compared to site W1 where plant root effects extend to depths greater than 0.5 m. That most of the profiles for sites F2, W1 and W2 are similar is encouraging since they are similar with respect to hydrology and vegetation, suggesting that carbon cycling at the created site (F2) is operating similar to the natural analog (W1, W2). Methane profiles from the created sites are depressed compared to levels observed in the natural wetlands. Either lack of CH_4 production or oxidation resulting from a more oxidizing environment (USGS, unpublished data) within the created site likely controls the observed profiles.

Small-scale sampling – Within the sampling interval spanned by the CIMEs (20 cm), large variations in chemistry are evident near the surface porewaters (Figures 5, 6 and 7), and were not necessarily characterized by the discrete, intermediate sampling (Table 3). The degree to which the intermediate-scale sample from the same depth interval adequately represents the CIME profile depended on the analyte. Lysimeter samples appeared to represent NO_3 + NO_2 correctly and underestimate the amount of NH_4 present at the near surface in both the natural and constructed wetlands (Table 3). Similar to the water table well/lysimeter comparisons, it is likely that different portions of the profile were contributing disproportionate amounts of water to the suction lysimeter. The segregation of flow in peats (into matrix and macropore flow) has been noted by others (e.g., Harvey et al. 1995; Harvey & Nuttle, 1995). Although Hunt et al. (in press) have shown that, based on stable isotopes of water, macropore flow is not dominant under unstressed conditions, the

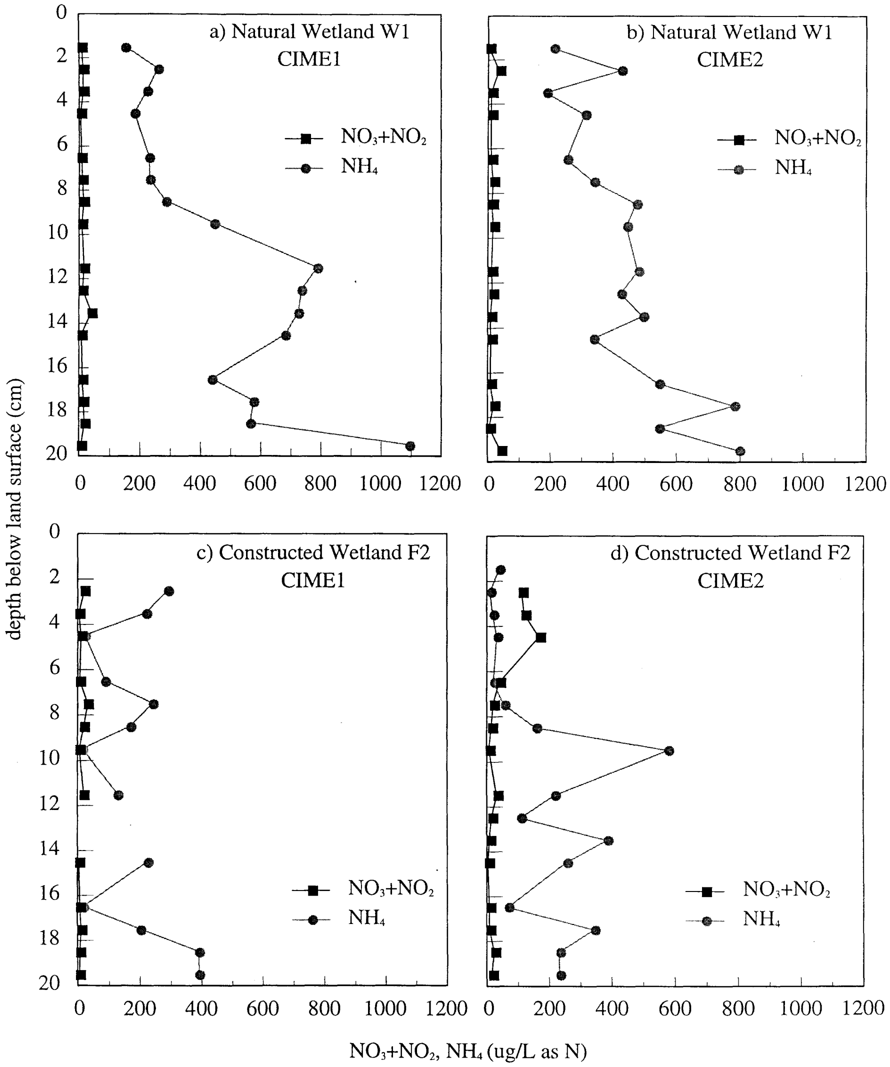

Figure 5. Comparison of sampling using replicate CIMEs emplaced 1 meter apart in natural wetland site W1 (5a, 5b) and in constructed wetland site F2 (5c, 5d). While the general trends are similar, concentrations measured in samples from replicate CIMEs at a given depth are considerably different. Profile average, median, and maximum values are compared to 0.15 m lysimeter concentrations in Table 3. The concentrations are reported as ug/L as N.

vacuum applied to the lysimeter appears to stress the system sufficiently to cause segregated flow.

To demonstrate the variability of porewater profiles over short horizontal distances, two CIMEs were placed approximately one meter apart in the

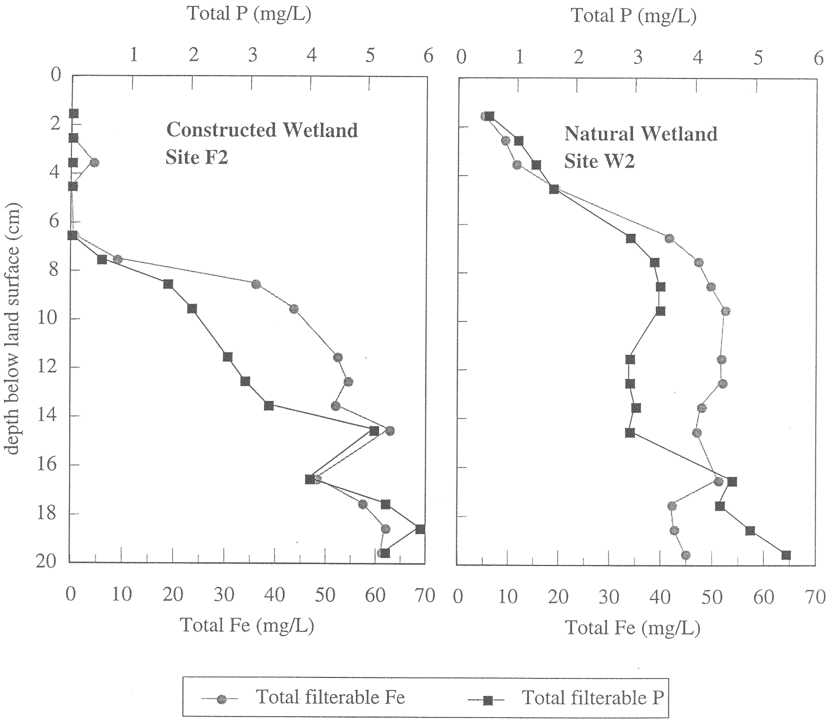

Figure 6. Profiles of iron and total phosphorous from sampling CIMEs at natural wetland site W2 and constructed wetland site F2. Profiles reveal large chemical heterogeneity that exists on a 1 cm scale in the shallow wetland porewaters, which is likely due to changes in the redox state of the system.

natural and constructed wetland (Figure 5). While the same general trends were apparent in both the profiles, the concentrations at a given depth in each profile can vary significantly. This emphasizes that while vertical differences in geochemistry are important, horizontal spatial variations may be important as well. While not widely recognized in the literature, these horizontal variations could be important in the location of “representative” sites in a given wetland.

A set of CIMEs was installed in both the natural and the constructed wetlands in May 1993 and October 1995 (Figure 6 and 7) to examine iron (Fe) and phosphorus profiles – constituents important to wetland vegetation and the assessment of the wetland water quality function. Profiles of Total P and Fe in May 1993 showed considerable variation; from non-detectable to 1 and 10s of mg/L, respectively, in the 20 cm vertical profile encompassed by the CIME (Figure 6). The total phosphorus levels shown here are much higher than those commonly assumed for pristine wetlands (< 100 ug/L), and those disturbed

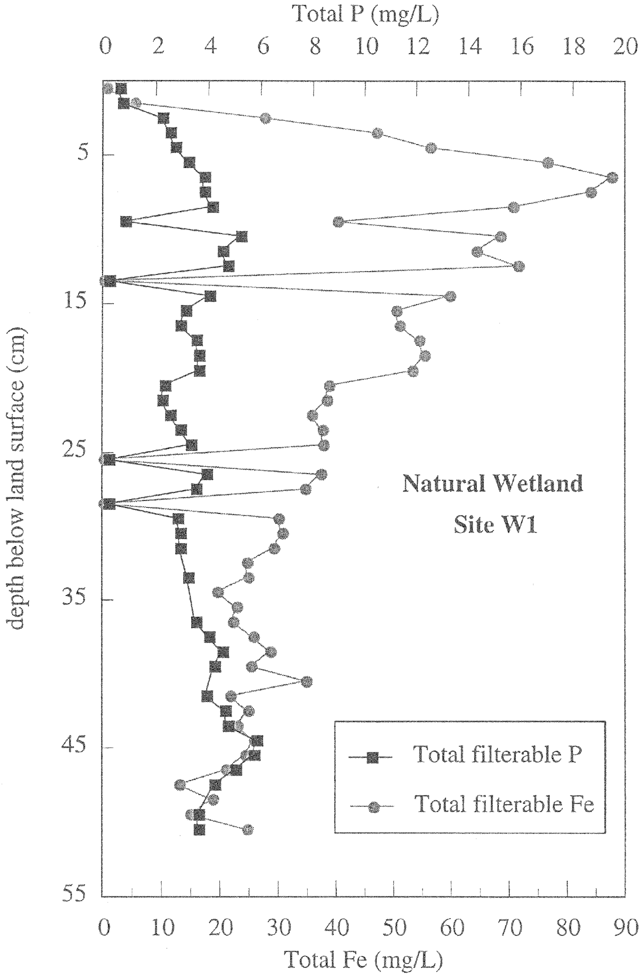

Figure 7. Profiles of Fe and P from an extended CIME (52 cm long) deployed at natural wetland site W1 in October 1995. The top of the profile shows the same Fe to P relation at shallow depths that is shown in Figure 6, but at greater depths Fe concentrations follow a general declining trend, and both constituents show near quantitative losses at small intervals, presumably in response to oxygen introduced by rhizomes.

by anthropogenic influences (700 ug/L, Kadlec and Knight 1995, pg. 102). These high concentrations also raise questions regarding the assumption that these systems are phosphorus limited. While the magnitude of the gradient is surprising, the existence of a gradient in these parameters is expected given the redox stresses present at the saturated zone/unsaturated zone interface, the proximity to plant roots, and the sensitivity of these parameters to redox conditions. The top 5 cm of the CIMEs were commonly stained with iron-hydroxide. The generally low levels of phosphorus at shallow depths is likely a result of scavenging of phosphorus by iron-hydroxide (e.g., Chambers et al. 1992), and uptake by plant roots.

The CIME installed at natural wetland site W1 in October 1995 was considerably longer than those deployed previously (52 cm versus 20 cm), which allowed us to determine if the high total P and Fe concentrations at the bottom of the profiles observed in May 1993 continued. Profiles from the longer CIME showed a similar close correspondence between total P and Fe, but it also revealed a general trend toward lower Fe concentrations with depth (Figure 7). At very distinct intervals concentrations of both total P and Fe show near quantitative losses of both constituents, presumably due to the intersection with rhizomes where local oxic zones prevail, and ferric hydroxide formation and phosphorus sequestration results. The longer profile also indicates that the total P and Fe profiles are controlled by recycling over the top 30 cm, and not due to upward transport of these constituents from below.

The observed small-scale chemical heterogeneities result from a number of factors, including the proximity of the reduced saturated zone to the oxidized unsaturated zone, water table/capillary fringe evapotranspiration, location in areas of higher macropore content, effects of vegetation, and the microbial community type and distribution. Given that such variability is likely the norm in wetland environments, it is unlikely that the use of lysimeters can adequately represent “average” conditions of the near surface. Furthermore, the magnitude of the variation casts doubt on whether determination of an “average” condition for shallow wetland porewater has value. It should be noted, however, that the CIMEs were installed at ground surface, and only reflect on the adequacy of samples from the uppermost lysimeter to represent the upper saturated zone. Because the unsaturated/saturated zone interface is dynamic and is routinely stressed in wetlands, it is likely that this example represents the most extreme case in the profile.

Comparison of Spatial and Temporal Differences – The effects of seasonality on water chemistry in various aquatic ecosystems are relatively well-known, and sophisticated techniques have been developed to address the effects of temporal variation (e.g., Hirsch et al. 1982). Similar to the analysis of spatial heterogeneity, a Kruskal-Wallis test for significance was performed to determine whether the median profile concentration of $NO_3 + NO_2$, DIP, or DIC at a specific site changed significantly between sampling dates. Results of this analysis showed that only two of 12 tests showed significant ($p < 0.05$) temporal variability (i.e., had at least one profile median statistically different from profile medians measured during the other months). So, while a specific

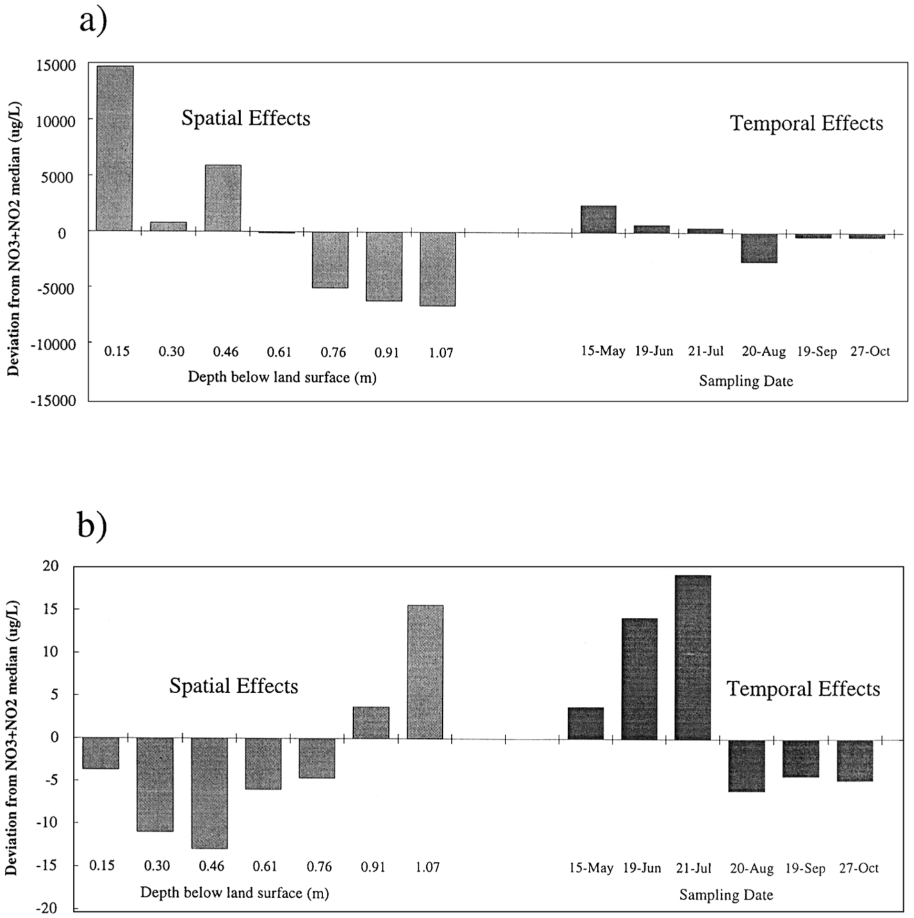

Figure 8. Comparison of median polishing results for NO_3 + NO_2 data from the constructed wetland F1, which portrays our general observation that spatial heterogeneity is larger than temporal heterogeneity (8a), and a case of an exception to our general observation where spatial heterogeneity and temporal heterogeneity are equally important (8b).

analyte showed considerable variability both among and within sites, the pattern observed for an individual profile was reproducible. To further evaluate the relative importance of spatial versus temporal variations in our chemical data, we performed a statistical analysis (median polishing, Emerson & Hoaglin 1983; Emerson & Wong 1985; Helsel & Hirsch 1992) to evaluate the relative magnitudes of spatial and temporal effects on the geochemistry in our study wetlands. Median polishing is an iterative, robust technique for exploring a two-way table of values. It calculates a resistant estimate of the overall median, as well as estimates of the row and column effects (spatial and temporal variations). Spatial effects were larger than temporal effects in nine of the twelve comparisons, as exemplified by Figure 8a. In three of the twelve cases temporal effects were equal to or greater than the spatial effects; a example of this case is shown in Figure 8b. The latter result occurred only where concentrations were very low (< 50 ug/L) throughout the profile indicating that the magnitude of spatial effects were small, not that the temporal effects were larger.

Comparison of the natural to the constructed wetlands and related implications

Contrary to a widely held view that chemical heterogeneity is important only at large horizontal sampling scales (e.g., Kadlec & Knight 1995, pg. 109), the results presented here indicate that geochemical comparison of wetlands must take into account small-scale chemical heterogeneity. This is especially important in wetlands where the water quality function is identified as an important or desired function. Using the discrete sampling data presented here, the following comparison of the natural and constructed wetlands can be made. Site F1 in the constructed wetland has significantly greater NO_3 + NO_2 concentrations and significantly lower DIP than F2 and W1 and lower DIC than the other three sites; this phenomenon is a result of the application of off-site SMS and downward transport of NO_3 + NO_2 by infiltrating rain. Site F2, on the other hand, was geochemically more similar to the natural wetland sites (Table 1). Therefore, because site F2 has nutrient concentrations and distribution (as well as source of water) more similar to the adjoining natural wetlands than site F1, we conclude that it should also more closely resemble the natural counterpart as the site matures.

It is important to note that there were differences between the two adjacent *natural* wetlands as well. Average DIP concentrations were four times greater in the sedge meadow site W1 than at the riparian site W2 (Table 1). In addition, DIC concentrations in the sedge meadow site were nearly twice that measured in the riparian wetland. While this finding is a topic for future work, it is likely related to the differences in the vegetation type and the related differences in root respiration and nutrient sequestering.

If evaluations of the constructed wetland sites had been made using only sample analyses from water table wells, all four sites would have appeared to have similar soil-water DIP and DIC concentrations (Table 1) and the high NO_3 + NO_2 concentrations at F1 would have gone unnoticed. Samples from water table wells indicated F2 had NO_3 + NO_2 concentrations that were lower than W1 and W2; average, median and maximum intermediate-scale measurements from the profile were of the same order of magnitude (Table 1). A notable result of this work is that the importance, presence, or absence of processes occurring in the wetlands would not have been revealed if water table wells were the sole method for collecting water samples. Furthermore, any assessment of the "water quality function" would have been incomplete at best, and incorrect at worst.

Conclusions

Four fundamental conclusions can be drawn from this study:

- First, we have demonstrated that significant spatial chemical heterogeneity exists on a 0.15 m scale for all nutrients (N, P and C) near the water table, and that these variations can be much larger than previously reported for freshwater wetlands. Samples from water table wells did not capture this heterogeneity, and commonly did not represent the profile's average or median concentration. This occurred because certain depths of the screened interval contribute disproportionate amounts of water to the well from localized zones of increased hydraulic conductivity.
- Second, variations in geochemistry were also very large on the 1.5 cm scale, at times ranging eighteenfold over a 20 cm interval. As a result of these chemical heterogeneities, even sampling with lysimeters on a 0.15 m scale may be inadequate to characterize the heterogeneity and related profiles present in the upper 20 cm of the saturated zone. The large variations may be explained by a combination of factors, such as the proximity of the chemically reduced saturated zone to the oxidized unsaturated zone, evapotranspiration, and a vigorous microbial community.
- Third, temporal variations in chemistry over the growing season are less important than spatial heterogeneity. Temporal variations were similar in the natural and constructed wetlands, and were larger than spatial variations only when concentrations within the profile were low (< 50 ug/L). More information is gained in geochemical studies of wetlands by placing emphasis on spatial sampling.
- Fourth, there are significant differences between the constructed wetland and natural counterpart when the systems are investigated using intermediate and small-scale samplers. Furthermore, there are also significant differences between the two natural wetland sampling sites. This result demonstrates the variability present across wetland type and argues for careful assessments of wetland communities slated for destruction, as well as the constructed wetlands used to mitigate their loss.

The results presented here underscore the importance of choosing the appropriate sampling scale for the research question, and the inadequacy of water table wells to characterize this wetland system. Studies of nutrient dynamics and cycling in this wetland, and likely other wetlands, require smaller-scale sampling than has traditionally been used in groundwater studies. Such sampling should include the region near the root zone using close-interval membrane equilibrators. Without study on this scale, chemical heterogeneities present will not be recognized, and erroneous interpretations may result.

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