

Impact of Groundwater Sulfate Delivery on Anaerobic Respiration and Dissolved CO₂ Concentrations in a Rich Fen in Central New York.

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by
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Abstract:

This study examines the interactions between groundwater flow and porewater chemical concentrations to elucidate controls on dissolved CO₂ concentration and the rate of anaerobic carbon mineralization along a transect in a wetland fed by ground water, Junius Ponds Fen, in central New York. Three hypotheses were tested: (1) groundwater flow paths influence pool sizes of sulfate and nitrate in shallow peat, (2) supply of sulfate through groundwater flow is responsible for high dissolved CO₂ concentrations within the fen, and (3) response of anaerobic CO₂ production to sulfate addition in vitro will be correlated with rates of sulfate supply via ground water, as indicated by sulfate pool sizes. Ground water rich in sulfate is entering the fen both laterally from the adjacent upland, and through a deep plume that reaches the surface of the fen. Groundwater gradients in sulfate, nitrate, dissolved organic carbon, and dissolved inorganic carbon were found to follow paths of groundwater flow, and to be spatially related to the dissolved carbon dioxide concentrations across the fen. Sulfate-amendment incubations did not show a significant increase in soil respiration rate as a result of sulfate addition, but did show a response to carbon addition in some cases. Incubations also failed to show a spatial response to sulfate addition. The high bulk density of peat at this site, in conjunction with the incubation data, suggest that labile carbon availability may be more important in controlling the rate of anaerobic carbon mineralization than sulfate pool size.

Introduction:

Rich fens are a type of wetland that is strongly influenced by ground water inputs (Bedford and Godwin 2003). In New York State, as well as in the Upper Midwest and England, fens have a relatively constant supply of ground water that keeps the plant-rooting zone saturated for the majority of the year. The chemistry of this ground water reflects the chemistry of the surrounding geologic material and local land use practices (Godwin et al, 2002; Bedford and Godwin, 2003). Understanding the biogeochemical function of the wetland requires consideration of the fen in the context of its landscape framework, including catchment hydrology, because of the close ties between groundwater chemistry and surrounding surficial geology. Given the anaerobic conditions that typically prevail in saturated soils in fens, ground water can play an important role in delivering alternate electron acceptors to microbial communities, thus further affecting groundwater chemistry in plant-rooting zones.

Within fens, anaerobic microbial respiration reactions are the dominant metabolic pathways, and the supply of alternate electron acceptors is critical. Nitrate reduction is the most energetically favorable anaerobic carbon mineralization pathway, although this process is likely insignificant in rich fens because of low nitrate concentrations and the tendency for anaerobic conditions to prohibit nitrate formation via aerobic N-mineralization (Lang et al. 1993). Sulfate reduction has not generally been thought to be as important in freshwater wetlands as in coastal wetlands because of limited sulfur inputs. However, the sulfate pool in peatlands can turn over rapidly and support high rates of sulfate reduction (Wieder et al., 1990; Vile et al., 2003). Therefore, sulfur inputs can play an important role in the total respiration of a wetland system. In sulfate

reduction, two moles of carbon are mineralized for every mole of sulfate reduced (Conrad, 1989). Thus, an increase in the supply of sulfate may have a potentially large impact on the carbon dioxide production resulting from microbial respiration through higher carbon mineralization rates in systems with high sulfate inputs compared to other anaerobic processes where the ratio of electron acceptor consumption to CO₂ produced is one to one.

Previous studies have investigated the importance of sulfate reduction to salt marsh and marine sediments (e.g., Howarth and Jorgenson 1984). However, few studies have examined the importance of dissimilatory sulfate reduction in freshwater peat. A study by Wieder et al. (1990) found that sulfate reduction contributed substantially to carbon dioxide production and anaerobic carbon mineralization in two bogs in the Appalachians. However, Vile et al. (2003) showed through a multi-year sulfate fertilization experiment designed to simulate heightened atmospheric sulfate deposition that sulfate addition did not significantly increase rates of sulfate reduction in a bog. Therefore, it is still uncertain whether this process is important in peatland systems.

In this paper, I examine how hydrologic flow and groundwater chemical supply influence sub-surface pool sizes of sulfate, nitrate, dissolved organic carbon, dissolved inorganic carbon, and the distribution of dissolved CO₂ in a rich fen with significant inputs of sulfate via groundwater flow from a gypsum-dominated watershed. Three hypotheses were tested: (1) groundwater flow paths influence pool sizes of sulfate and nitrate in shallow peat, (2) supply of sulfate through groundwater flow is responsible for high dissolved CO₂ concentrations within the fen, and (3) response of anaerobic CO₂ production to sulfate addition in vitro will be correlated with rates of sulfate supply via

ground water, as indicated by sulfate pool sizes. If mineralization of carbon compounds is limited by the availability of electron acceptors, which is likely in a low-nitrate system, then stimulation of sulfate reduction could increase CO₂ production and dissolved CO₂ concentrations in the rooting zone. I relate hydrologic flow data to spatial patterns in pools of sulfate, nitrate, dissolved CO₂, dissolved inorganic carbon, dissolved organic carbon and pH within Junius Pond Fen. To examine the influence of sulfate supply on CO₂ production and the spatial distribution of sulfate reduction, peat samples taken along a transect of groundwater flow were incubated with carbon- and sulfate-amended water.

Site Description:

Junius Pond Fen (JPF) is located in the Finger Lakes Region of central New York at (*lat, long*). It is characterized by both subsurface and deep groundwater flows, which maintain a stable water table just below the peat surface. The site is located in a watershed dominated by gypsum (calcium sulfate) surficial geology, which plays a dominant role in determining subsurface groundwater chemistry (Bailey 2004). JPF is a rich fen, and thus it is characterized by very low levels of available nitrogen and phosphorus (Bedford and Godwin 2003). Since variations in the groundwater chemistry within a wetland may result from the interactions of different flow systems (Carter and Novitzki, 1988), the intersection of two groundwater flow paths of different depth and flow direction in JPF may play an important role in local groundwater chemistry. Previous work on JPF has shown that there are clear correlations between hydrologic and hydrochemical gradients within the fen, and that the water table is relatively constant, varying 10cm or less from May through December, and remaining at or just below the

peat surface (Bailey 2004). For this study, five locations (JP2, JP6, JP7.5, JP8.5, and JP10) were considered within the fen. These locations fall along a transect running perpendicular to the pond toward the upland (Figure 1). Sampling locations JP6-JP10 are located within the fen and JP 2 is located closer to the upland in a forested swamp area adjacent to the fen. These sites were chosen to represent areas subject to different ground water influences based on the hydrologic data from previous years (Bailey 2004).

Methods:

To examine the link between groundwater flow and hydrochemical patterns, I first measured hydraulic head from piezometer clusters at various locations along the transect. I then compared these measurements to previous head measurements from the same transect (Bailey 2004), to construct a groundwater flow map of the site. From a subset of the piezometers, I took water samples for chemical analysis to characterize chemical pool sizes which I could later relate to the results of incubation experiments. Based on chemical data from previous years (Bailey, 2004), I identified sites that had different groundwater characteristics, both in their location on the flowpaths, and in their groundwater chemistry.

To test hypotheses (2) and (3), I obtained peat cores from each selected location from both the surface peat (~14 cm) and the bottom of the peat layer (30-150 cm depending on site), for two in vitro incubations. The first experiment was a reciprocal ground water incubation of surface peat to determine if groundwater chemistry or peat composition was affecting CO₂ production rates more strongly between two locations on the groundwater flow path. The second incubation was a sulfate-amendment incubation,

where I fertilized peat cores taken from five different locations along the groundwater flow path with either sulfate, glucose, or both sulfate and glucose. The response of cores to the sulfate amendments allowed me to assess if sulfate supply could increase the rate of CO₂ production to answer hypothesis (2). The difference in response of incubations from different locations along the flowpath allowed me to assess the spatial pattern of the response of peat to sulfate amendment at locations with different groundwater sulfate characteristics. This allowed me to approximate the relative populations of sulfate reducing bacteria present in peat samples, and to make inferences about field sulfate reduction to answer hypothesis (3).

Groundwater hydrology and chemistry

Piezometer installation and hydrometric measurement methods were done in a manner similar to Hill et al. (2000). Piezometer clusters were installed in the fen and swamp, approximately ten meters apart, along a transect that ran parallel to the direction of subsurface groundwater flow. Additional wells were installed in areas where preliminary data suggested that flow and/or chemistry were changing rapidly (Bailey, 2004). The transect begins at the pond and runs toward the upland parallel to the direction of groundwater flow. Most piezometer clusters were made of PVC pipes (1.25cm ID) with a 15cm slot zone at depths ranging from 0.5-2.5m below the peat surface. I installed additional wells to supplement depths available at existing clusters, and to add 15-30cm depth wells. These were made of 1.5-inch diameter PVC pipes with 15cm slot zones. I surveyed the relative heights of all piezometers to normalize elevations to a common benchmark. Groundwater hydrologic data were collected on July

7, 2003 to compare with previous hydrologic data gathered by Bailey (2004), and groundwater chemistry data were collected in mid-August 2003. Dissolved carbon dioxide measurements were taken on July 17, 2002, June 16, 2003, and June 25, 2003 to characterize the distribution of CO₂ concentrations prior to sampling for incubations.

Hydraulic head was measured by inserting quarter-inch plastic tubing into each piezometer until it contacted the water surface and recording this depth. Depths then were calibrated to a common benchmark following surveying. Prior to chemical sampling, piezometers were purged using a hand-operated pump. Temperature, pH and conductivity were taken using electronic field probes (Fisher Scientific) from wells prior to sample collection. Fresh groundwater samples were withdrawn using Nalgene tubing and sample bottles in-line with the pump for chemical analysis. Samples were stored in coolers to transport back to the laboratory, where they were stored at 4°C for a maximum of 24 hours, before being filtered through a 0.2 um membrane filter and stored again at 4°C for later NH₄⁺, NO₃⁻, SO₄²⁻, DOC, and elemental analyses. I analyzed NO₃⁻ on a Lachat QuikChem 8000 flow injector analyzer, and analyzed SO₄²⁻ using an ion chromatograph. Samples for DOC, NH₄⁺, and elemental analysis were sent to the Cornell Nutrient Analysis Laboratory.

Field samples for DIC were collected in 20 mL syringes (10mL water) and brought back to the lab where a 10 mL headspace was added. The sample was acidified to a pH value between 1 and 2 rigorously shaken to convert all DIC into CO₂. The headspace then was subsampled and analyzed on a Varian gas chromatograph. At pH 2, all DIC present should be in the form of CO₂, in equilibrium between the water and air,

allowing use of Henry's law and the concentration of CO₂ in the syringe headspace to calculate the total DIC in the water sample.

Samples for groundwater dissolved CO₂ were taken based on the methods of Hope et al. (1995) and Kling et al. (1991, 1992). Twenty milliliters of ground water were collected from piezometers using syringes fitted with a three-way stopcock on the Luer end to prevent contact with ambient air during pumping. A 20mL nitrogen headspace then was introduced from a gas bag, and the syringe was shaken for five minutes. The headspace was subsampled in a 20mL syringe and stored in the dark, at ambient temperature, for transport to the lab to prevent gas contamination due to volumetric changes. Carbon dioxide concentration was measured on a Varian gas chromatograph, and Henry's Law was used to calculate dissolved CO₂ in the original ground water sample (Hope et al. 1995).

Reciprocal Ground Water Incubation

A reciprocal ground water incubation was undertaken to determine if differences in groundwater chemistry could be responsible for the observed differences in field CO₂ concentrations. I chose two sampling locations based on groundwater chemistry data from 2000 (Bailey, 2004). One location (JP7.5) was chosen assuming its hydrology was dominated by the lateral flow zone, prior to the upwelling of deeper ground water. The other location (JP8.5) was assumed to be located in the upwelling zone, and thus assumed to experience different groundwater chemistry than JP7.5. However, the close proximity of these sites and more recent hydrologic data suggests that these sites may not be seeing

large differences in their groundwater nitrate, sulfate, and other ions examined in this study.

In an attempt to determine if groundwater chemistry or peat characteristics were influencing soil respiration rates, I incubated peat samples from each location in vitro in ground water from both sample locations. Three cores were taken from each sample location in 14 cm long, 5.2 cm diameter PVC cores, minimizing air exposure, and were transported to the laboratory in a cold dark cooler. The bottom centimeter was cut off each core and discarded. I then carefully cut off the next centimeter (from ~13cm below the peat surface) and divided it into four sections to be used in the incubations, noting if there were visible differences in the peat composition. I measured the wet weight of each section for later conversion to dry weight. Additional samples from the centimeter above the section sampled for incubation were weighed and dried to determine percent moisture. The volume of peat used in the incubations was chosen based on the size of the incubation jars, the estimated CO₂ production rates, and the sensitivity of the gas chromatograph.

Two sections from each core then were placed on a sieve and washed with 2 mL of the water in which they would be incubated (either from JP7.5 or JP8.5). Water from each of the two locations were taken from ~30 cm below the peat surface using piezometers. Each soil section was placed in a 0.355 L mason jar with 15mL of treatment water with no pre-incubation. The jars were sealed and flushed with N₂ eight times to create an anaerobic environment. The jars were incubated in a dark, temperature-controlled room at approximately 23°C. The headspace was subsampled via syringe (after light swirling to mix the gasses) at regular intervals for 24 hours, and carbon

dioxide concentration was determined by gas chromatography. I approximated soil respiration by measuring CO₂ increase in each incubation jar over time, assuming that this increase would be proportional to the amount of carbon respired by microbes in the peat. I then performed an analysis of variance to determine if the effects of soil and water significantly impacted CO₂ accumulation rates.

Sulfate Amendment Experiment

To investigate the effect of sulfate on carbon dioxide production, cores were taken with a peat corer at either two or three depths at each location along the transect (JP2, JP6, JP7.5, JP8.5, and JP10). If the total peat depth was shallow (less than 1m), two cores were taken, one from 5-20 cm below the surface and one at the bottom of the peat, including some of the adjacent mineral soil. Where the peat was >1m deep (JP2) three cores were taken, one from 5-20 cm below the surface, one from the bottom of the peat layer (~1.5 m), and one from an intermediate depth, of approximately 50 cm, to compare to the same depth as the deep cores from the other sample locations.

I took subsamples from the middle of each surface core (below the water table), and from 2-5 cm above the mineral soil boundary for deep cores. One subsample was used to determine percent moisture in each core, and other subsamples of approximately the same wet weight (~20 g) were placed into mason jars along with 30 mL of distilled water. The jars were evacuated and flushed eight times each with nitrogen gas and set in the dark for five days to allow the microbial community to utilize the sulfate originally present in the peat. After the five days, I took an initial sample of the headspace and analyzed it on a gas chromatograph for CO₂ concentration. I then added the treatments;

to the control I added 2 mL DI, to the sulfur treatment I added SO_4^{2-} solution to bring the sulfate concentration in the jar to 1 mM, to the carbon treatment I added 2 mg glucose per gram dry peat (Joe Yavitt, Cornell University, personal communication), and to the “both” treatment I added SO_4^{2-} to 1 mM and glucose to 2 mg/g. I sampled the headspace regularly over 48 hours and analyzed the gas samples on a gas chromatograph. I used a linear regression to determine the CO_2 accumulation rate in each incubation jar, and ran an analysis of variance and Tukey multivariate analysis using the S-Plus statistical software package to examine differences among treatments.

Results

Groundwater Flow Data

The JPF ground water system is dominated by two major flowpaths (Figure 2, Bailey 2004). The first is just below the land surface, with flows from the upland end of the transect (by JP1) toward the pond just beyond JP11. I refer to this flowpath as the subsurface flow. A second flowpath appears to flow from deeper within the peat, below JP1 and JP2, toward the surface in the middle of the fen, in the vicinity of JP6 and JP7, where this ground water presumably mixes with water from the subsurface flow. I refer to this flowpath as the deep flow. Previous groundwater chemistry analysis (Bailey 2004) indicates that this deep flow might be influencing local groundwater chemistry by supplying sulfate-rich water to surface peat.

In general, groundwater flow patterns at JPF are similar over time (Bailey 2004). The hydraulic head data gathered in June 2003 showed the same general flowpaths as in 2002, and substantiate the idea that hydrologic flow is relatively constant in this system.

The water table as measured in 2003 varied less than 5cm from the average water table data taken by Bailey (2004) which incorporated 9 sampling dates between May and December 2002, so these average values were used to interpret chemical data in this study.

Dissolved carbon dioxide analysis

Groundwater-dissolved carbon concentrations for 2002 generally were greater near the surface, and decrease with depth (Figure 3). The largest concentrations were found at JP6 (158 mg C/L), followed by JP7 (111.5mgC/L). CO₂ concentrations farther back along the deep groundwater flowpath (from JP2 to JP5) and are much lower than the concentrations at JP6 and JP7, indicating that these large surface values are not likely to be a result of greater CO₂ delivery from groundwater flow. Dissolved carbon dioxide measurements taken in June 2003 show a pattern of carbon dioxide concentration similar to the 2002 data, with the highest values at the surface and lower values with depth (Figure 4). The highest observed CO₂ concentration remained at JP6 (97.06 mgC/L), and was less than the value observed in the previous year, which *may be due to differences in climate during the time the samples were taken*. Also, there was an unusually low CO₂ concentration at JP7.5 in 2003 (14.04 mgC/L) which does not fit the overall pattern of highest CO₂ concentrations in water near the fen surface.

Groundwater sulfate concentrations

The highest concentration of sulfate in ground water in 2003 was found at the surface at JP6 (70.3 mg/L) (Figure 5). The general pattern was one of greater sulfate

concentrations 50 cm or more below the peat surface and lower concentrations nearer the surface. Surface concentrations directly downgradient from JP6 are much lower. In 2002, sulfate concentrations are similar, with the highest values at JP6, JP7, and JP9 and generally lower values with depth (Bailey 2004). The lack of a clear spatial pattern in sulfate concentration suggests that something in addition to groundwater flow is controlling dissolved sulfate pool size across the transect.

Other groundwater chemistry

Groundwater ammonium analysis showed very low levels of ammonium across the fen. Most samples were below detection limits, with the highest concentration reaching 0.5mg/L N-NH₄. Nitrate analysis also showed very low nitrate levels across the transect (Figure 6). The highest level was found at JP6 (0.3mg/L N-NO₃), with most below 0.2mg/L. Levels were higher with depth at JP2, suggesting that groundwater flow might be partly responsible for the higher values at the surface at JP6.

The pH was circumneutral across the site, with highest values closest to the pond and the lowest value at site JP6 (Figure 7). This is not surprising considering the high values of dissolved CO₂ at JP6 and the interconnectedness of carbon equilibria and pH. A plot of pH against the measured CO₂ in ground water shows a negative correlation, which explains 65% of the variability in observed pH across the fen (Figure 8).

Dissolved organic carbon concentrations (DOC) are higher near the surface and generally decrease with depth (Figure 9). They also seem to decrease with proximity to the pond. Dissolved inorganic carbon (DIC) concentrations show a similar pattern as the DOC, with concentration generally decreasing with depth (Figure 10). However, DOC

begins to greatly increase near the surface at JP8.5 and continues to do so toward the end of the transect at JP10.

Ground water influence on soil respiration

Carbon dioxide accumulation rates from the control incubations with both soil and water from the same site (either JP7.5 or JP8.5) showed statistically higher rates of CO₂ accumulation for incubations from JP8.5 than incubations from JP7.5 (Figure 11). Regardless of peat origin, rates of CO₂ accumulation were higher in incubations conducted with ground water from JP8.5, than with ground water from JP7.5 (Figure 11, Table 1). Origin of the peat did not appear to have a significant effect on CO₂ accumulation rate. Analysis of variance indicated that there was a statistically significant effect of water type on CO₂ accumulation rate (P=0.01), but not of soil origin (P=0.97).

Sulfate amendment incubation

Carbon dioxide concentrations in the incubation jars of all treatments increased linearly in the beginning of the incubation, and continued to increase over the remainder of the incubation. The rates of CO₂ accumulation for each jar were found by conducting a linear regression analysis using the least-squares fit model, to obtain the rate of change of CO₂ over the first approximately 8 hours. Rates of CO₂ accumulation in the jars ranged from 0.1 to 0.4 umol CO₂/g dry soil/hour (Figure 12).

Peat from sampling location JP2 was the most responsive to incubation treatment (Figure 12a). At all three depths sampled, the addition of glucose increased the rate of CO₂ accumulation in the headspace. Also, shallow peat incubations showed an increase

in CO₂ accumulation rate in glucose and sulfate amendments compared with the glucose-only treatments. At JP8.5 and JP10, rates of CO₂ accumulation at both depths did not differ significantly from the control under any treatment (Figures 14c, 14d; Table 2). Peat from sampling locations JP6 and JP7.5 showed increased CO₂ flux only with glucose amendment to surface peat (Figures 12a, 12b; Table 2).

Within each of the five sampling locations, there was a distinct difference in CO₂ accumulation rate between surface and deep peat samples (Figures 12a-e). Rates of accumulation in surface samples were higher in almost all instances than in deeper peat samples from the same location. Within each site, there were differences in the response of peat slurries to the various treatments. Overall, there was a larger response to incubation treatment on surface peat samples and in samples from sites that were closer to JP2 (Table 3).

Discussion:

Interaction between hydrologic gradients and groundwater chemistry

There appears to be a correlation between hydrologic gradients and groundwater chemical pool sizes. The hydrologic profiles and patterns of groundwater flow, as well as water table levels, have stayed relatively stable between 2002 (Bailey, 2004) and 2003. This stable flow of water appears to affect electron acceptor pools and groundwater chemistry in surface peat at Junius Ponds Fen.

Location JP6 has unusually high concentrations of many measured hydrochemicals, including carbon dioxide, sulfate, nitrate, and DIC compared to other locations in the fen. It seems likely that this is a result of groundwater flow and the

interface between peat and mineral soil. At JP5 there is an abrupt decrease in peat depth, forming an interface between peat and mineral soil that slopes toward the surface between JP5 and JP6. Because the underlying mineral soil has a greater bulk density than the peat (Bailey 2004), ground water likely will be deflected upward toward the surface where it encounters this interface. The hydraulic head contours and position of the water table indicate that there also is a significant flow of ground water in the peat near the surface of the fen, intersection the water table around JP6. From the sulfate data, we see that the deeper ground water is enriched compared to surface water, so deep ground water upwelling at JP6 would contribute further to the sulfate supply from lateral flow at this location. This would cause a concentration of ground water at JP6, and an accompanying concentration of ions carried in ground water. Location JP2 also has higher sulfate pool concentrations than other locations along the transect. In this case, its position near the interface with the upland would cause it to experience a larger influx of sulfate in laterally flowing ground water from the adjacent upland.

Nitrate concentrations show the same spatial patterns as sulfate, although the concentrations are below 0.5 mg/L, and are not likely large enough to provide a significant source of alternate electron acceptors unless they are being consumed too quickly to maintain a larger pool size. High competition for nitrate as a plant nutrient makes it likely that rapid uptake as an electron acceptor would be limited. Similar results have been found in many other studies of fen hydrochemistry, showing that groundwater flow is a major factor in supply and cycling of nitrate, phosphate and sulfate within a wetland (e.g., Hill et al., 2000; Carlyle and Hill, 2001; Devito and Hill, 1997). The similarities between the spatial patterns of nitrate and sulfate, in conjunction with the

hydrologic contours, provides evidence that groundwater flow patterns are a major factor controlling electron acceptor pool sizes within the fen.

Implications for dissolved carbon dioxide

Understanding the processes that influence dissolved CO₂ concentrations is important to understanding the ecological function of a fen. From a geochemical perspective, dissolved CO₂ influences speciation of carbonate minerals and the availability of nitrogen and phosphorus to wetland plants. This is particularly important in the rich fens of New York because species diversity has been shown to relate to the availability of nitrogen and phosphorus (Bedford and Bailey, unpublished data). Another potential impact of high dissolved CO₂ levels is that high levels can decrease local pH values, which in turn could contribute to the dissolution of calcite minerals. An increase in the partial pressure of CO₂ has been shown to inhibit calcite precipitation, causing an increase in phosphorus mobilization (Komor 1994, Boyer and Wheeler 1989). Thus, by better understanding the controls on CO₂ production, and spatial patterns of CO₂ concentrations in ground water within a fen, we can gain insight into the controls on phosphorus availability in rich fens.

Preliminary groundwater sulfate data suggest that sulfate might be responsible for the high CO₂ concentrations observed at JP6. Concentrations in the surface peat at sites other than JP6 within the peat layer are low enough to limit rates of sulfate reduction. Generally, rates of sulfate reduction are thought to be limited at concentrations below 200uM (19.2mg/L) (Joseph Yavitt, Cornell University, personal communication), which suggests that the high sulfate concentration at JP6 (70.3mg/L) has the potential to

overcome sulfate limitation and stimulate sulfate reduction. Previous studies have shown that sulfate reduction rates can be positively correlated with sulfate pool size under certain site conditions (such as high labile carbon), which suggests that sulfate reduction could be limited by sulfate concentration (Wieder et al., 1990; Lamers et al. 1998).

Hydrochemical effect on soil respiration

The reciprocal ground water incubation data suggest that groundwater chemistry can be important in stimulating rates of CO₂ production in peat from JPF. If ground water were not an important factor in CO₂ production, we would expect either no difference in CO₂ production rate, or higher rates for each peat when incubated in its own ground water (in control treatments). However, ground water from JP8.5 stimulated higher CO₂ production rates in peat from both sites, which suggests that groundwater chemistry is affecting CO₂ production in the field.

However, the analyses of groundwater chemistry conducted after the incubation indicated that the only significant difference in measured chemical species between the sites is in dissolved inorganic carbon (DIC), which varied from 17.8 mg/L at JP7.5 to 39.1 mg/L at JP8.5, and paralleled the CO₂ gradient between these two sites (Figures 3, 10). Repeating this experiment with samples from more locations with distinctly different groundwater chemistries along the groundwater flow path, including JP6, would provide more insight into this relationship. Also, to account for variations in dissolved CO₂ in the ground water during the incubation, bubbling with an inert gas would remove any differences in degassing from the water column during the experiment, giving a more accurate measurement of CO₂ production.

Sulfate effect on soil respiration

Data from the sulfate amendment incubation do not support the hypothesis that sulfate supply is responsible for high CO₂ concentrations in ground water at JPF. If sulfate supply was responsible for higher field CO₂ concentrations, we would expect fertilization of peat cores with sulfate in the laboratory to result in higher CO₂ production. This result was not obtained from laboratory incubations. Only peat from the surface at JP2 showed a response to sulfate and glucose amendments. This may be because this site is closest to the upland in a more heavily vegetated area, and receives higher input of fresh organic matter to support higher microbial populations. This suggests that at JP2, sulfate may play a significant role in CO₂ production, however, the lack of surface CO₂ and sulfate concentration data from this location makes it difficult to substantiate this result in the field. Based on the data obtained in this experiment, it does not appear that sulfate supply is responsible for the large dissolved CO₂ pool found at JP6.

Patterns of sulfate reduction along the groundwater flow path

Data from the sulfate amendment incubation do not support the hypothesis that sulfate reduction will be restricted to areas with high groundwater sulfate supply. If sulfate reduction is only occurring in areas of the fen with high sulfate ground water input, we would expect to see the greatest response to sulfate additions in incubations with peat from areas with high field sulfate concentrations. We would expect higher populations of sulfate reducers to be present in the peat samples, thus supporting a larger base population to respond to sulfate amendment in the laboratory. Thus, we also would expect peat taken from JP6 to respond more strongly to sulfate additions than peat from

locations with low field sulfate concentrations. The incubation data, however, do not show this expected pattern of response. Although rates of CO₂ production in control incubations were highest in peat samples from JP6 and JP2 (the locations with highest sulfate delivery), incubations from JP6 failed to show any stimulation with addition of sulfate and glucose as would be expected if high populations of sulfate reducing bacteria were present. One reason may be that partial re-oxidation of sulfur is required for sulfate reduction, since some bacteria use other forms of sulfur to fuel reduction, including thiols and elemental sulfur. This would explain the lack of response that I predicted assuming sulfate was the principal form of sulfur utilized.

Implications for the role of sulfate

Sulfate supply does not appear to be responsible for the very high dissolved CO₂ found at JP6, despite the very high sulfate concentration found at this site. Based on the magnitude of the dissolved carbon dioxide found there, and the assumption that two moles of carbon are mineralized for each mole of sulfate reduced (Conrad, 1989), we can calculate roughly how much sulfate would be required to produce a pool of this magnitude. To produce 97 mg CO₂ entirely by sulfate reduction, 106 mg of sulfate would be necessary, which is larger than the sulfate pool at this site. Sulfate could be entering in groundwater flux and cycling actively within the peat to maintain a high enough viable supply to produce this much carbon dioxide, however reduction of this much sulfate would produce 70.5 mg of sulfide. Hydrogen sulfide released in this amount would be highly toxic unless oxidized rapidly, and we did not smell sulfide above the peat surface. We did detect sulfide in the ground water from some piezometers,

suggesting that some sulfate reduction is taking place. Nonetheless, the incubation data show that it is not likely the dominant form of anaerobic decomposition. Experimentally determining the actual rates of sulfate reduction along the site could provide insight toward the quantitative role of sulfate reduction in total anaerobic metabolism, and examination of iron dynamics (and possible Fe-P precipitates) and alkalinity (and possible marl formation) could provide insight toward the potential fate of sulfide in the system.

Implications for labile carbon availability

An interesting outcome of the glucose amendment incubations is that not all peat samples responded to glucose addition. Only samples from JP2 and the surface of JP6 and JP7.5 showed increased CO₂ production with glucose addition. One explanation for the lack of response to glucose amendments by the microbial community in some cases is that microbial populations in the field may be very low. When the lability of carbon in the field is considered, this appears to be a viable explanation. For example, rates of CO₂ production in the laboratory were higher for surface peat samples than for deep peat samples from the same sampling location. We would expect this, because higher labile carbon is usually present in surface peat that is not as decomposed as deeper peat. This higher availability of labile carbon would support higher microbial populations which, when brought into the laboratory, would show a higher respiration rate per weight of dry soil and would show more response to incubation conditions. However, the failure of surface peat from sites JP8.5 and JP10 to respond to glucose amendments suggests that factors other than labile carbon supply in the field might be involved. It is unlikely that

these surface locations had microbial populations that were too low to respond to laboratory incubation. One possibility is that during the pre-incubation the microbial community exhausted the supply of available electron acceptors, so that upon glucose addition the community did not have the means to carry out anaerobic carbon dioxide production. Repeating the experiment with nitrate addition would allow a more in-depth look into the impact of electron acceptor availability compared to carbon quality.

Peat samples taken from along the transect at JPF had bulk densities that ranged from 0.24 g/cm³ (at JP5) to 0.77 g/cm³ (at JP1) (Bailey 2004), which is much higher than typical values for wetland peat (Mitsch and Gosselink, 1993). These substantiate the field observation that the peat at JPF appears very decomposed. According to the ranges in bulk density reported for peat of varying decomposition stages by Verry and Boelter (1978), the observed bulk densities of peat samples collected at JPF fall in the range for sapric peat, which is characterized as having at least two-thirds of the organic material decomposed (Mitsch and Gosselink, 1993). In fact, much of the peat at JPF is well above the minimum bulk density for sapric peat, indicating that it is much more than two-thirds decomposed, and likely has very low labile organic carbon content.

DIC values at JPF (12-41 mg/L) were generally in the same range found in bogs by Yavitt (1994) (6-30 mg/L) despite the differences in site pH. Concentrations of DOC found at JPF were lower than in other peatlands. Yavitt (1994) found DOC concentrations in bogs of West Virginia and Maryland to be between 4000 and 12000 μ M (48-144 mg/L), which was higher than reported values in similar ecosystems (24-59 mg/L). The DOC numbers found in JPF were between 1 and 13 mg/L, much lower than the low range of these values. This further suggests that carbon availability may be

limiting in this fen, or that aerobic decomposition at the very surface of the peat is causing conversion directly to CO₂, with no accompanying DOC production.

Other studies have shown that rates of sulfate reduction in wetlands can be limited by the supply of labile organic matter. Lamers et al. (1998) showed that in a mesocosm, sulfate availability was initially limiting the rate of sulfate reduction; over time the supply of labile organic matter became limiting as its supply was depleted. Vile et al. (2003) found in a freshwater bog fertilized to mimic increased sulfate from atmospheric deposition that initial sulfate reduction rates were limited by sulfate availability, but over time labile carbon availability became limiting. A similar result has been found in coastal marine sediments where sulfate is in abundant supply. Berner and Westrich (1985) found that factors associated with organic matter availability are the primary factors limiting rates of sulfate reduction in a coastal wetland.

Implications for ecosystem function

Peat from JPF has a higher bulk density than most surface peat samples from other rich fens across central New York (Bedford and Bailey, unpublished data). The fen also is the only of these fens to be situated in a calcium-sulfate terrane rather than the more typical calcium-carbonate geology of the region. This suggests a tentative link between catchment geology and decomposition in fens. Since the vast majority of the peat surface at JPF, and many of the other fens in central New York, is below the water table (Bedford and Bailey, unpublished data), anaerobic decomposition is the primary pathway of carbon mineralization. Thus decomposition typically takes place slowly, allowing for the accumulation of carbon-rich peat. At JPF, high sulfate delivery rate as a

result of groundwater flow could be increasing anaerobic decomposition of new organic matter in comparison with other fens, explaining the highly decomposed peat at JPF. Since much of the labile organic carbon has been utilized, further sulfate amendment likely would not significantly stimulate anaerobic respiration rates in the field, potentially explaining how high sulfate pool sizes at the site. Also, populations of microbes may be able to sustain moderate rates of sulfate reduction in the field fed by a continuously replenishing supply of labile carbon, even though they didn't respond to short-term laboratory incubations. This would support the field observation that there is hydrogen sulfide present in ground water.

Alternative explanations for trends in carbon dioxide

Another interesting pattern emerges when considering iron concentrations in the ground water across the site. At the site with the highest sulfate and CO₂ values, concentrations of dissolved iron also are much higher than elsewhere in the site (Hayn, unpublished data). There also is lower total iron in the peat at this location than in the immediately surrounding area. This suggests the possibility that dissolved iron is accumulating in this area as a result of the groundwater flow paths and could be participating in redox chemistry. Iron is a more energetically favorable alternate electron acceptor than sulfate (Mitsch and Gosselink, 1993) and can be re-oxidized and recycled within the loop in situations with very low dissolved oxygen conditions (William Ghiorse, Cornell University, personal communication), such as those found around plant roots. Iron reduction may be the reason why sulfide can be smelled in ground water samples, but not above the peat surface, since reduced iron may precipitate with sulfide.

Further study into iron cycling and transport at JPF would elucidate its effect on anaerobic metabolism within the fen.

Conclusion:

Groundwater chemistry is influencing both surface groundwater chemistry and dissolved CO₂ levels across Junius Pond Fen, and this pattern persists over time. However, it does not appear that the pattern in CO₂ concentrations is a result of sulfate delivery stimulating anaerobic dissimilatory sulfate reduction, despite the substantial delivery of sulfate derived from the local gypsum catchment geology. This experiment suggests that carbon lability may be more important in regulating field levels of soil respiration, although further study would be necessary to determine if this is occurring at JPF.

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Figure Legends:

Figure 1. Junius Ponds Fen location of the ground water transect, shown in gray.

Figure 2. Vertical cross-section along the transect, showing piezometer slot zone (diamonds) and equipotential lines of hydraulic head contours over 2002 (Bailey 2004) and 2003. Arrows show general direction of groundwater flow, which is perpendicular to equipotential lines.

Figure 3. Dissolved CO₂ concentrations (mg/L CO₂) in ground water along the transect in late July 2002. Lines are contours of equal carbon dioxide concentration. The highest concentration is at the surface at JP6.

Figure 4. Dissolved CO₂ concentrations (mg/L CO₂) in ground water along a section of the transect in late June 2003. Lines are contours of equal carbon dioxide concentration. The highest concentration is at the surface at JP6.

Figure 5. Sulfate concentration (mg/L SO₄) in ground water along the transect in mid-August 2003. Lines are contours of equal sulfate concentration. The highest sulfate concentration is at the surface at JP6.

Figure 6. Nitrate concentration (mg/L N-NO₃) in ground water along the transect in mid-August 2003. Lines are contours of equal nitrate concentration.

Figure 7. pH values along the transect in mid-August 2003. Lines are contours of equal pH.

Figure 8. pH values of soil water at various sites across Junius Pond Fen plotted as a function of the amount of dissolved CO₂ in the ground water at each site.

Figure 9. Dissolved organic carbon (DOC) concentration (mg/L C) in ground water in August 2003. Lines are contours of equal DOC concentration. There is very little variation in surface DOC values across the site.

Figure 10. Dissolved inorganic carbon (DIC) concentration (mg/L C) in ground water in mid-August 2003. Lines are contours of equal DIC concentration.

Figure 11. Results from reciprocal ground water incubation. Bars represent the average CO₂ accumulation rate for each treatment. Incubations with water from JP8.5 show higher CO₂ accumulation rates than incubations with water from JP7.5. Error bars show twice the standard error for each set of measurements. S=location from which soil core was taken. W=location from which ground water was taken. Stars and bullets identify statistically significant differences based on analysis of variance (Table 1).

Figure 12a-e. Carbon dioxide accumulation rates in sulfate and glucose amendment incubations. Figures a-e represent data from sites JP2, JP6, JP7.5, JP8.5, and JP10, respectively. Higher rates were observed in surface peat incubations, and the most consistent response was of the surface peat to glucose-only amendments. At JP2 peat from the mid depth corresponds with the deep depth from the other sites. For the "both" treatment, the three replicates have been averaged, and their SE adjusted accordingly. Error bars represent two standard errors. Statistically significant differences are summarized in Table 3 based on analysis of variance (Table 2).

Table 1. Summary of analysis of variance, examining CO₂ production as a function of treatment. Pr(F) values lower than 0.05 indicate significance to 95% confidence.

a. Reciprocal ground water experiment; CO₂ production as a function of soil and water type used in the incubation

	Df	Sum of Sq	Mean Sq	F Value	Pr(F)
soil	1	0.000327	0.000327	0.00156	0.9697571
water	1	2.401000	2.401000	11.48010	0.0147077
soil:water	1	0.048167	0.048167	0.23030	0.6482923
Residuals	6	1.254867	0.209144		

Table 2. Tukey multivariate analysis test results for comparison of significance of treatment effects on CO₂ accumulation rates for peat samples from each of 11 sampling locations (JP2 through JP10, s=surface, m=mid, and d=deep). Treatment comparisons that do not include zero are significantly different. The numbers (e.g. 1-2, 1-3 etc.) indicate comparisons between treatments, where treatments 1-4 are assigned as control, +SO₄²⁻, +sugar, and +sugar and SO₄²⁻, respectively.

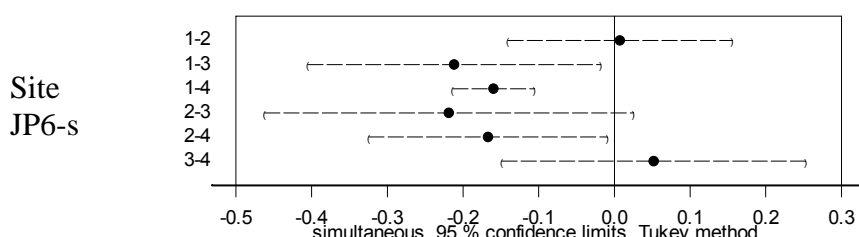
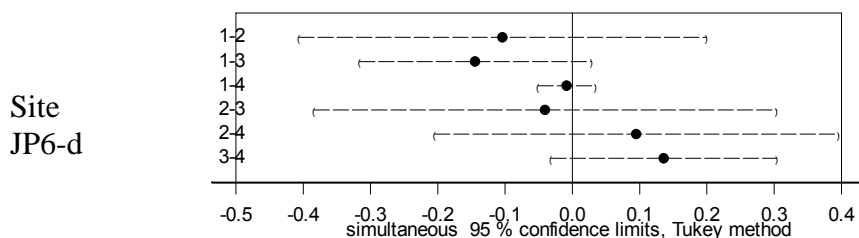
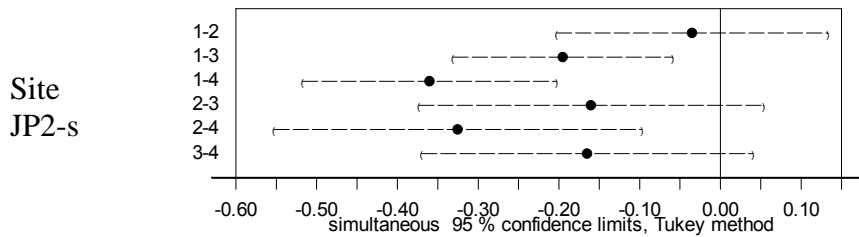
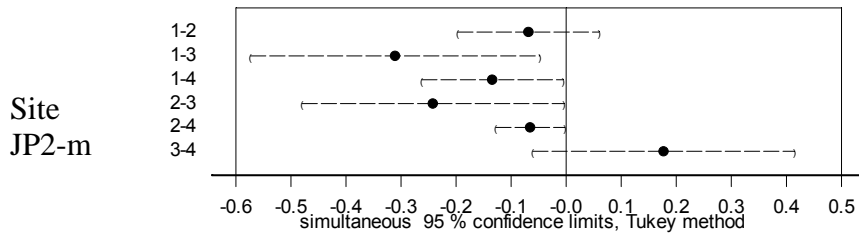
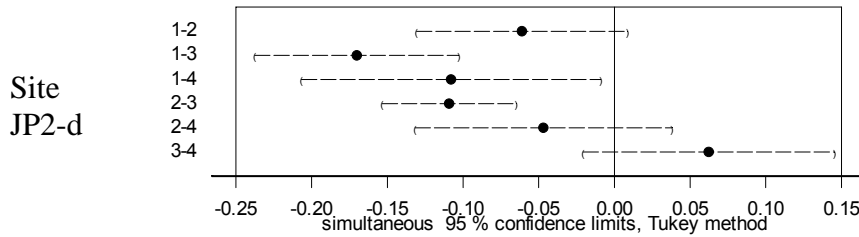


Table 2. Continued.

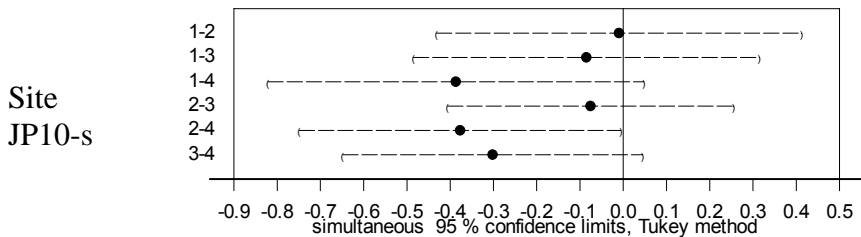
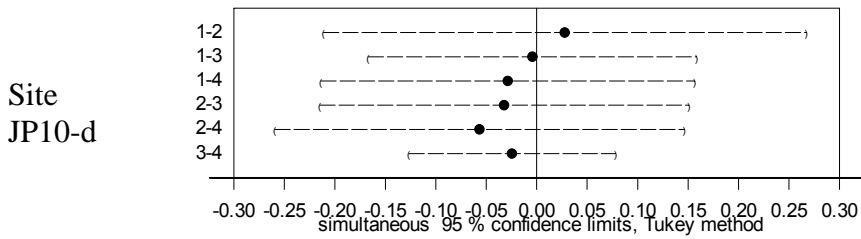
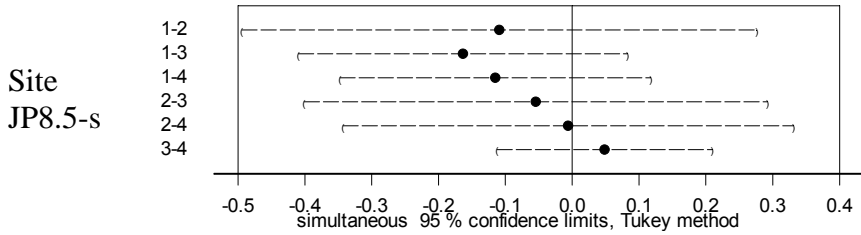
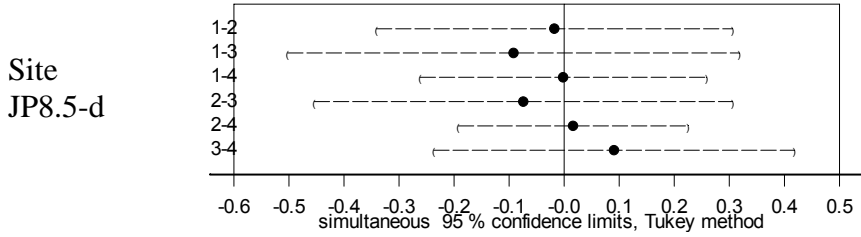
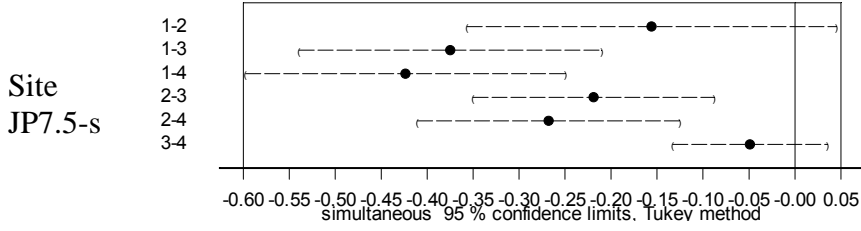
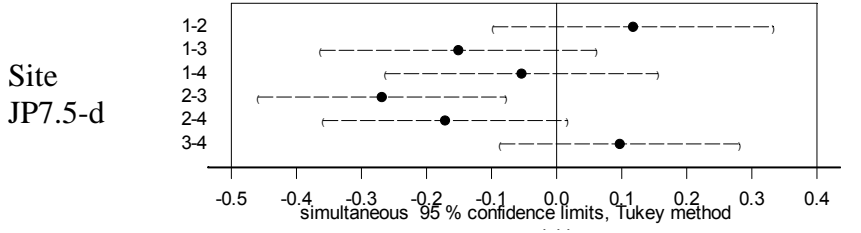


Table 3. Summary of treatments that produced significant increases in CO₂ accumulation rate in incubating jars from five sites in Junius Pond Fen. Boxes indicate an increase in accumulation rate compared to the control jars from the same peat source (for single treatments) or compared to the glucose only for the multiple treatment (both SO₄ and glucose addition). Significance was determined using analysis of variance/Tukey multicomparison tests found in Table 2. It was hypothesized that peat from JP6 would be influenced by both SO₄&glucose based on the hydrologic flow regime.

	SO ₄ only	glucose only	both SO ₄ &glucose
JP2-s		■	■
JP2-m		■	
JP2-d		■	
JP6-s		■	
JP6-d			
JP7.5-s		■	
JP7.5-d			
JP8.5-s			
JP8.5-d			
JP10-s			
JP10-d			

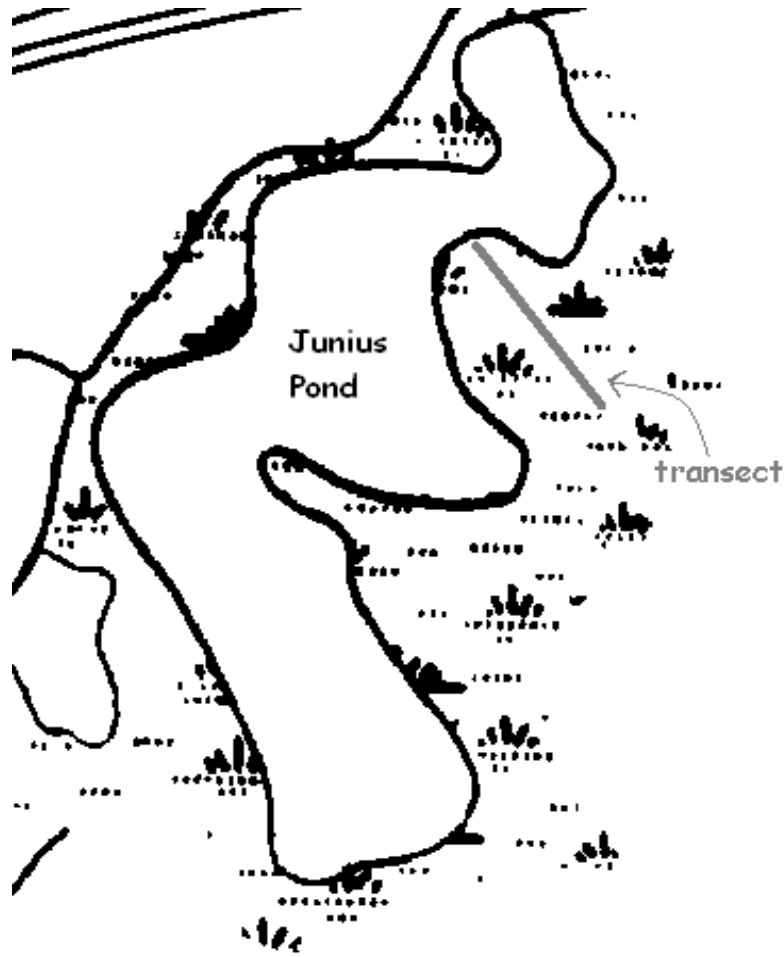


Figure 1. Junius Ponds Fen and location of the groundwater transect, shown in gray.

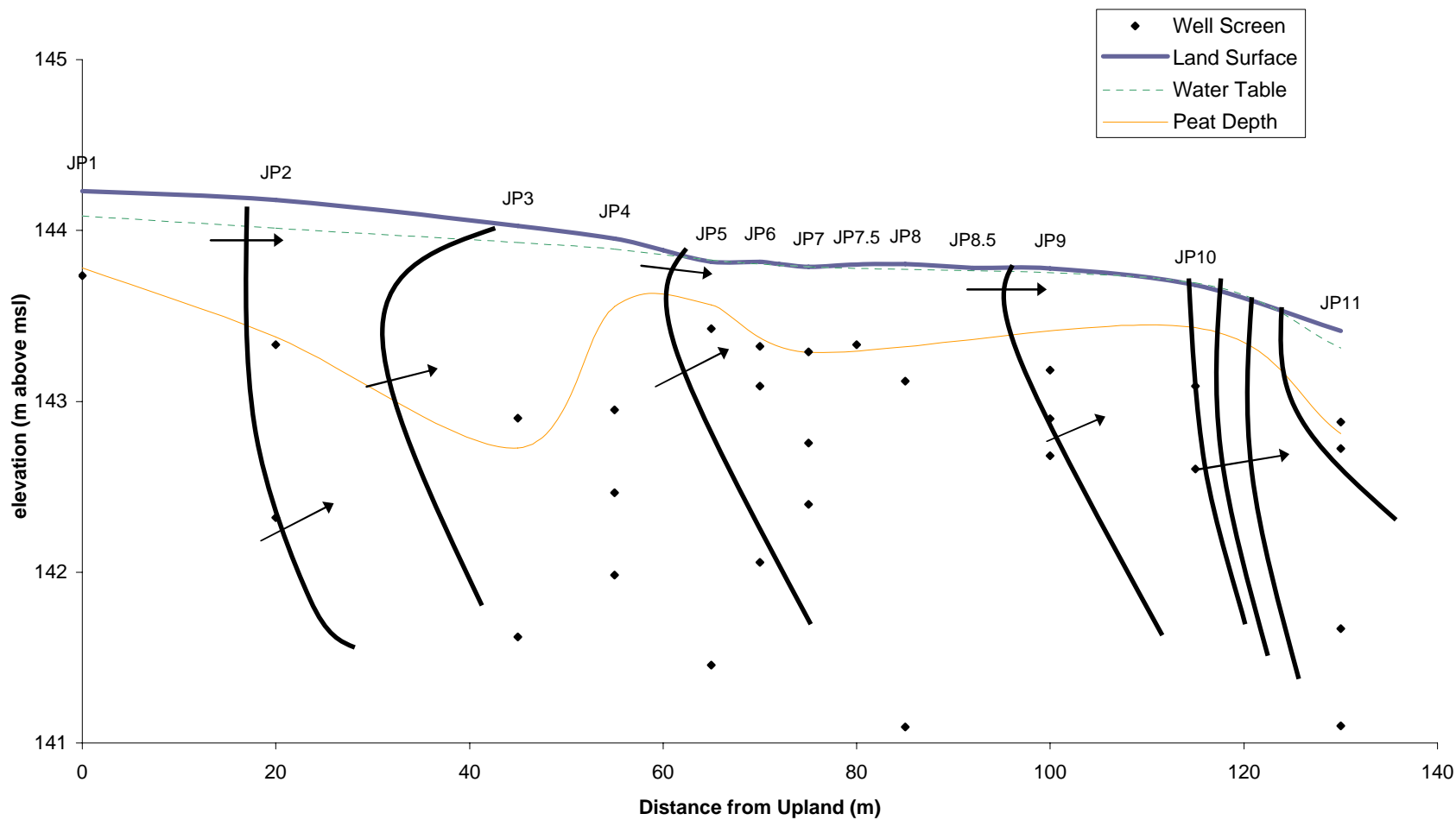


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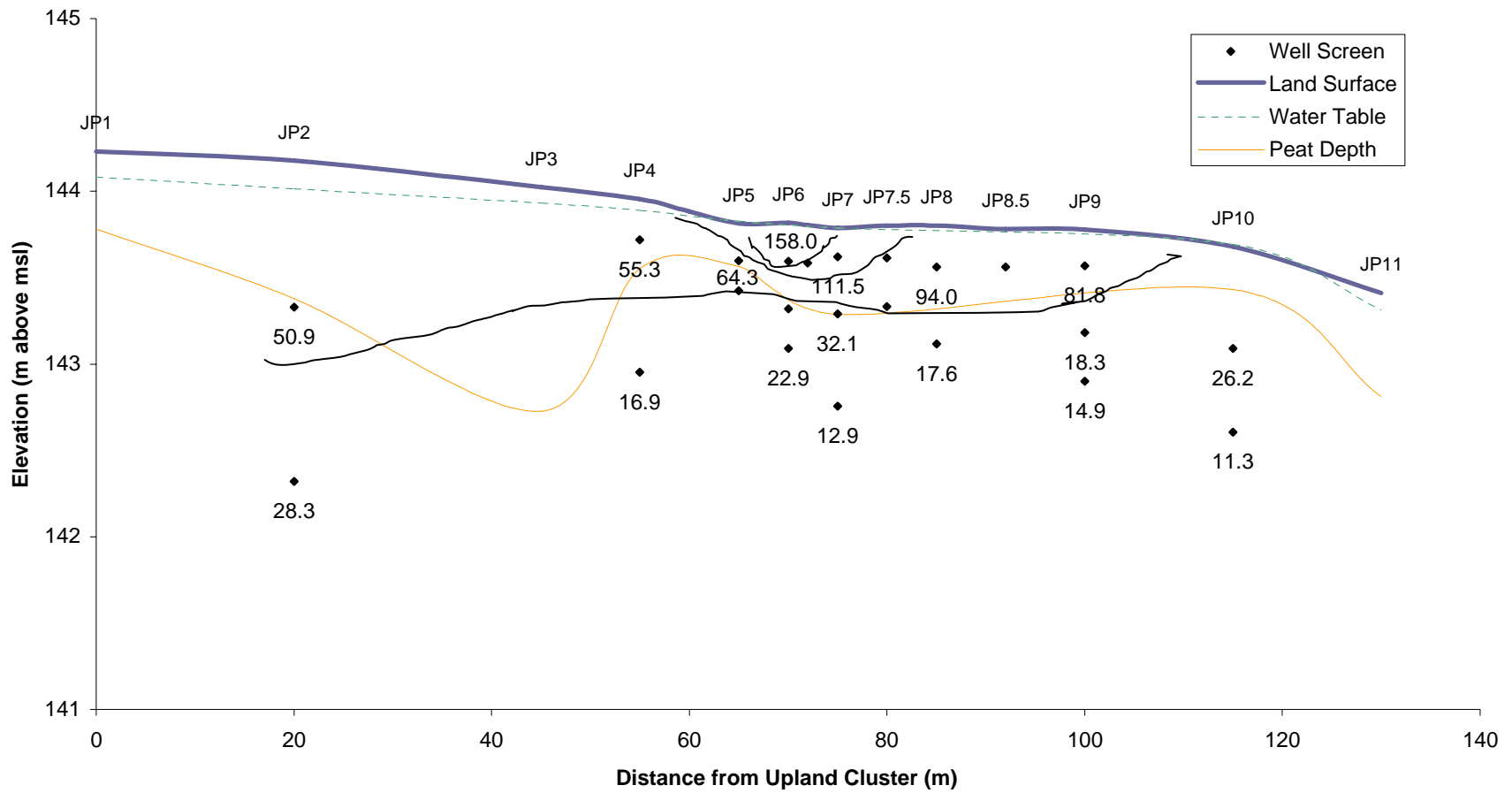


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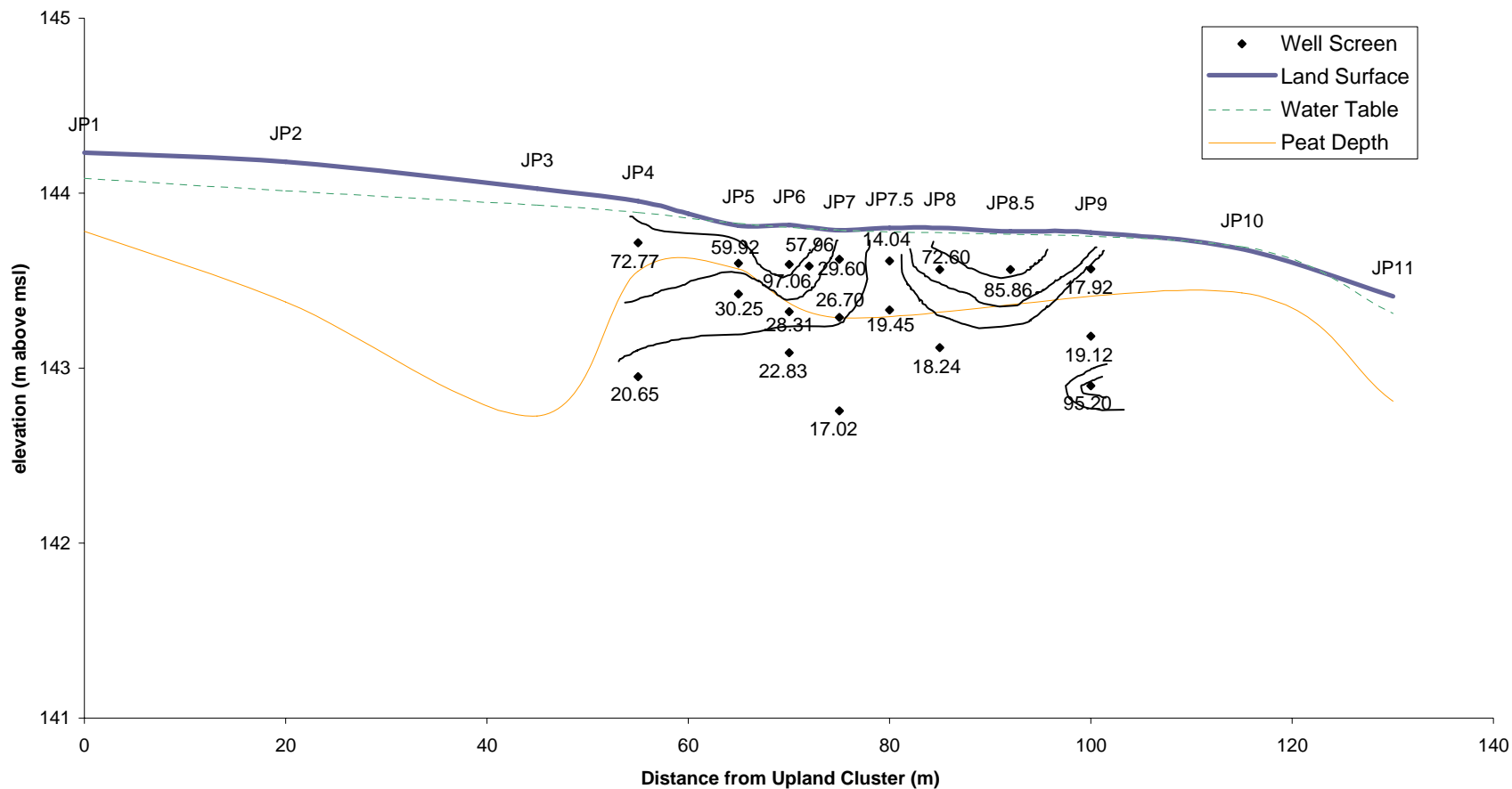


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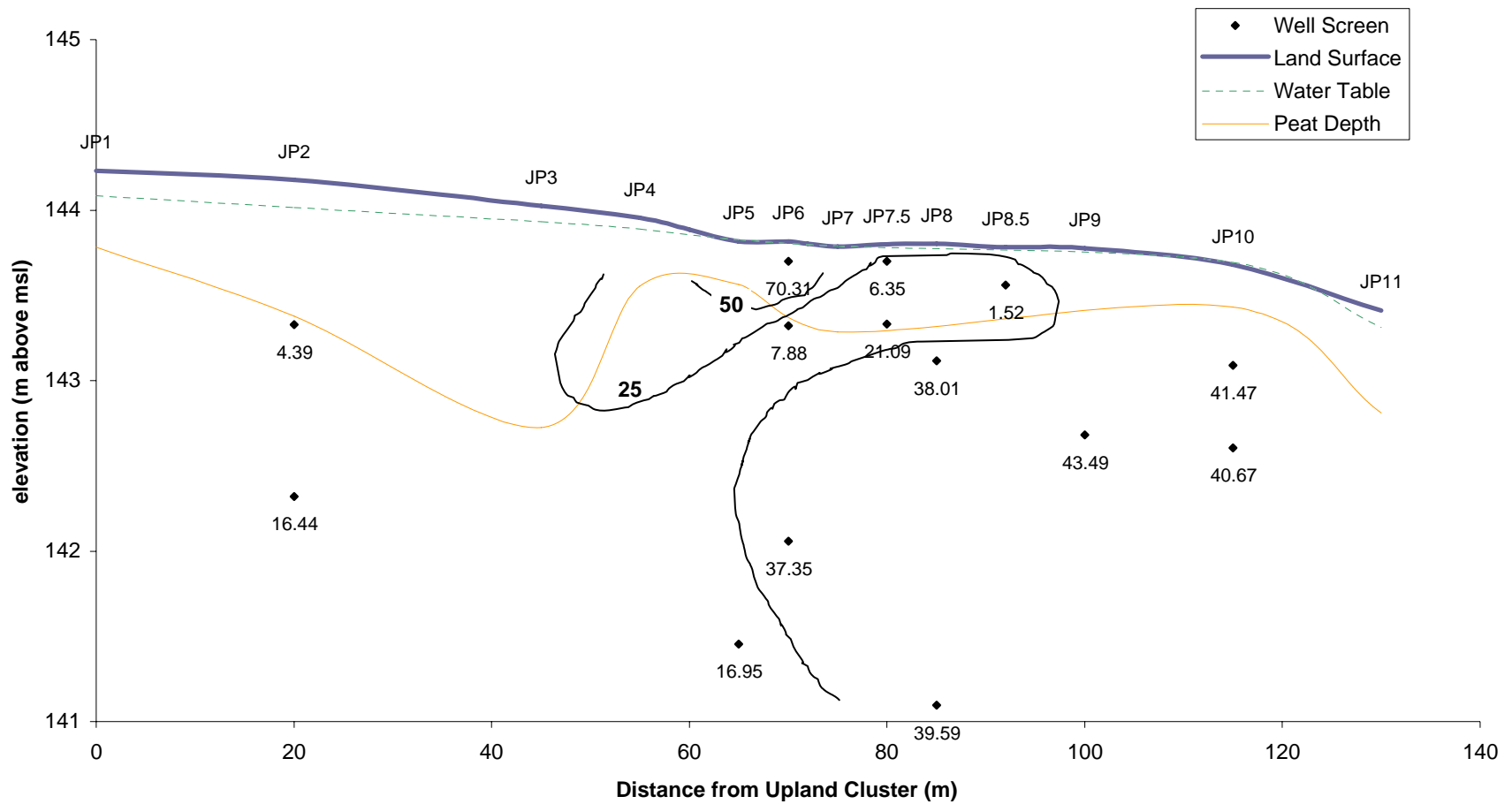


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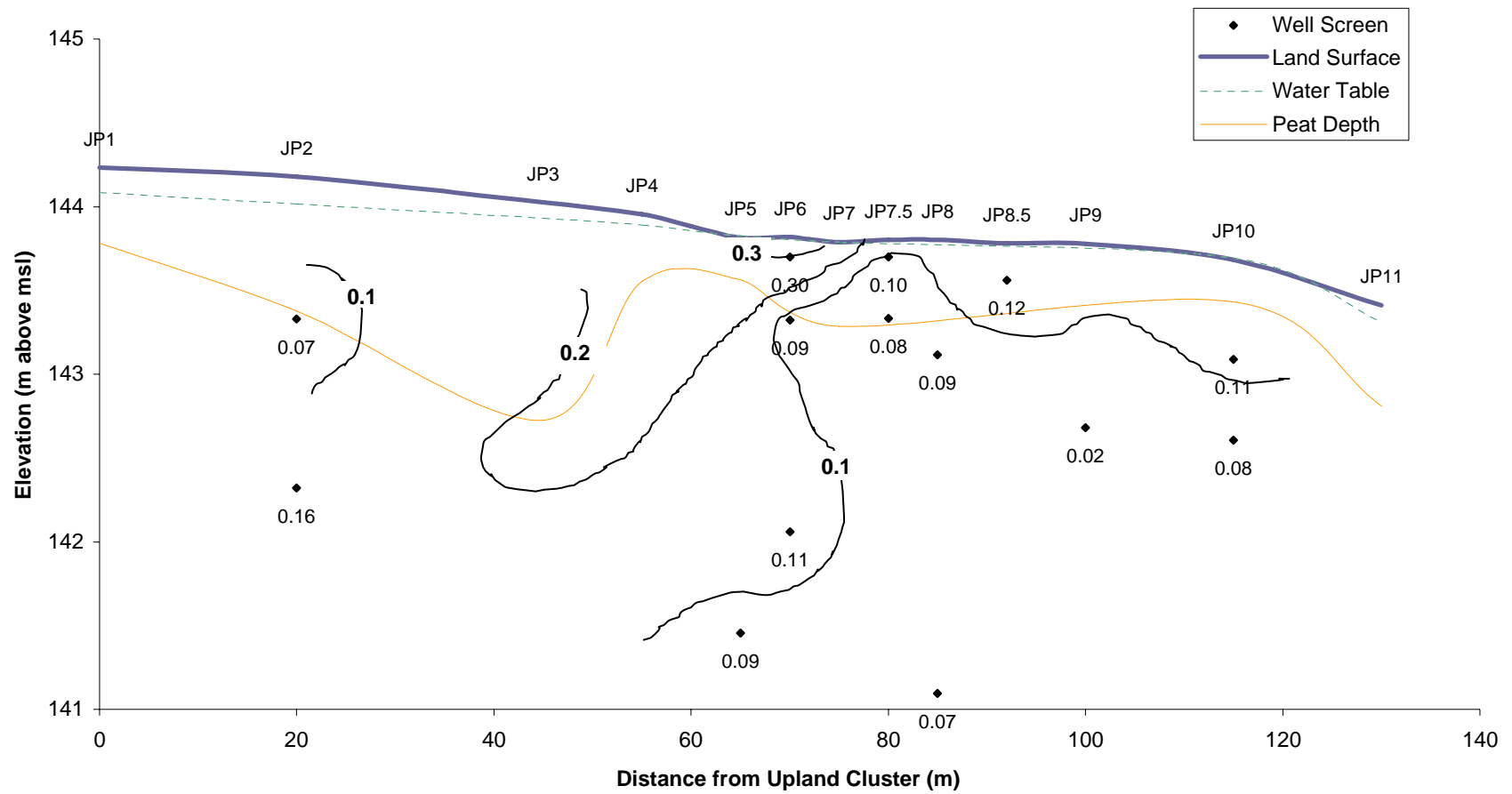


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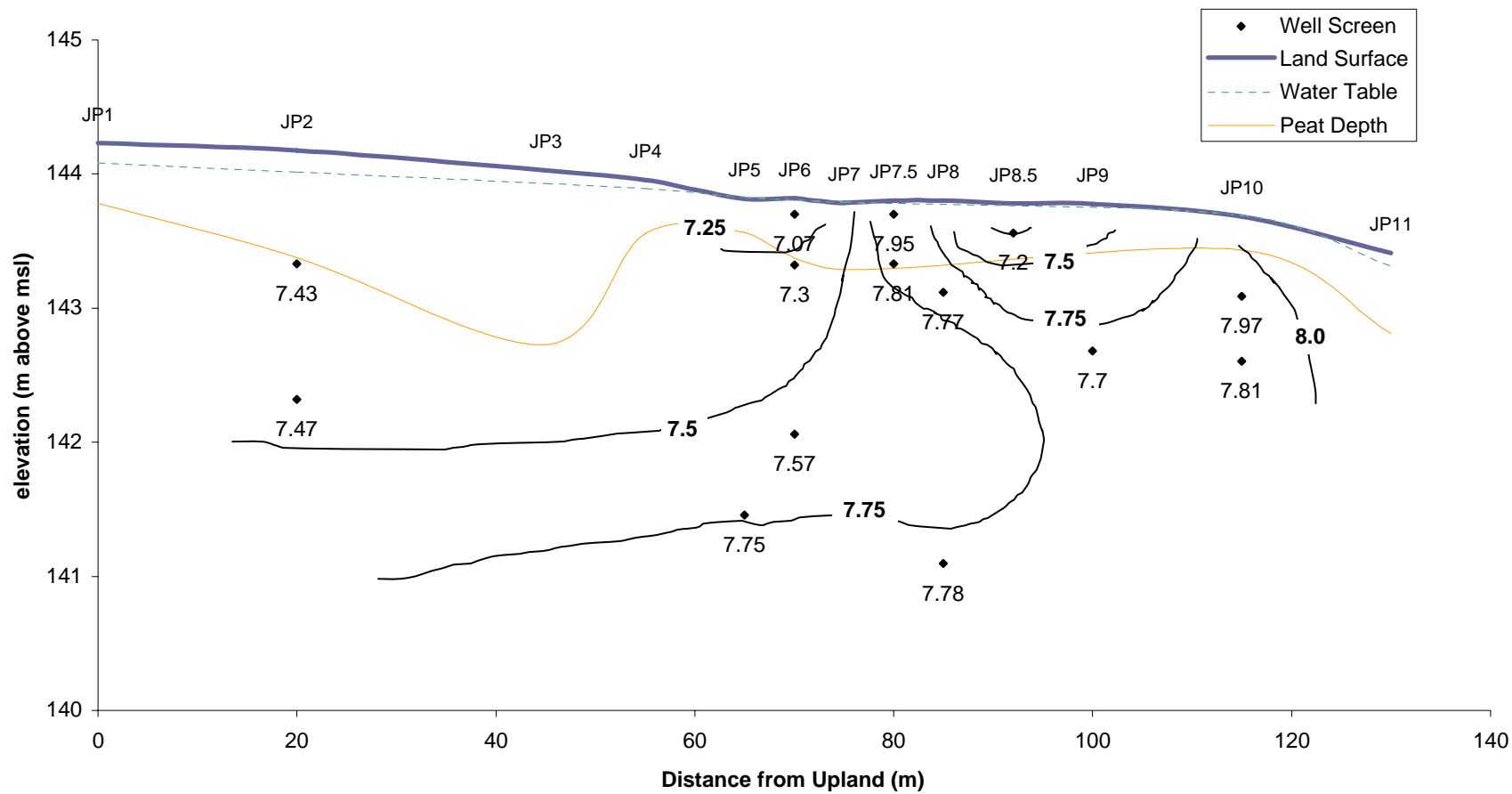


Figure 7. pH values along the transect in mid-August 2003. Lines are contours of equal pH.

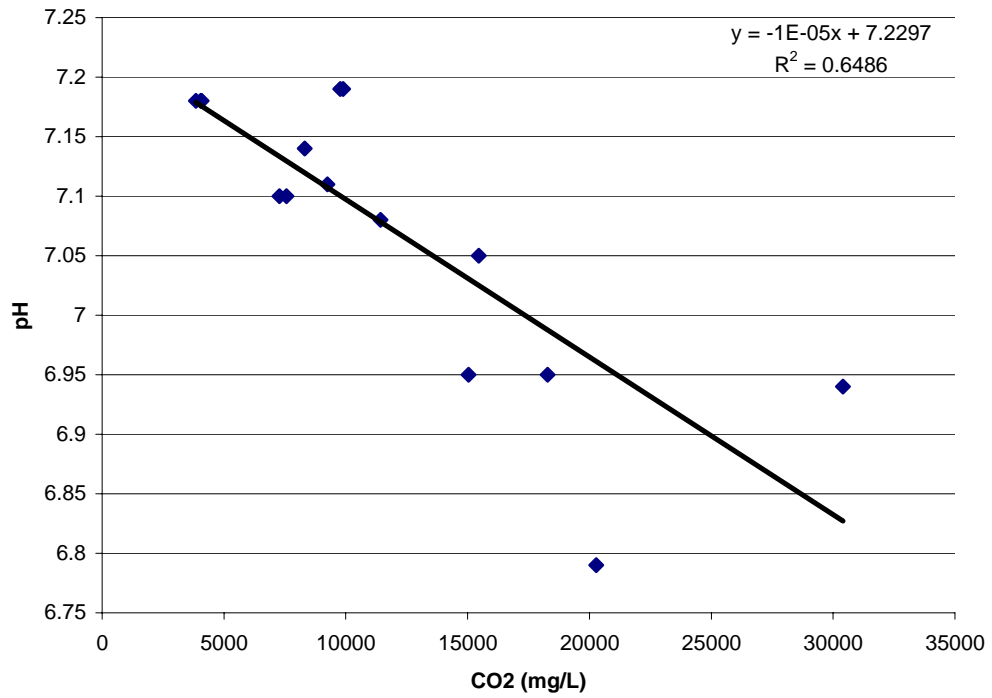


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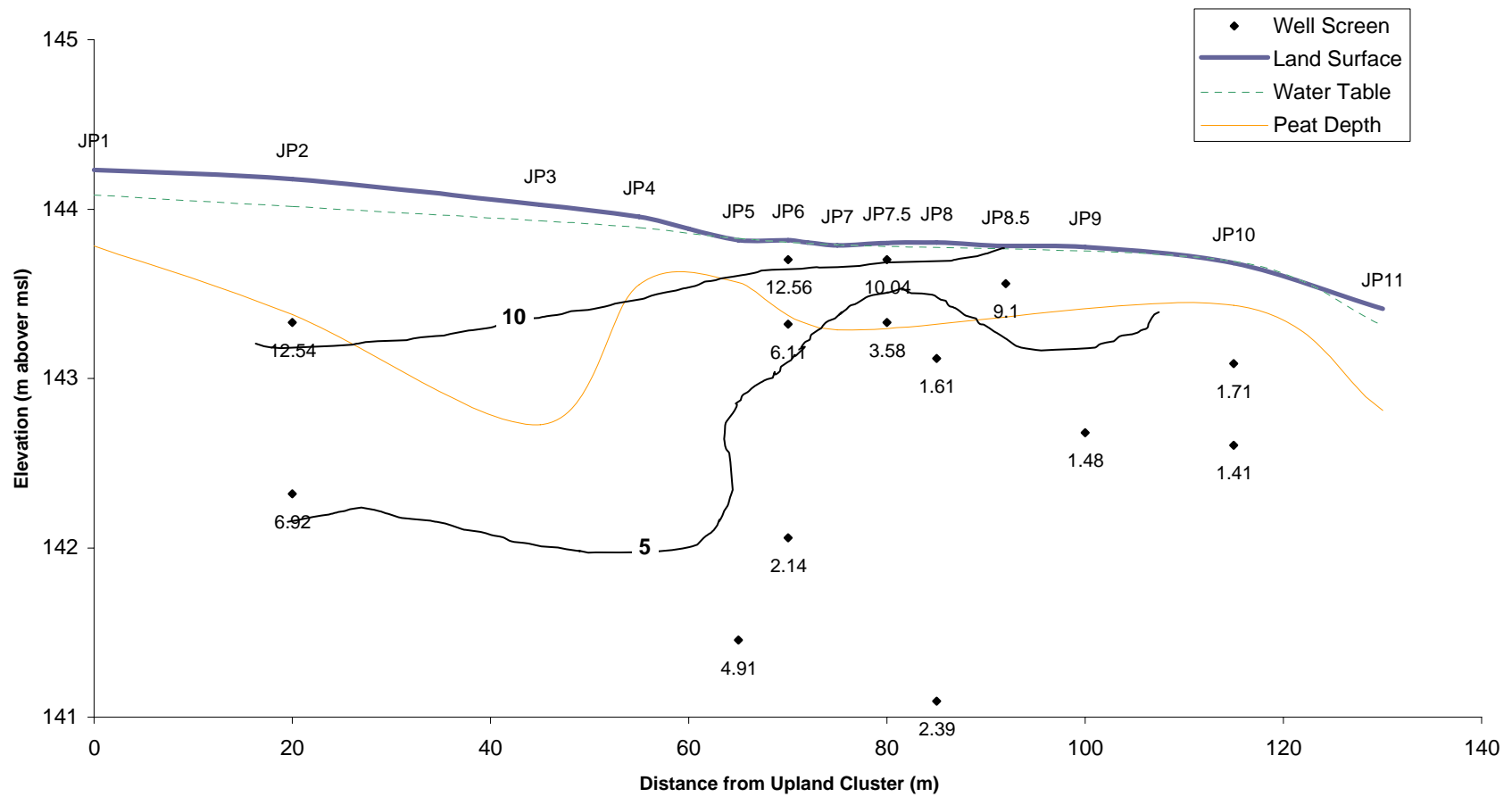


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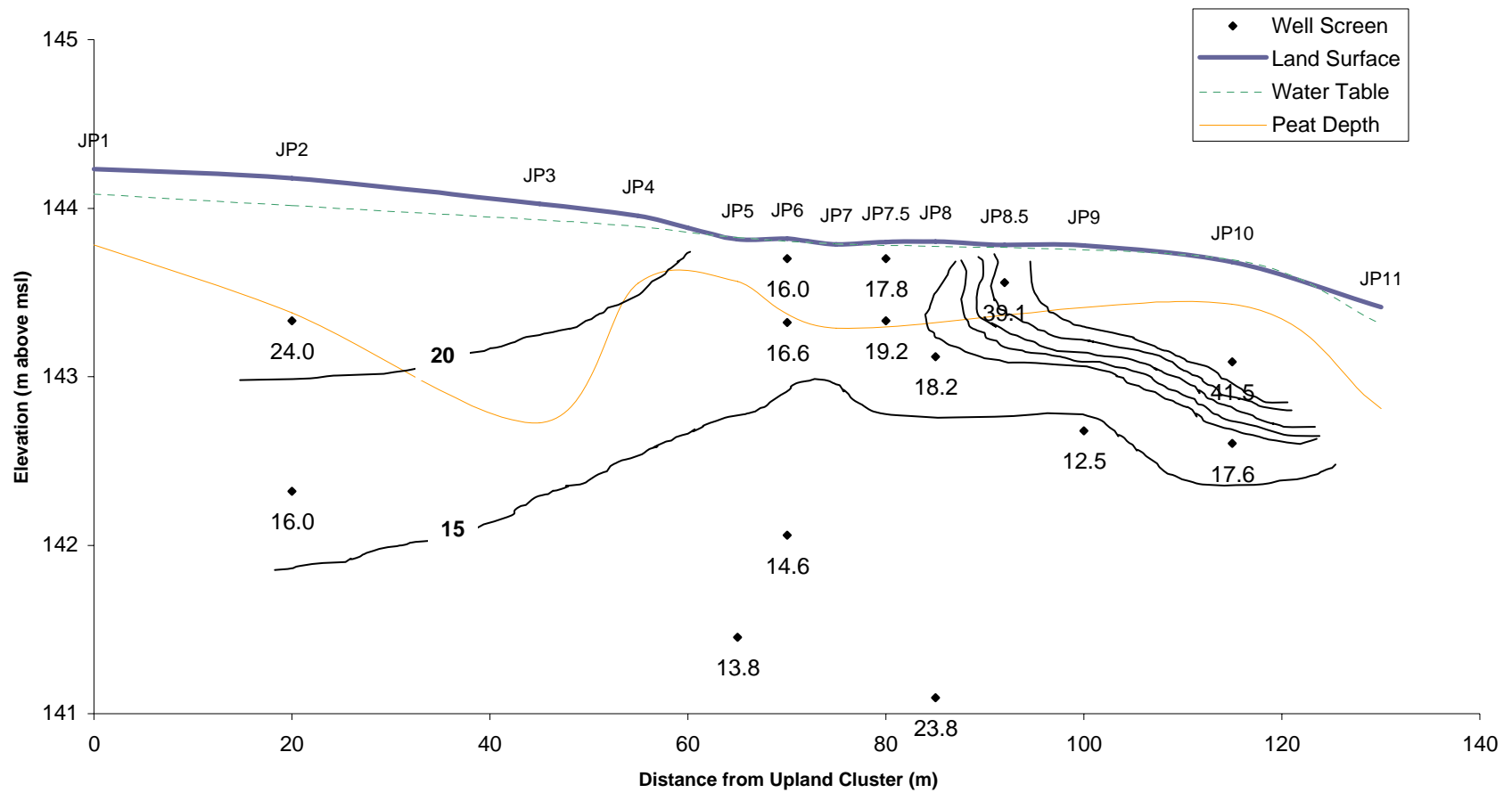
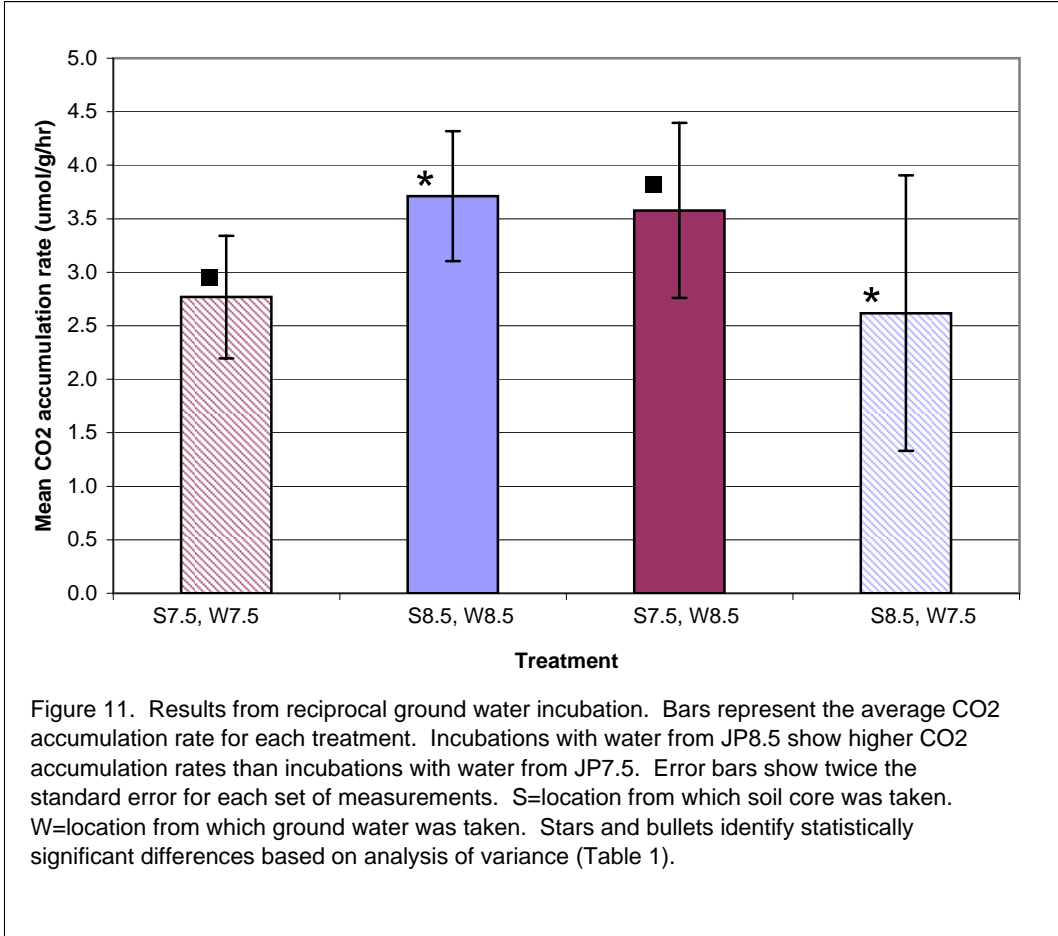


Figure 10. Dissolved inorganic carbon (DIC) concentration (mg/L C) in ground water in mid-August 2003. Lines are contours of equal DIC concentration.



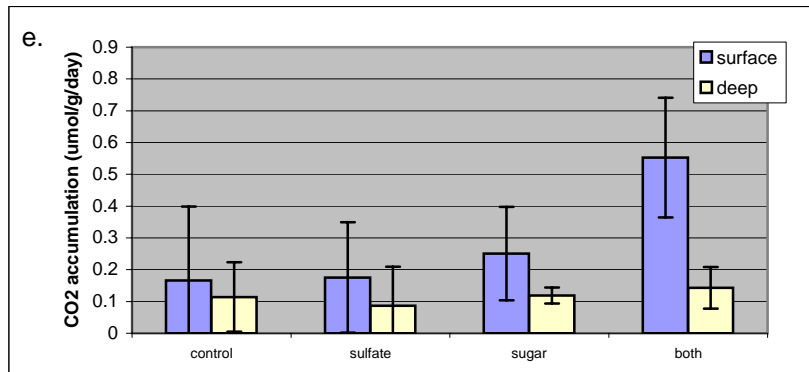
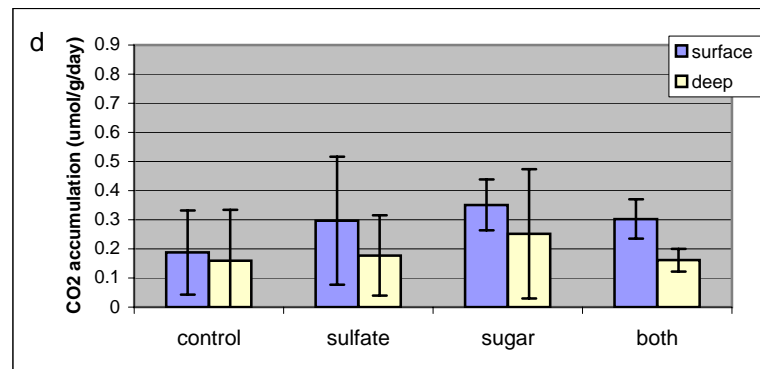
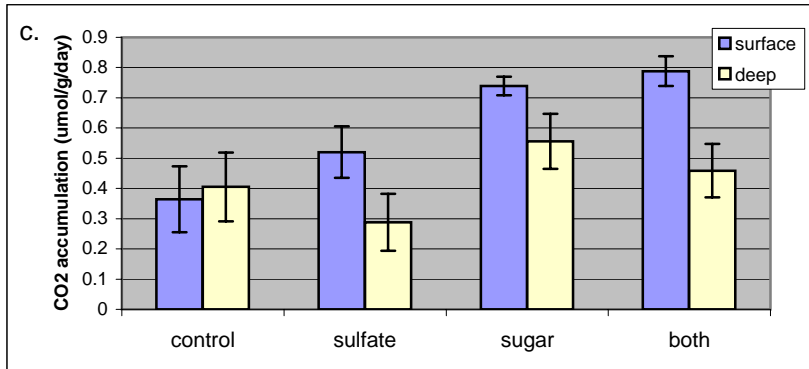
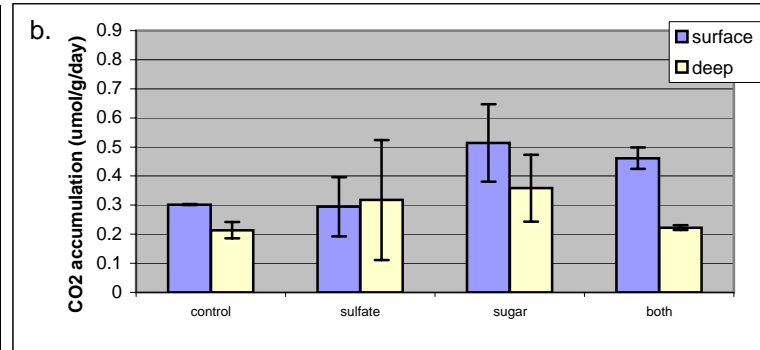
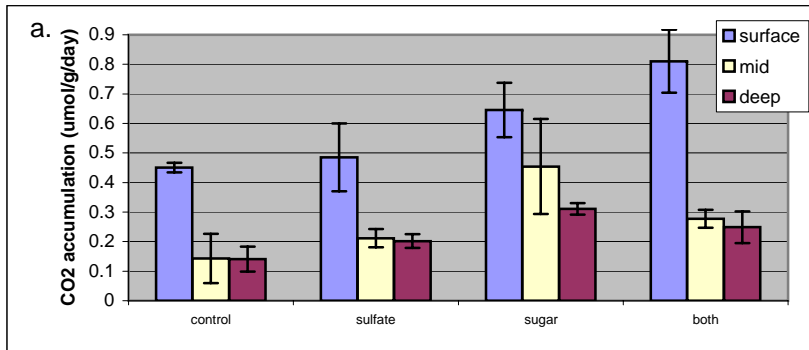


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