

Assessing the Role of Oxbow Deposits in Carbon and Nitrogen Dynamics within Alpine Watersheds

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Abstract

Despite their abundance, floodplains are poorly understood components of the global carbon cycle that are not well represented in Earth system models. The hydrology of floodplains was thought to be the major factor in controlling the chemical state and microbial activity within their sediments and groundwater. This paper seeks to characterize the impact of changing water levels on carbon and nitrogen cycling within alpine floodplains. This study took place in a meander in the East River floodplain in Central Colorado, where the summer drawdown causes a rapid decline in the floodplain's groundwater. Although carbon and nitrogen data have not been received at the time of writing, reduced iron was found to increase throughout the meander over time even as groundwater levels fell, with an unexpected peak in the center of the meander. This peak suggests that there is also a peak in metabolized organic carbon in the same location, which tends to drive the reduction of iron. We expect that ammonium (reduced nitrogen) will follow the same trend as reduced iron, while nitrate should follow the opposite trend, as nitrogen and iron are both redox-active. Dissolved oxygen was low in the center of the meander but occurred in higher concentrations along the riverbanks. Plants in the floodplain, which can oxygenate the subsurface via their roots, may be the cause of the oxicity of the downstream edge of the meander. Overall, it is clear that there are other major controls on floodplain chemical cycling beyond hydrology.

Introduction

Despite their abundance and constant interaction with the atmosphere through CO₂ in- and effluxing as well as with rivers through advection and diffusion, floodplains are poorly understood components of the global carbon cycle that are not well represented in Earth system models. This is partly due to a lack of knowledge about carbon fluxes in soils and groundwater, especially from sources below the rhizosphere (Arora et al., 2016; Tokunaga et al., 2016). The high rate of microbial respiration within floodplains also makes them important players in metal and nutrient cycling for redox active element such as nitrogen, iron, and uranium. It is known that changes in hydrological conditions (e.g. high vs. low flow) help drive the biogeochemical cycling of nutrients (Bormann & Likens, 1967). What remains elusive, however, is the extent of these hydrological controls on microbially-induced organic matter degradation and nutrient cycling through space and time.

The East River floodplain in central Colorado is a small-scale example of an active floodplain within a pristine alpine watershed. Insights to processes occurring within the East River floodplain could inform our understanding of those same processes in larger

floodplains (such as those of the Ganges and Brahmaputra rivers), which have a significant imprint on global carbon dynamics. Additionally, because East River is a tributary of the Colorado River, changes within its floodplain dynamics can have widespread impacts throughout the Southwestern United States. Understanding upstream nutrient dynamics might help us predict the impacts of a changing climate on downstream water quality. The Colorado River supplies water for roughly 40 million people, so investigating the various biogeochemical processes within its tributaries is of utmost importance for all of its dependents (Connor, 2012).

The purpose of this study is to investigate how the hydrology of the diffusion-limited organic-rich deposits (oxbow deposits) that result from river meanders influences carbon and nitrogen dynamics within pristine alpine watersheds. The fine-grained nature of oxbow deposits produces a near-zero rate of water flow through them, which inhibits nearly all advective chemical exchange and therefore limits chemical transport to diffusion below the water table (Stief, 2001). Hydrologic cycles, such as the spring melt transitioning to summer drawdown, lead to varying states of saturation within the oxbow deposits of alpine watersheds like the East River floodplain in Central Colorado. The periodic changes in water saturation levels affect the concentration of dissolved oxygen within the deposits themselves—oxygen is free to dissolve into the groundwater under low water conditions when unsaturated soil pores are exposed to the atmosphere, but high groundwater levels produce a diffusion-limited environment that results in anoxic conditions (Yabusaki et al., 2017). This is because diffusion-limitation leads to oxygen being consumed more quickly than it can be supplied, so areas with flowing water or atmospheric exposure receive oxygen at much higher rates than submerged areas.

This type of anoxic environment triggers a sequence of biogeochemical reactions that play significant roles in the cycling of nutrients (especially carbon and nitrogen) and metals (such as iron). In the absence of oxygen as a terminal electron acceptor, the subsurface community shifts towards microbes that use metals and other elements as electron acceptors for their metabolism, such as *Geobacter*, which reduces Fe(III) to Fe(II) (Lovley & Phillips, 1986; Straub, Benz, & Schink, 2000). Additionally, although the

abundance of these electron acceptors changes with depth (they are preferentially metabolized according to their reduction potentials), their localized concentration within anoxic environments creates locally reduced zones (Arora et al., 2016; Moore, Reddy, & Graetz, 1992). This means that the locally reduced zones within diffusion-limited floodplains and oxbow deposits are also excellent sinks for redox-active metals that are immobile in their reduced state, like chromium and uranium.

The use of elements besides oxygen as electron acceptors has an impact on rates of carbon mineralization and nutrient dynamics—for both carbon and nitrogen—because they are redox active. In the case of nitrogen, which can act as a productive terminal electron acceptor for microbes in the absence of oxygen, it follows that it would be reduced to ammonium (NH_4^+) under anoxic conditions. Under oxic conditions, however, oxygen will outcompete nitrate as an electron acceptor (and ammonium does not act as an electron acceptor), so nitrogen should be oxidized to nitrate (NO_3^-) under oxic conditions. Therefore, we hypothesized that ammonium would be released from oxbow deposits during periods of anoxic flow, which occurs when groundwater levels are high, and that nitrate would be released with oxic flow, which occurs when groundwater levels are low.

Alternative microbial electron acceptors like nitrogen do not produce as much energy as oxygen upon being reduced, so microbial activity, which directly determines the rate of carbon mineralization within oxbow deposits, tends to slow in anoxic environments. Although carbon continues to be mineralized from cellulose under anoxic conditions, the microbial enzymes that cleave cellulose grow much more active when conditions are oxic, which frees large amounts of dissolved organic carbon (DOC) for mineralization (Leschine, 1995). We hypothesized that the surge in enzymatic activity following the transition into an oxic regime resulting from falling groundwater levels would outpace the microbes' capacity to metabolize the newly available carbon, and therefore that greater quantities of DOC would be released from oxbow deposits during periods of oxic flow (low water) than during anoxic flow (high water).

Methods

Study Site

This study was conducted at the pumphouse field site in the East River floodplain (38.923° N, 106.950° W) at the Rocky Mountain Biological Laboratory (RMBL) in Gothic, Colorado (Figure 1). Data collection took place throughout the summer, from early June to late August, when the East River receives 46 mm of monthly rainfall. The melting snowpack, produced from 769 mm of monthly snowfall (equivalent to approximately 77 mm of rain) during winter and spring (Nov-Apr), creates the bulk of the East River headwater, while monsoons provide summer precipitation in the subalpine climate (WRCC, 2017). Although the floodplain outside of the river channel was initially flooded under nearly one foot of water in June, the water level had retreated to two feet below the riverbanks by mid-July, after the initial summer drawdown.

The soils within the East River oxbow deposits consist primarily of fine-grained mollisols, and the deposits themselves are highly vegetated, mainly by willows (*Salix spp.*), lupine (*Lupinus spp.*), corn lily (*Veratrum sp.*), and grasses. Alluvial sediments dominate the riverbed along the edges of the meanders within the river channel. The upstream river valley between the pumphouse site and RMBL (5.4 km apart) is unused by humans, but the land immediately downstream is used for private cattle ranching, which necessitated the installation of protective fencing around each of our sampling piezometers.

Experimental Design

In order to examine the underlying hydrology of the East River floodplain as well as the chemical state of the groundwater over time, we installed a total of 17 piezometers over two transects across the meander (east-west) nearest to the pumphouse shed. One transect consisted of four clusters of three piezometers of different depths (labeled as “shallow,” “mid,” and “deep” at each cluster), and the other contained five individual piezometers. Clusters or individual piezometers were spaced 10-15 m apart within each transect (Figure 2). The piezometers themselves were made of PVC pipe with slits cut into the bottom 20 cm, which were surrounded by a mesh screen to allow for the intake of

groundwater free from large soil particles. Piezometers were either 2.5 or 5 cm in diameter and were installed at depths of 40-60 cm (shallow), 60-80 cm (mid), or 80-100 cm (deep).

The piezometers were installed by auguring cores in the sediment and lowering them to the appropriate depth, as indicated by a pre-measured mark on the side of the pipe. Bentonite clay was used to seal the joint between the pipe and the soil in order to prevent air from entering or water from escaping the sampling shaft. The piezometers were developed after installation by pushing clean water down the pipes through the mesh screen with a PVC plunger in order to clear mud out of the screens and expedite their groundwater production.

In order to examine the relationship between hydrology and the chemical state of the groundwater, the piezometers were sampled three times per week for groundwater levels and a variety of chemical parameters. Groundwater levels were measured at each piezometer using an electric tape. Prior to sampling, either 500 mL or 1 L of groundwater (for the 2.5 and 5 cm diameter pipes, respectively) was purged out of each piezometer to minimize atmospheric influences on the sampling process. After purging, a multiparameter probe was used to record groundwater pH, conductivity, redox potential, and temperature in the field. Dissolved oxygen and iron(II) concentrations were also measured in the field with a CHEMetrics spectrophotometer and the appropriate reagent kits for each measurement.

To determine the carbon and nitrogen fluxes within the oxbow sediments, groundwater samples were collected in vials to be analyzed for dissolved cation, anion, and total inorganic and organic carbon (TICTOC) content at Lawrence Berkeley National Laboratory (LBNL). Vials were collected at the same time as the other physical and chemical measurements as a part of the overall piezometer sampling process. In order to prepare and preserve the groundwater samples for analysis, the cation samples were acidified with concentrated nitric acid, the anion samples were frozen, and the TICTOC samples were refrigerated. Samples were shipped to LBNL for analysis, and concentrations of DOC, NO_3^- , and NH_4^+ are being determined with a TOC analyzer, ion chromatography, and mass spectroscopy. Carbon and nitrogen data had not yet been received from LBNL at

the time of writing, but the samples are expected to be processed within the next one or two months.

Data Analysis

All analyses were performed using Microsoft Excel 2011 and R version 3.4.0 with the packages “gdata” (Warnes et al., 2017), “plyr” (Wickham, 2011), “AER” (Kleiber and Zeileis, 2008), “plotrix” (Lemon, 2006), and “effects” (Fox, 2003). Because the carbon and nitrogen groundwater samples had not yet been processed at LBNL, our analyses focused on the other properties of the East River groundwater, especially the relationship between groundwater depth and dissolved oxygen and iron(II). We first performed unpaired t-tests between the MCP and MCT-2 transects to determine whether they were effective replicates of each other for both dissolved oxygen and iron(II). We then created linear models to examine the variations in dissolved oxygen and iron(II) content within the groundwater as a function of several chemical and physical factors, namely the groundwater depth, pH, temperature, conductivity, ORP, and number of days since commencing sampling. Dissolved oxygen and iron(II) were placed on logarithmic scales within the models due to their exponential increases under changing conditions. We also created linear models for each individual chemical parameter (dissolved oxygen and iron(II), pH, temperature, conductivity, and ORP) as functions of time and groundwater depth, as well as groundwater depth itself as a function of time, within each transect to investigate the trends occurring across the meander. We used type II ANOVA tests to determine the significance of the predictors in all of our models. Finally, we used pairwise t-tests to determine whether there were significant differences between individual piezometers within a common transect for each chemical parameter. Analyses of carbon and nitrogen data will be performed after receiving the complete dataset from LBNL, which should be within the next one or two months.

Results

All of the piezometers that were sampleable for more than one week (which includes all but MCT2-4S, which dried up shortly after being developed) experienced a statistically significant (ANOVA, $p < 1.17 \times 10^{-6}$) drop in groundwater levels throughout the

summer (Figure 3, Figure 10, Figure 11). During the same time period, only the mid-depth piezometer at the MCT2-1 piezometer cluster (MCT2-1M) showed a significant trend (an increase) in dissolved oxygen content, but both the MCP and MCT2 transects as a whole experience either significant (ANOVA, $p = 0.0409$ for MCP) or near-significant ($p = 0.0591$ for MCT2) dissolved oxygen increases over time (Figure 4). Dissolved oxygen was significantly higher at MCT2-4 (t-test, $p < 0.009$) and noticeably higher at MCT2-1 than at the MCT2 clusters not adjacent to a riverbank.

In the MCP transect, only the MCP1 piezometer, on the upstream riverbank, showed a significant increase (ANOVA, $p = 0.0209$) in dissolved iron(II) over time (Figure 11), but, of the MCT2 piezometers that remained sampleable after the end of June, most of the deep and medium-depth wells (MCT2-1D, 2D, and 3D, as well as MCT2-1M and 2M) exhibited a significant increase (ANOVA, $p < 0.0255$ for deep, $p < 0.01163$ for medium-depth) in dissolved iron(II) over time (Figure 5, Figure 10). Similarly, the MCP transect as a whole did not display a significant trend (ANOVA, $p = 0.364$) in dissolved iron(II), while the overall MCT2 transect experienced a significant increase through the summer months (ANOVA, $p < 2 \times 10^{-16}$). Iron(II) content was significantly higher (t-test, $p < 1.8 \times 10^{-11}$ for MCT2 and $< 2 \times 10^{-16}$ for MCP) at the piezometers in the center of the meander, i.e. MCT2-2 and MCP-2 and 3, than at the other piezometers within their respective transects.

The MCP and MCT2 transects were statistically similar, and therefore effective replicates, for dissolved iron(II) content (t-test, $p = 0.9058$) but were not for dissolved oxygen (t-test, $p = 8.155 \times 10^{-6}$). The two transects became statistically similar (t-test, $p = 0.4782$) for dissolved oxygen content, however, upon only considering the MCT2 piezometer clusters not adjacent to a riverbank (i.e. MCT2-2 and 3), effectively removing the effects of the dissolved oxygen peaks observed along the bank at piezometer clusters MCT2-1 and 4.

Groundwater depth was a significant predictor for both dissolved oxygen concentrations (ANOVA, $p = 0.000154$) and dissolved iron(II) (ANOVA, $p = 7.36 \times 10^{-10}$) across the meander, with higher groundwater levels producing lower dissolved oxygen (Figure 7) and higher dissolved iron(II) concentrations (Figure 8). Groundwater depth was

also a significant predictor for ORP throughout both transects (ANOVA, $p = 3.11 \times 10^{-6}$ for MCP; $p = 4.43 \times 10^{-6}$ for MCT2), which highly paralleled the trends observed in dissolved oxygen and iron(II) (Figure 6). ORP also significantly increased (ANOVA, $p = 5.76 \times 10^{-16}$) as groundwater levels dropped across the meander as a whole (Figure 9). Finally, ORP itself was a significant predictor for both dissolved oxygen (ANOVA, $p = 2.8 \times 10^{-9}$) and dissolved iron(II) (ANOVA, $p = 4.46 \times 10^{-12}$), although its intermediary relationship with groundwater depth and dissolved groundwater contents warrants further discussion.

Discussion

We hypothesized that the rate of organic carbon release would increase as groundwater levels declined, and that ammonium (reduced nitrogen) would be released from oxbow deposits during periods of anoxic flow/high groundwater, whereas nitrate (oxidized nitrogen) would be released with oxic flow/low groundwater. In the absence of actual carbon and nitrogen data from LBNL, we cannot yet make any hard conclusions on those fronts. However, the trends observed in groundwater depth, ORP, and dissolved oxygen and iron(II), as well as the relationship between these trends, can provide us with some clues.

Because groundwater elevations decreased across the meander throughout the summer, the rise in Fe(II) concentrations at each individual piezometer over time may seem to contradict the significant relationship between higher groundwater elevation and higher Fe(II) levels. This apparent contradiction, however, is at least partially explained by the fact that piezometers with deeper groundwater levels also contained lower levels of dissolved iron(II), with the same trend holding true for shallower groundwater and higher iron(II) content (Figure 8). This relationship supports the initial logical foundation for our hypotheses—that submerged regions are generally diffusion-limited and therefore oxygen-depleted and that the atmosphere is only able to be an effective oxygen source above the water table.

If hydrology were truly the main control on subsurface chemical cycling, however, we would expect to see a continuous decrease in dissolved oxygen accompanied by an

increase in iron(II) physically across the meander. This is because oxygenated groundwater would rapidly lose its dissolved oxygen to microbial metabolism while flowing from the riverbed through the diffusion-limited oxbow sediments, and would increasingly accumulate other reduced terminal electron acceptors (such as ferrous iron) while approaching the downstream edge of the meander. We observed the expected accumulation of reduced conditions on the upstream side of the pumphouse meander, but saw the opposite trend in the piezometers on the downstream half, when dissolved oxygen concentrations increased as reduced iron levels fell. This symmetrical pattern across the meander, along with the relatively low variations in dissolved oxygen and iron(II) concentrations as groundwater levels dropped over time, suggests that there are other major factors in addition to floodplain hydrology that control subsurface microbial metabolism and chemical cycling.

The continued increase in iron(II) concentrations observed over the summer, even during a sustained period of descending groundwater levels, was unexpected, and is the main instance of a process in the East River floodplain that must have major controls beyond hydrology. Determining these other controls will be of great importance due to the inherent linkage between iron reduction and subsurface carbon metabolism. As found by Boye et al. (2017), the presence of large quantities of organic carbon that is thermodynamically favorable for microbial metabolism can continue to drive the reduction of terminal electron acceptors beyond what would otherwise be expected based on an area's oxygen content. Additionally, Nealson and Myers (1992) suggested that the microbial ability to reduce iron under anoxic conditions may be much more common than previously thought, which is a reasonable conclusion, especially given that subsurface carbon and iron mineralogy can shape entire microbial communities (Lentini, Wankel, & Hansel, 2012). We observed significantly higher concentrations of reduced iron in areas with a lower ORP, and iron(II) concentrations within floodplains are known to be higher within naturally reduced zones, where this type of thermodynamically favorable carbon-driven microbial reduction takes place (Arora et al., 2016). Therefore, based on our observations, microbial carbon metabolism is likely the predominant process that determines the chemical conditions in the center of the pumphouse meander. The source

and fate of this organic carbon is not yet clear, but we hope that analysis of the upcoming carbon data from LBNL will elucidate more information about this process.

The high ORP and dissolved oxygen concentrations in the downstream half of the meander indicate that must be an additional source of oxygen apart from that supplied by the initial groundwater input into the upstream half of the meander. Without an additional oxygen source, we would instead expect to find near-total oxygen depletion in the groundwater by the time it reemerges from the meander sediment into the river channel. Because the floodplain became noticeably more vegetated throughout the summer in conjunction with the monsoon season, one possible source for this additional dissolved oxygen is from the plants that vegetated the pumphouse meander. Floodplain-inhabiting plants such as willows, which were dominant throughout the meander, are known to provide atmospheric oxygen to their roots and the adjacent soil through aerenchyma and other aerated tissue adaptations (Blom & Voeselek, 1996; Jackson & Attwood, 1996). Additionally, the oxygenated surface water in the river channel adjacent to the downstream edge of the meander could serve as another potential oxygen source through advection over a limited distance through the oxbow sediment. Although this could only take place in the case of retrograde groundwater flow (i.e. from the river into the meander on the downstream edge), which we do not anticipate observing, further hydraulic gradient analysis is needed to confirm the path of groundwater flow through the meander. We expect to find that the groundwater flows in a straight line from the western side of the meander (upstream, high head) to the eastern side (downstream, low head) (Figure 2).

Although it is difficult to make conclusions about nitrogen dynamics within the East River floodplain without having received the nitrogen data from LBNL, it is known that the absence of oxygen in the subsurface drives the reduction of other less energetic terminal electron acceptors, such as iron and nitrogen (Baldwin & Mitchell, 2000; Nealson & Myers, 1992; Yabusaki et al., 2017). It therefore follows that nitrogen would obey the same general reduction and oxidation trends as those observed for iron (i.e. more ammonia present in areas with higher iron(II) concentrations, and vice versa for nitrate), as both are redox-active terminal electron acceptors. Due to the transition between anoxic and oxic

conditions over time, it is also important to consider the effects of denitrification on nitrogen availability within the floodplain. Because denitrification occurs exclusively in anoxic environments, it is likely that we will observe decreasing denitrification rates over time due to the increasingly oxic conditions resulting from the lower groundwater levels. Thus, we expect to see higher mineral nitrogen availability in the East River floodplain over time—at least in the sediments near the riverbanks, which experienced the largest increased in dissolved oxygen concentrations—due to decreased losses to denitrification in the newly oxic sediments (Baldwin & Mitchell, 2000).

Although hydrology appears to be only one of several controls on floodplain chemical cycling, it is clear that shifts in hydrology can still produce significant changes within the subsurface chemical environment. Changes in rainfall, snowmelt, and overall hydrological characteristics are to be expected in the face of a changing climate. With the reduced snowpack and rainfall levels—and therefore lower flow rates in rivers—that will likely accompany future warming, we should expect to see the current end-of-summer trends, which are at least partially driven by low groundwater levels, become the new norm (Gregory et al., 1997; McCabe & Hay, 1995). As discussed previously, the significant rise in iron(II) concentrations in conjunction with the falling groundwater indicates that a shift into an oxic groundwater regime causes large stores of organic carbon to be mobilized from cellulose and metabolized by microbes, resulting in the continued reduction of terminal electron acceptors like iron. If it turns out to be the case that the organic carbon generally remains stationary within the floodplain after being cleaved from cellulose, then it is possible that floodplain sediments could as even larger short-term carbon stores in a warmer future with lower water levels than they do today.

As for future implications for nitrogen, lower average groundwater elevation and higher oxicity could reduce denitrification rates, and higher ORP levels could cause oxygen to displace nitrogen as an electron acceptor. This could lead to higher overall levels of available mineral nitrogen in rivers and floodplains, with nitrate representing a greater fraction of that available nitrogen. Elevated nitrate levels could boost the presence of algae communities within rivers and thereby shift river ecosystems by displacing other aquatic

organisms (Venkateswarlu, 1969). In terms of drinking water quality, however, it is unlikely that shifts in hydrology would produce high enough levels of nitrate to cause harm to humans, such as through blue baby syndrome (Richard, Diaz, & Kaye, 2014; Speijers & Fawell, 2011).

Even though the findings presented in this study rely on a currently incomplete dataset (specifically for carbon and nitrogen), it appears that they still have the potential to build our understanding of the controls on chemical cycling within floodplains based on the observations that have been made so far. The greatest limitation of our findings, however, is their localized nature within East River. Therefore, future studies could address this limitation by applying these localized findings to larger river systems like the Ganges and Brahmaputra rivers, which have large impacts on the short-term global carbon cycle and therefore play significant roles in global carbon models. This type of research would help facilitate future scientific studies of the earth system, technological developments in sustainable energy, and policy decisions regarding global carbon management (including carbon capture and sequestration, for example), all of which rely on accurate models of global carbon cycling.

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Tables and Figures

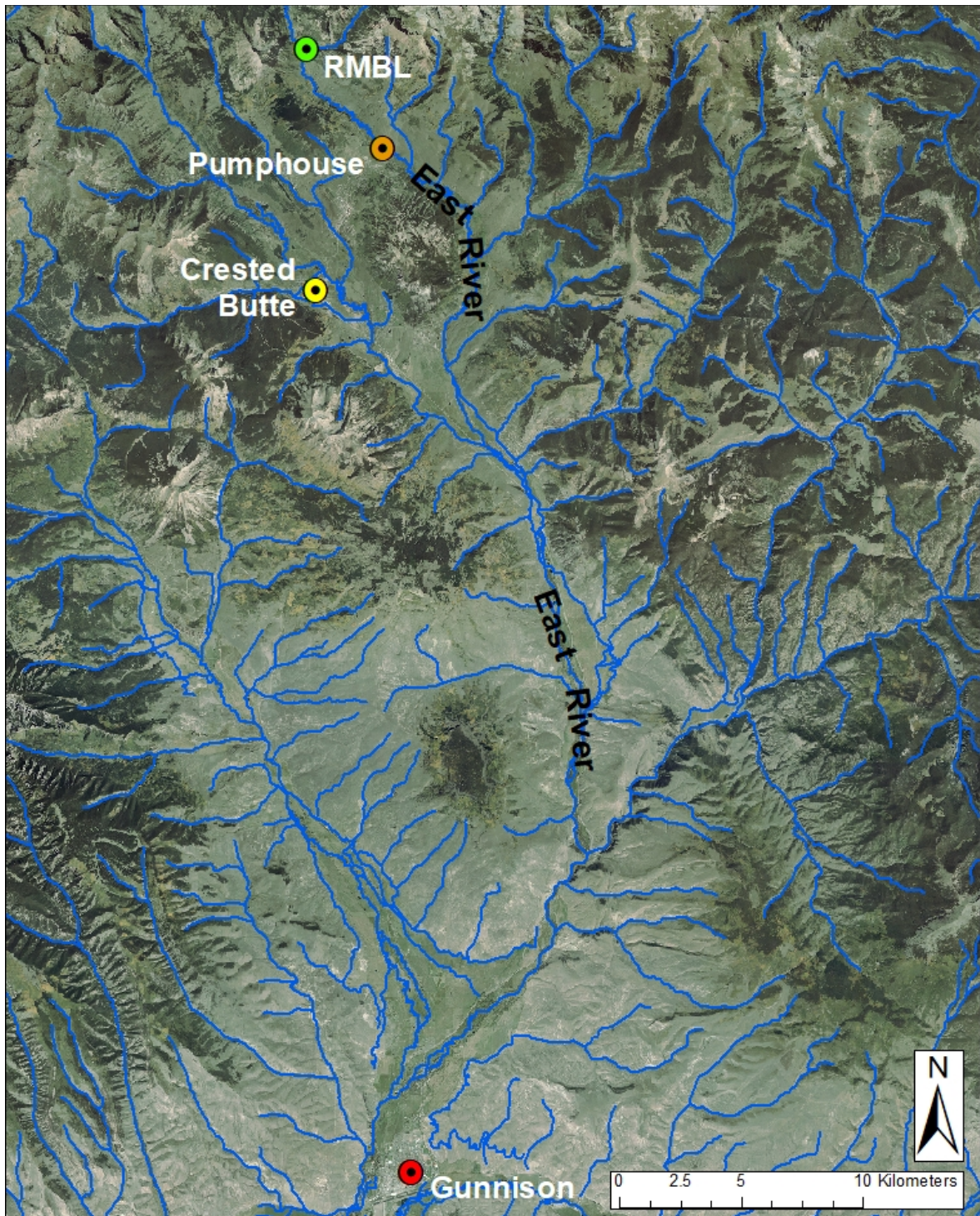


Figure 1. The location of the pumphouse field site in the East River valley in Gunnison County, CO. The pumphouse lies approximately 5.4 km away from RMBL, and the river valley between the two locations is unused by humans.

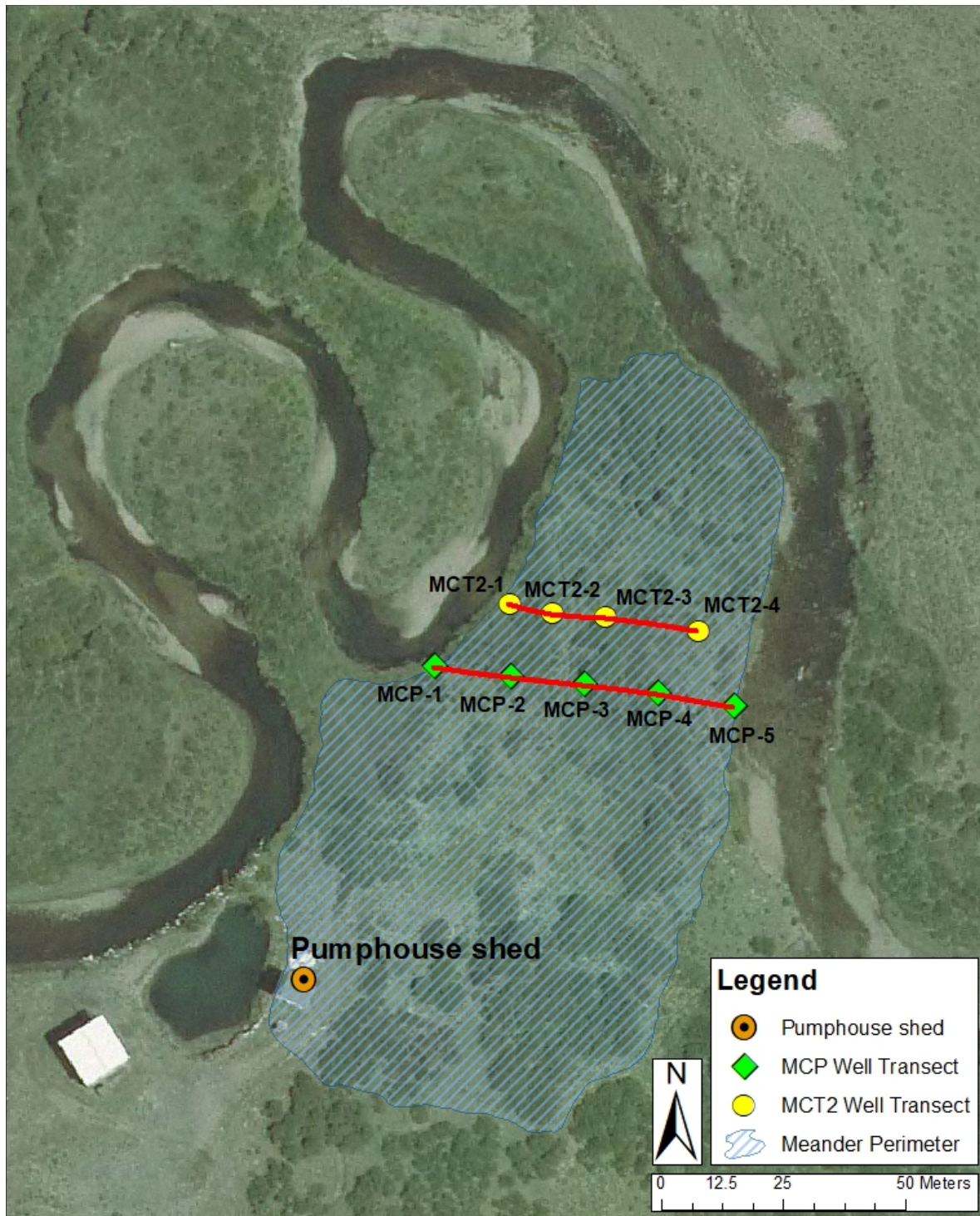


Figure 2. The distribution of piezometers across the pumphouse meander within the East River floodplain. The MCT2 transect contained four clusters of three piezometers of different depths, while the MCP transect contained five individual piezometers of the same depth. The pumphouse shed is located at 38.923° N, 106.950° W.

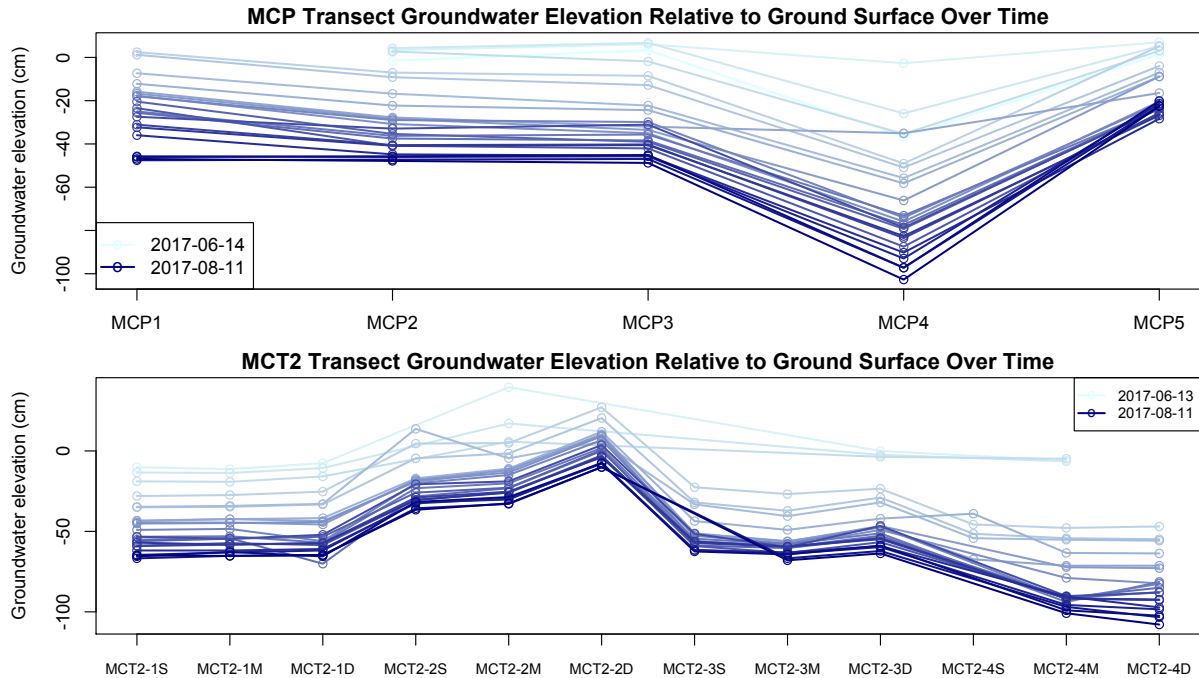


Figure 3. Groundwater elevation relative to the ground surface across both transects over time, as measured with an electric tape. Both transects experienced significant declines in groundwater levels over time. Measurements are displayed on a gradient from light to dark blue in chronological order (more recent measurements are shown as darker), and deeper groundwater levels are shown as more negative elevations on the y-axis.

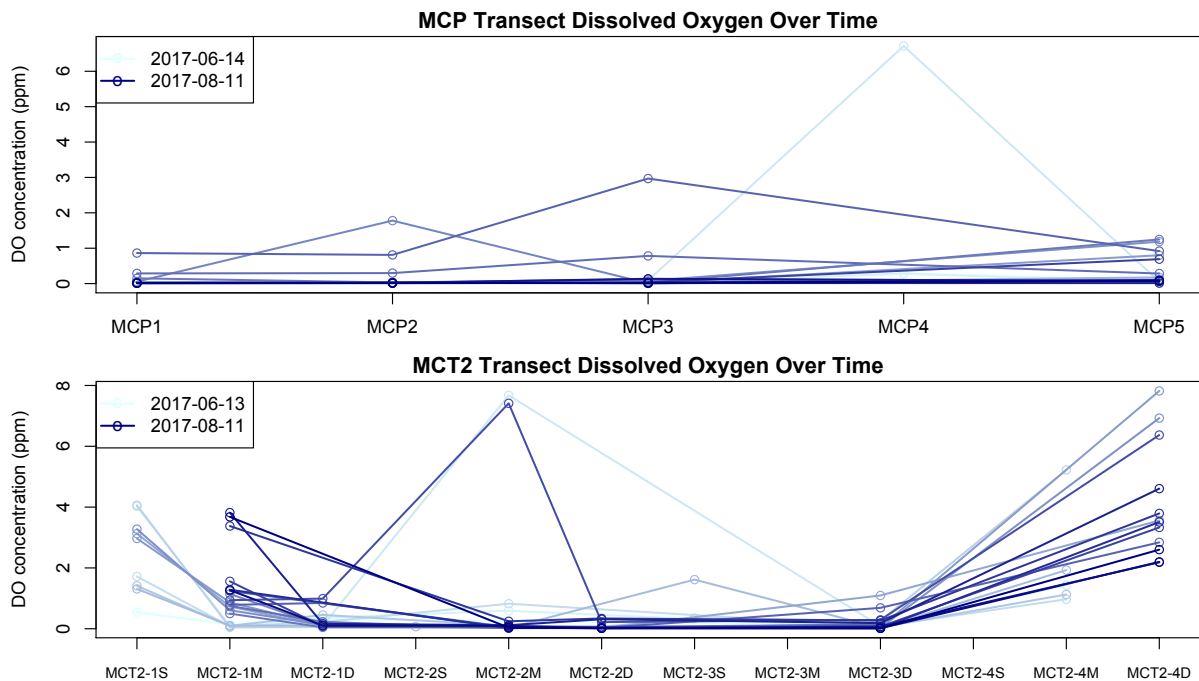


Figure 4. Dissolved oxygen content across both transects over time, as measured with a CHEMetrics spectrophotometer and dissolved oxygen vacu-vial kit. Measurements are displayed from light to dark blue in chronological order (more recent measurements are shown as darker). Although MCT2-1M was the only piezometer to show a significant increase in dissolved oxygen over time, both the MCP and MCT2 transects as a whole experienced significant increases in dissolved oxygen over time. The peaks at MCP4 and MCT2-2M are almost certainly anomalous and due to bubbles while sampling.

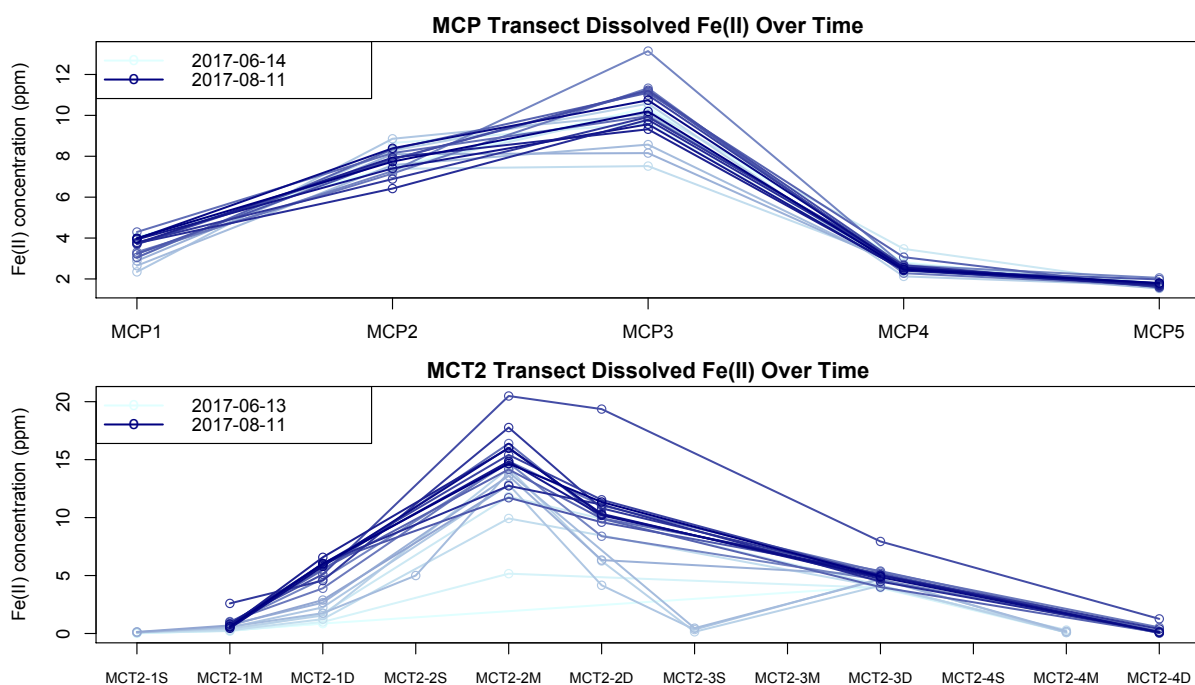


Figure 5. Dissolved iron(II) content across both transects over time, as measured with a CHEMetrics spectrophotometer and ferrous iron vacu-vial kit. Measurements are displayed from light to dark blue in chronological order (more recent measurements are shown as darker). There was no significant trend at any of the MCP piezometers, but several of the MCT2 piezometers (MCT2-1M/D, 2M/D, and 3M) showed significant increases in iron(II) content over time. Both the MCP and MCT2 transects as a whole experienced significant or near-significant increases, respectively, in dissolved iron(II) content over time.

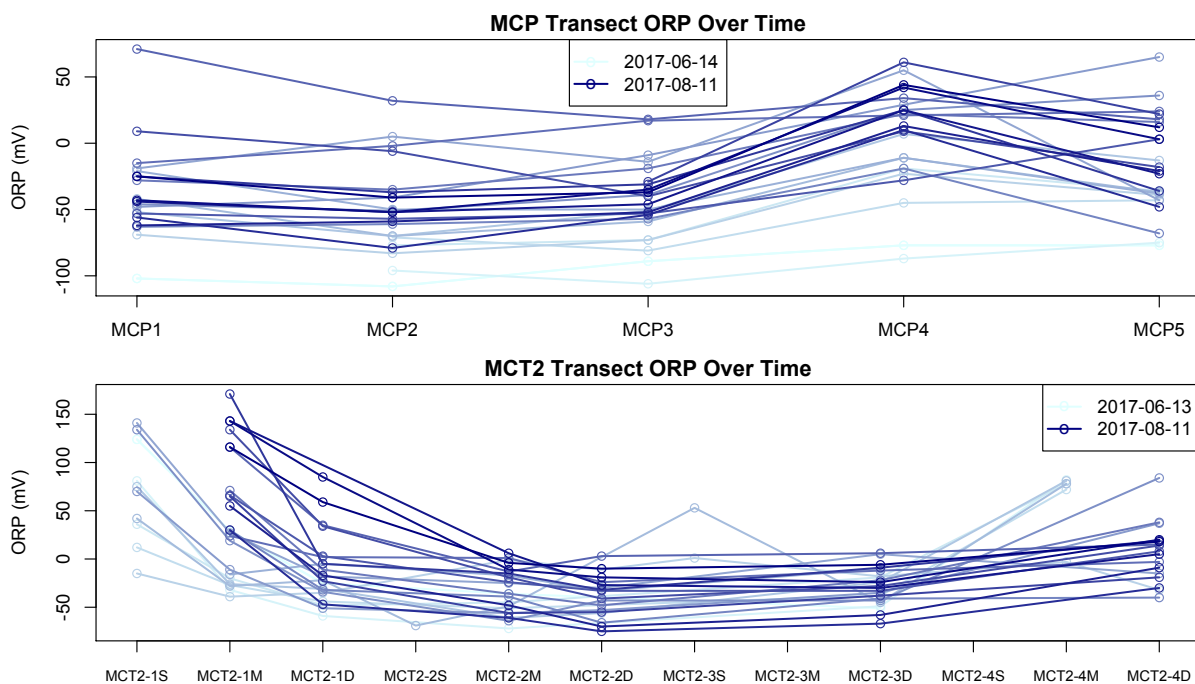


Figure 6. ORP across both transects over time, as measured by a multiparameter probe. Both transects experienced a significant increase in ORP as water levels declined. The ORP trends parallel those of dissolved oxygen and iron(II).

Dissolved oxygen vs. groundwater elevation across all piezometers

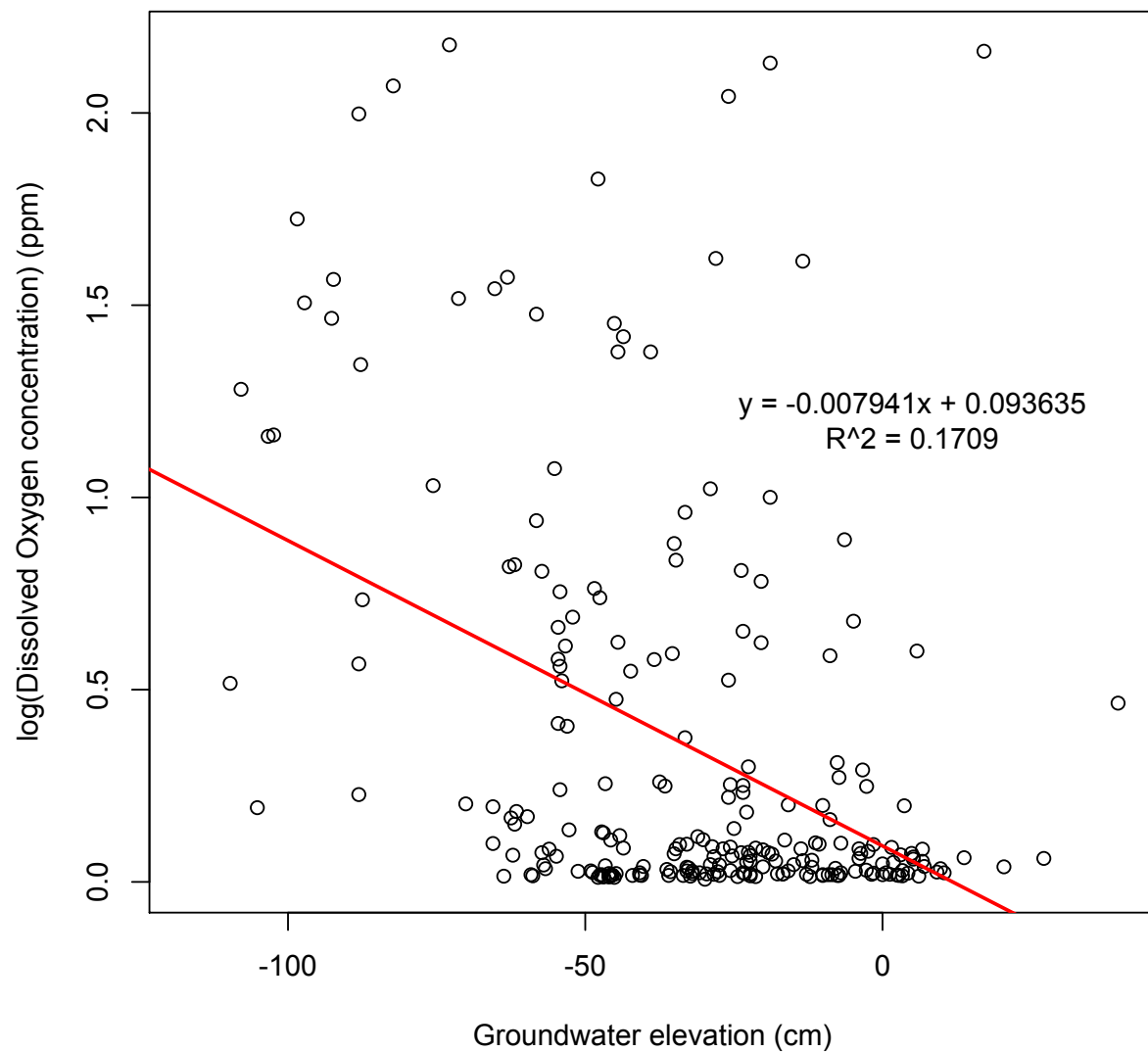


Figure 7. Dissolved oxygen concentration as a function of groundwater elevation (relative to the ground surface) at all of the pumphouse piezometers. Dissolved oxygen is shown on a log scale due to its exponential increase under low groundwater conditions. A more positive groundwater elevation indicates higher groundwater levels. The pumphouse meander showed a significant increase in dissolved oxygen concentrations as groundwater levels declined.

Dissolved Fe(II) vs. groundwater elevation across all piezometers

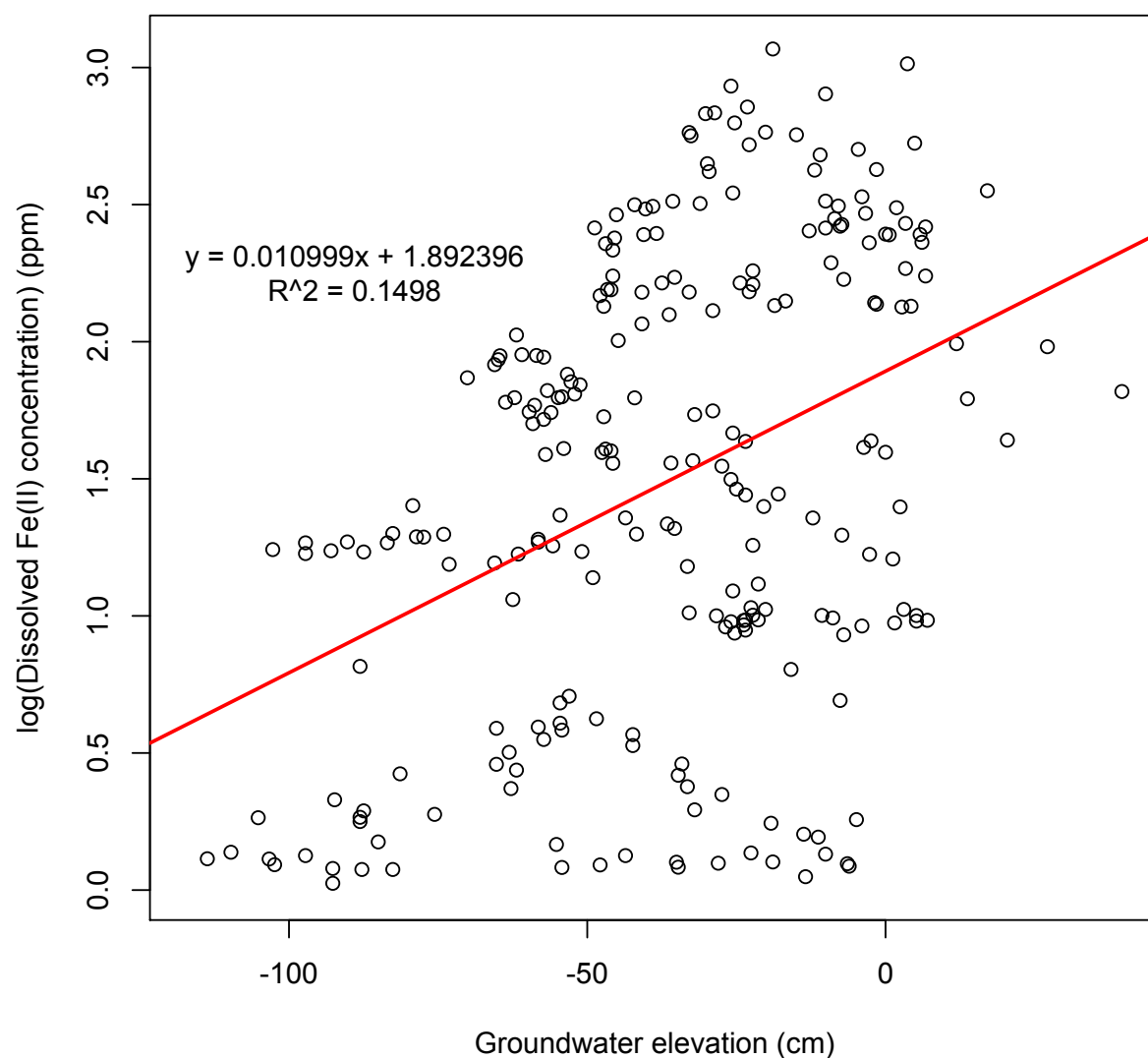


Figure 8. Dissolved iron(II) concentration as a function of groundwater elevation (relative to the ground surface) at all of the pumphouse piezometers. Dissolved iron(II) is shown on a log scale due to its exponential increase under high groundwater conditions. A more positive groundwater elevation indicates higher groundwater levels. There was a significant positive relationship between groundwater elevation and iron(II) concentrations.

ORP vs. groundwater elevation across all piezometers

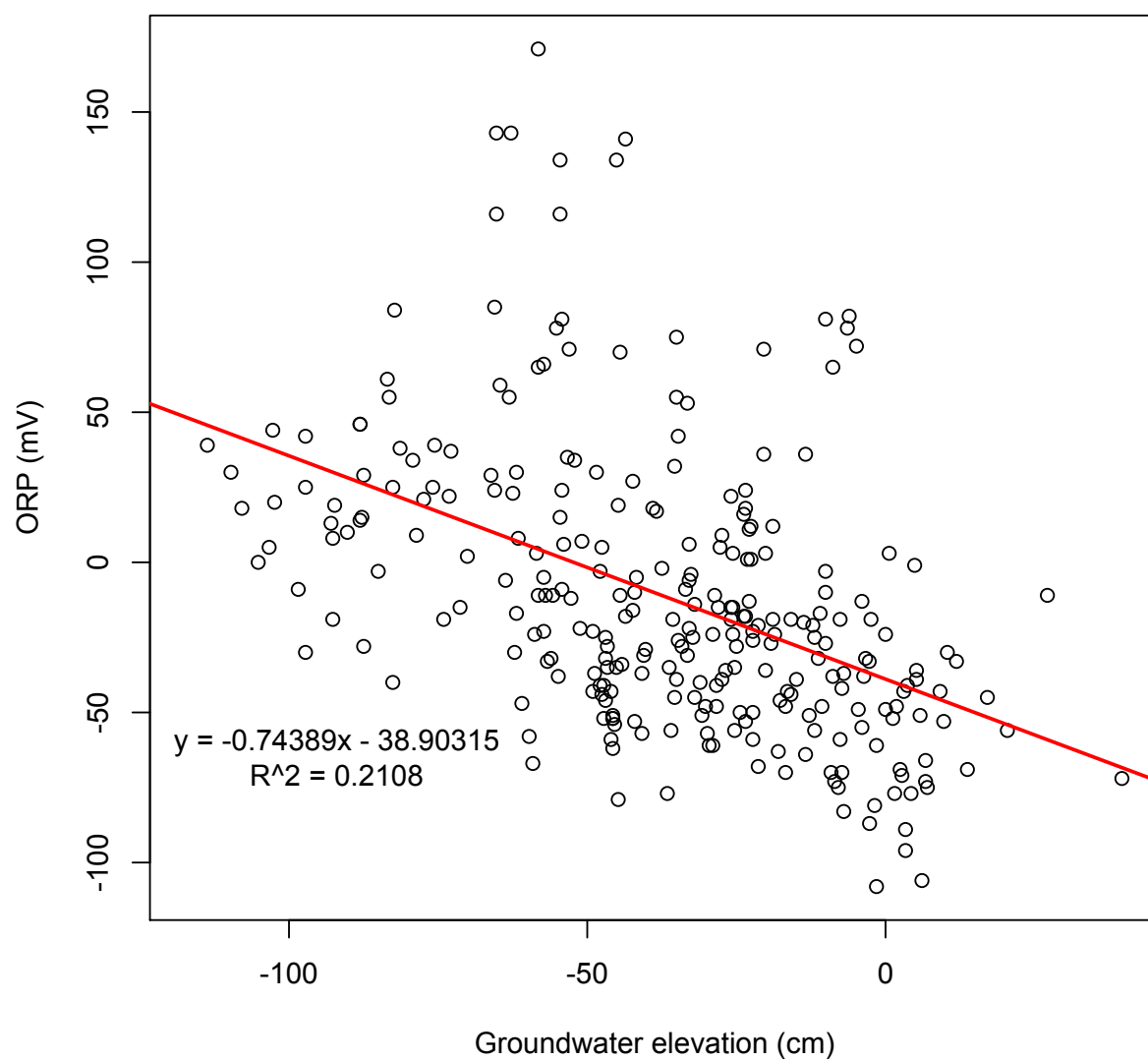


Figure 9. Redox potential (ORP) as a function of groundwater elevation (relative to the ground surface) at all of the pumphouse piezometers. A more positive groundwater elevation indicates higher groundwater levels. There was a significant negative relationship between groundwater elevation and ORP.

MCT2-1D groundwater elevation and dissolved contents over time

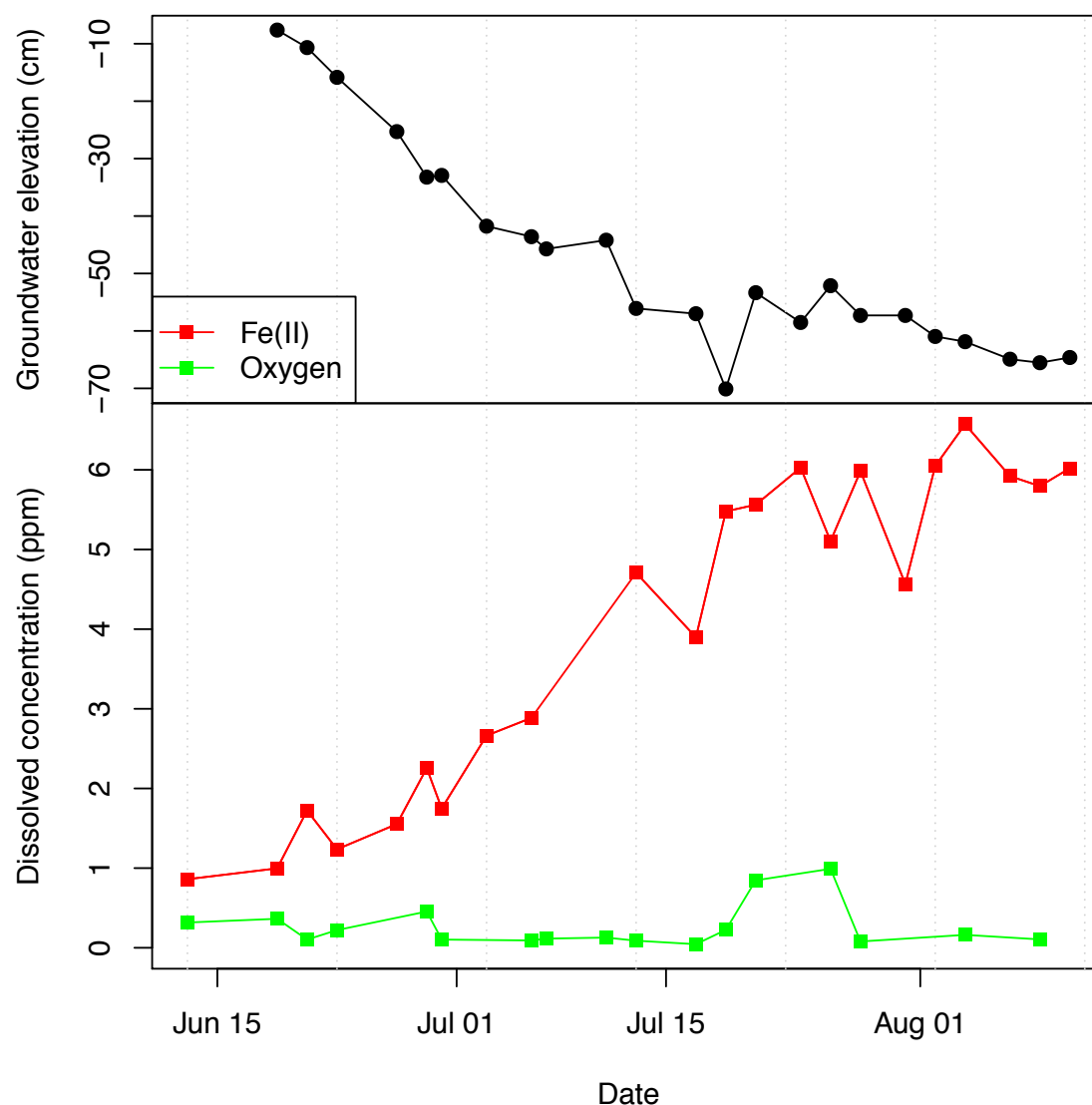


Figure 10. Groundwater elevation alongside dissolved oxygen and iron(II) content at the deep piezometer at MCT2-1 over time. The significant decline in groundwater, significant increase in iron(II), and the stability of the low dissolved oxygen concentrations were typical of most wells in the MCT2 transect. Groundwater levels were measured with an electric tape, and dissolved concentrations were measured with a CHEMetrics spectrophotometer and the appropriate vacu-vial kit for each chemical parameter.

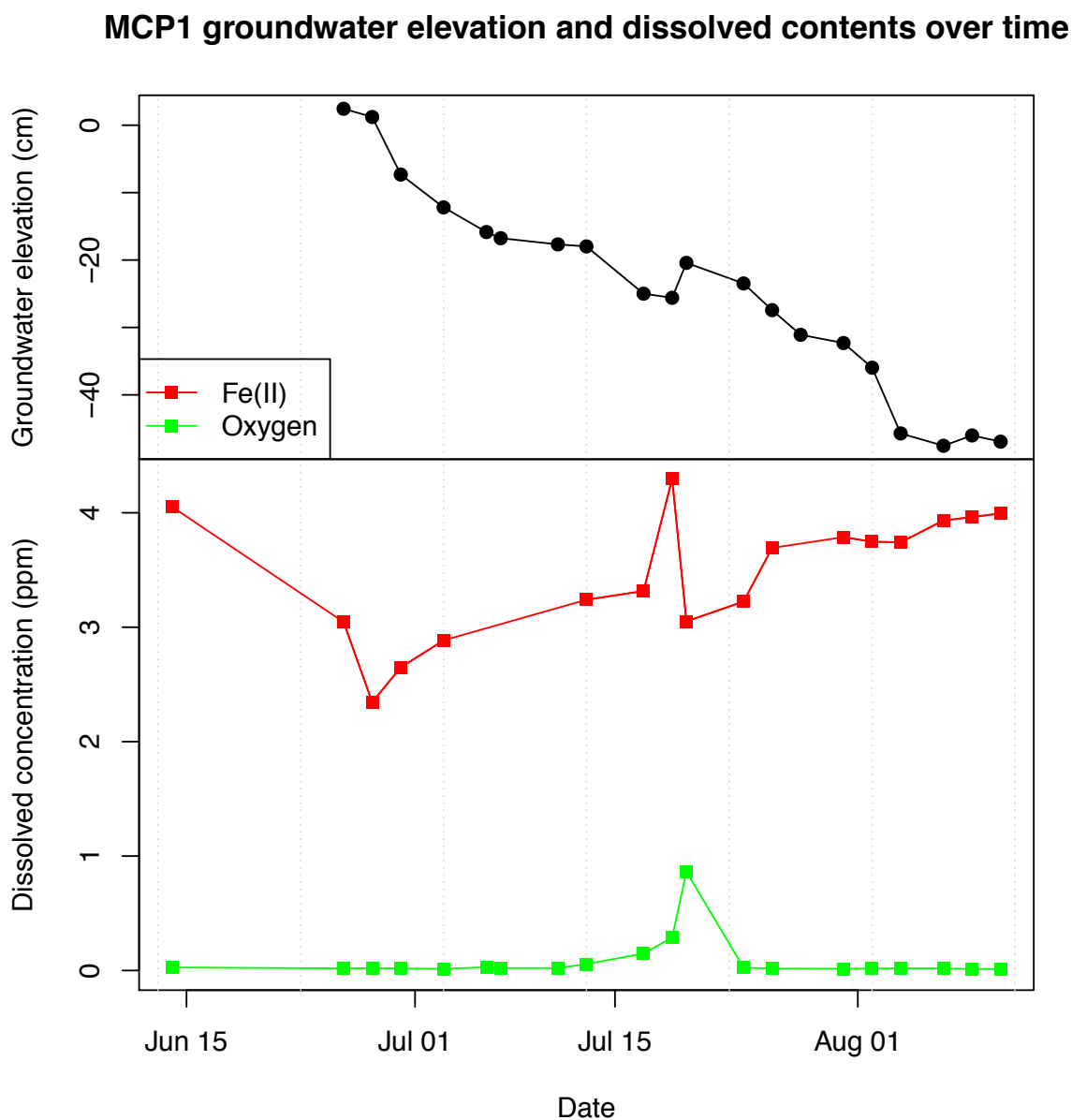


Figure 11. Groundwater elevation alongside dissolved oxygen and iron(II) content at the MCP1 piezometer. The significant decline in groundwater and the general stability of the low dissolved oxygen and high iron(II) concentrations were typical of the wells in the MCP transect. Groundwater levels were measured with an electric tape, and dissolved concentrations were measured with a CHEMetrics spectrophotometer and the appropriate vacu-vial kit for each chemical parameter.