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Degradation of Chlorinated Hydrocarbons in Groundwater Passing Through the Treatment Wetland at Wright-Patterson Air Force Base: Analysis of Results Collected During 2001-'06

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Degradation of Chlorinated Hydrocarbons in Groundwater Passing Through the Treatment Wetland at Wright-Patterson Air Force Base: Analysis of Results Collected During 2001-'06

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By

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      I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY <u>Annamarie Therrien</u> ENTITLED <u>"Degradation of Chlorinated Hydrocarbons in Groundwater Passing Through the Treatment Wetland at Wright-Patterson Air Force Base: Analysis of Results Collected During 2001-'06"</u>BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF <u>Master of Science</u>.

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Abstract

Therrien, Annamarie F. M.S. Department of Earth and Environmental Studies, Wright State University, 2012. Degradation of Chlorinated Hydrocarbons in Groundwater Passing Through the Treatment Wetland at Wright-Patterson Air Force Base: Analysis of Results Collected During 2001-'06.

Constructed wetlands are an efficient and cost effective means for chlorinated aliphatic hydrocarbon remediation, and will therefore continue to gain momentum as an accepted treatment by the US EPA (U.S. EPA, 1995; Amarante, 2000; Lien, 2001; WETPOL, 2009). The treatment options for chlorinated aliphatic hydrocarbons (CAHs), including wetlands, capitalize on aerobic/anaerobic interfaces in which bacterially mediated reduction-oxidation reactions degrade pollutants (Li, 1997; Bradley, 1998; Lorah and Voytek, 2004; Amon, 2007; Imfeld, 2008).

In August 2000, researchers at Wright State University (WSU) combined efforts with the United States Air Force Institute of Technology (AFIT) to construct a pilot-scale upward-flow treatment wetland on Wright-Patterson Air Force Base with parameters that could remediate perchloroethene (PCE) found in a nearby aquifer (Amon et al., 2007). Eleven studies of short duration have since documented the existance of anerobic and aerobic interfaces by measuring various terminal electron acceptors (sulfate, nitrate, methane, iron) and numerous other parameters. The studies evaluated PCE degradation rates, geochemical profiles, hydraulic conductivity and chlorinated ethene concentrations. (Bugg, 2002; Opperman, 2002; Clemmer, 2003; Kovacic, 2003; BonDurant, 2004; Sobolewski, 2004; Lach, 2004; Schlater, 2006; Mohamud, 2007; Waldron, 2007, Corbin, 2008).

The present research has attempted to compile, organize, and re-analyze the data collected by AFIT and WSU researchers during 2001-2006. Data was analyzed using Jenks

Optimization (goodness of variance fit) method to identify and remove outliers. Meta analysis of CAH concentrations and redox parameters was performed by creating data subsets of individual piezometer and depths, influent to effluent transect data and ArcGIS maps.

The present analysis concludes that a fully functioning wetland with strongly reducing geochemical conditions and flow patterns capable of PCE destruction developed at this site within 18-24 months. Dechlorination of CAHs was observed at every depth and at 63 of 66 sampled locations despite significant differences in hydraulic conductivity and available electron acceptors. Rate of dechlorination varied with depth and hydraulic conductivity. Strongest reducing conditions developed at Middle layer (0.69 m) and demonstrated the highest rates of PCE dechlorination. Maximum degradation of vinyl chloride (VC) and 1,2 dichloroethenes (DCE) occurred in Upper layer (0.23m) where conditions may have been more oxidizing.

The size of the pilot-scale treatment wetland generally allowed adequate residence time despite short circuits. However, two exceptions were observed: (i) near the effluent, increases in head pressure, due to laminar flow bring higher concentrations from gravel layer to surface quickly, and (ii) CAHs re transmitted quickly along the wetland's outer boundary, possibly along the soil-PVC liner. Despite these effects, with the exception of one researcher's results, the effluent concentrations for all CAH species remained below their respective MCLs after January 2003. The study suggests that the construction of wetland for the treatment PCE-contaminated groundwater include establishing and employing a grid monitoring system to ascertain geographical boundaries for problem areas, frequent sampling in initial 24 months and establishing controls on influent pumping system to adjust residence time as needed.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SUPPLEMENTAL FIGURES AND TABLES

I. Introduction

Background

Perchloroethene (PCE), a chlorinated aliphatic hydrocarbon (CAH), has been a contaminant of concern since 1970. Over the last 40 years, the magnitude of groundwater contamination from PCE and its daughter products, trichloroethene, dichloroethene isomers and vinyl chloride (VC) that typically form in reducing conditions, and are carcinogenic in nature, has propagated research into remediation technology (TOSC, 2001). PCE's continued commercial use as a solvent in paint stripping and dry cleaning(1950- present) and ineffective early disposal practices generated ubiquitous aquifer contamination by 1970 (McKetta,1979; Pankow and Cherry, 1996; Kenneke and Weber, 2003). Costly and inadequate pump-and-treat systems, first implemented in the 1980s (U.S. EPA, 2003), were not effective in remediation of solvent contaminated sites due to the movement and spreading behavior of CAHs, such as PCE (high specific gravity, low solubility in water, and hydrophobic sorption to soil organic matter).

The Technology Innovation and Field Service Division of the USEPA has since recognized *in situ* bioremediation, permeable reactive barriers, and natural attenuation as effective remediation technologies for chlorinated solvents such as PCE (U.S.EPA, 2011). These technologies capitalize on bacterially mediated oxidation-reduction processes in the subsurface, which can be self-sustaining in natural environments (Lorah and Olsen, 1999; Lee et al., 1998; USEPA, 2002; Lendvay et al., 2003; Baez-Cazull et al., 2008). Constructed wetlands offer a cost-effective approach for bioremediation, which facilitates degradation of PCE to benign daughter products (carbon dioxide, ethene or ethane and water) by exploiting aerobic/anaerobic

interfaces in wetlands (Kadlec and Hey 1994; Li, 1997; Bradley and Chappelle, 1998; Kenneke and Weber, 2003; Lorah and Voytek, 2004; Amon et al., 2007; Imfeld et al., 2008).

Biogeochemical Processes and Fate of CAHs in Wetland Environment

Increasing research in recent years elucidates the chemical processes in constructed wetlands that can degrade chlorinated ethenes (Lorah and Olsen, 1999; Kenneke and Weber, 2003; Lorah et al., 2004, 2007; Amon et al., 2007; Mander and Mitsch, 2009). In strongly reducing wetland soil, CAH compounds may degrade by reductive dechlorination processes, e.g., PCE can degrade to ethene and water. In iron reducing, sulfate reducing and methanogenic conditions, PCE can undergo reductive dechlorination by either hydrogenolysis or dichloroelimination (Supplements 1, 2) (McCarty and Semprini, 1994). Resulting daughter products include trichloroethene (TCE), 1,1 dichloroethene (1,1 DCE), *cis* and *trans* 1,2 dichloroethenes (1,2-DCE), and vinyl chloride (VC), which then can be reduced to ethylene.

PCE dechlorination can occur in iron reducing, sulfate reducing and methanogenic conditions (Lorah and Voytek, 2004), while daughter products, DCEs and VC, require sulfate-reducing/methanogenic or aerobic conditions to degrade (Supplement 2). However, DCEs and VC often persist in methanogenic conditions due to biogeochemical factors (Bradley and Chappelle, 1998; Lorah and Voytek, 2004). The competition for hydrogen (as an electron doner) with other microorganisms may contribute to persistence/slow-degradation of DCEs and VC in anaerobic environments (Lorah and Voytek 2004; Becker, 2006; Kassanga and Pardue, 2006). Sulfate reducing or methanogenic soil near aerobic interfaces around roots in wetlands can provide the necessary environments for destruction of DCE and VC via oxidation (Bradley and Chappelle, 1998; Arnold et al., 2002).

DCEs and VC degrade via metabolic and co-metabolic reactions in sulfate-reducing, methanogenic and oxidative conditions. In metabolic reactions (dehalorespiration), CAH is used as the electron acceptor, and an electron donor is required. DCEs may persist longer than VC as bacteria prefer VC substrate over DCE (Verse et al., 2002). This preference may be due to the fact that VC reactions provide an additional 1.6 kcal/mole. of energy compared to DCE reactions (Supplement 2) (Wiedmier et al., 1999). TCE, DCEs and VC can also biodegrade in aerobic conditions. During aerobic co-metabolic degradation reactions, bacteria require a growth substrate, such as methane or ethene, to produce a non-specific enzyme that can also oxidize certain CAHs, including TCE, DCEs and VC (Chang and Alverez-Cohen, 1996).

Additional mechanisms for CAH removal in wetland environments include phytochemical reactions, abiotic mineralization, volatilization and sorption to soil organic matter. In the phytochemical process of removal, after initial uptake by roots, CAH molecules can be mineralized and become attached to a glycoside in plant tissue. Once in tissue, the chlorinated alcohol is stored, degraded or volatilized leaving the plant free of the original contaminant (Shang et al., 2001). Though rates vary for each wetland, abiotic/biotic mineralization in iron reducing and methanogenic soils account for 10-34% of overall CAH degradation (Bradley and Chappelle, 1996; Bankston et al., 2002; Lorah and Voytek, 2004).

Sorption and volatilization may vary considerably at wetland sites depending upon soil type and available dissolved organic carbon. In a bench-scale study (Bankston et al., 2002), 50% of radiolabled TCE was lost due to volatilization. Lorah and Olsen (1999) reported significant CAH removal (~50%) due to sorption in their study of a tidal wetland. This suggests that considerable amounts of CAH loss may be attributed to sorption and volatilization alone and mechanisms of loss may differ for each wetland.

Reduction-oxidation reactions influence nitrogen, sulfur, iron and carbon cycling in natural wetlands and aquifers (Bradley and Chappelle 1996; Roden and Wetzel, 1996; Kostka et al., 2002; Sutten-Grier et al., 2011). A basic understanding of the biogeochemical cycling is necessary to evaluate what the changes in their concentrations reveal about CAH destruction potential in a constructed wetland (Bradley and Chappelle 1996; Roden and Wetzel, 1996; Kostka et al, 2002; Sutten-Grier et al 2011). This section focuses on nitrogen, sulfur and methane cycling in a natural wetland/aquifer system to correspond with data available for this study.

Abiotic and biotic chemical processes in natural wetlands both bind and release nitrogen species. Abiotic ammonification and mineralization in aerobic zones oxidize nitrogen species, thus increasing nitrate concentrations in the wetland (Golterman, 1995). In vegetated wetlands, however, plant uptake can reduce nitrates formed in the aerobic zones from mineralized ammonia. Denitrification by bacterially mediated processes, along with plant activity, consumes 40-90% of nitrogen in constructed or natural wetlands (Gilliam, 1994; Golterman, 1995; Vymazal, 2007). Reductive biotransformations of CAHs may occur only after nitrates are depleted. Therefore, presence of active denitrification can hasten CAH dechlorination (Supplement 2).

Sulfide minerals including, pyrite (FeS_2), are oxidized in wetland soils to form sulfate in oxygenated soils (D'Angelo and Reddy, 1999; Baez-Cazull et al, 2008). Multiple sulfide species, including hydrogen sulfide (H_2S) and thiosulfide ($S_2O_3^{-2}$) are oxidized abiotically or biotically to sulfate in aerobic wetland soil (Rickard and Luther, 2007). Sulfates from external

sources can also enter wetlands through run-off or from the surrounding aquifer. Plant-mediated reactions can release sulfate in the root zones upon uptake of atmospheric sulfur by leaves (Krairapanond et al, 1992). In some instances, certain roots can uptake sulfate from pore water, which undergoes assimilatory reduction to form amino acids in plant tissue (Mugford et al, 2011; Kahn et al, 2010); root uptake of sulfate may account for some loss of sulfate in the wetland. Bacterially mediated reduction reactions, which reduce sulfate to sulfide, dominate sulfur transformation reactions in the wetland, and they are key to PCE dechlorination (Wiedemier et al., 1999; Lorah and Voytek, 2004; Reddy and Delaune, 2008;). Therefore, a decrease in sulfate suggests ongoing sulfate reduction and probable CAH degradation in contaminated aquifers/wetlands (Lorah, 1999; Kassanga and Pardue, 2006; Amon et al, 2007).

Wetland-generated methane is the greatest source of global methane (Chappellaz et al., 1993; Mitchler et al., 2009). The mechanisms of methane production in wetlands include microbiological reduction of carbon dioxide (hydrogenotrophic methanogenesis), acetate fermentation (acetoclastic methanogenesis) associated with organic matter decomposition, UV-related aerobic plant processes and osmotic assimilation from the atmosphere (Keppler et al., 2006, 2008). In freshwater wetland soils, acetate fermentation is the dominant pathway for methanogenesis. The pathway of carbon dioxide reduction accounts for a minimum of 30% of methane contributed by the wetland (Conrad, 1999). In other words, at least 30% of methane concentrations in atmospheric background of 1750 ppb can be attributed to methanogenesis by microbial reduction of carbon dioxide (Wuebbles and Hayhoe, 2002). Temperature, pH, oxygen, wetland fauna type and growth, and rate of deposition of organic matter can alter the ratio of acetate fermentation to carbon dioxide reduction (Valentine et al., 1994; Chanton et al., 2004). Only after methanogenesis by acetate fermentation decreases in anaerobic soils can

methanogenesis by carbon dioxide reduction increase. Anaerobic soils in wetlands, which

support methanogenesis by carbon dioxide reduction, create an environment conducive to CAH

degradation (Little et al., 1988; Chang and Alverez, 1996; Kassenga and Pardue, 2004; Lorah

and Voytek, 2004; Kassenga et al., 2006).

Site Description: Pilot Scale Treatment Wetland at Wright Patterson AFB

In August 2000, researchers at Wright State University (WSU) combined efforts with the

United States Air Force Institute of Technology (AFIT) to construct a pilot-scale wetland on

Wright-Patterson Air Force Base, Ohio, that could treat PCE-contaminated groundwater brought

in from a nearby aquifer (Amon et al., 2007). An upward flow treatment wetland was

constructed by excavating a pit and removing ~1000 cubic meters of site soil (dimension: 37 m x

18 m x 1.5 m). The pit was then lined with a PVC geomembrane and filled with 3 layers of

hydric soil obtained from a nearby drained wetland (Amon et al., 2007).

A 21 cm thick layer of crushed gravel surrounds pipes and lies beneath 1.3 m of local

wetland soil. The lowest 43 cm of wetland soil is amended with wood chips to increase the

natural carbon in the wetland soil and provide electron donors in the form of hydrogen to support

halorespiration (Kassenga et al., 2004; Kassenga and Pardue 2006; Amon et al, 2007) (figure 1).

A pumping system was installed to bring PCE-contaminated groundwater to the wetland in the

gravel layer. The system employed three perforated PVC pipes to distribute contaminated water

across the gravel layer of the wetland and force water movement upward through the 3 layers of

hydric soil to the surface, where treated water exits over a weir into the local drainage system

(Supplement 3). Multiple varieties of hardy wetland plants (sedges), and augmented bacterial

seed were placed throughout the wetland (Clemmer, 2003; Amon et al., 2007).

In 2001, a monitoring system comprised of 66 nested piezometers arranged in a 6 x 11 grid was installed at the site to allow water sampling from 3 distinct depths: 0.23 m, 0.69 m and 1.14 m (figures 1, 2). Solinst Model 615S stainless steel piezometers resist degradation in various redox environments and insure integrity of sampling (Powell et al., 2010). The three sampling depths correspond to the upper, middle and lower layers of the wetland, and allow for geochemical analysis in three soil layers: Lower zone with high organic carbon, anaerobic Middle zone, and Upper plant-influenced aerobic zone (figure 1).

Established Flow Patterns in Wetland

Variations in hydraulic conductivity in wetlands influence flow patterns and can be caused by vegetation, heterogeneous soil, piezometer installation, higher transmissivity along outer walls of the wetland, and flow variations due to exiting water (Opperman, 2001; Entingh, 2002; Clemmer, 2003; Kassenga et al., 2003; Kenneke and Weber, 2003; Koskiaho, 2003; Lach, 2003; Lorah and Voytek, 2004; Giraldi et al., 2009; Imfeld et al., 2009; Lightbody et al., 2009). The suggested areas of increased flow can compromise wetland efficiency by creating fluidized soil zone of greater mixing and reduced residence time, which may also affect the microbiologic activities in the wetland soil. Therefore, it is important to know the flow patterns in the wetland.

The water flowpath in 3-D in the wetland was modeled using hydraulic head data gathered from 60 piezometers (Corbin, 2008). These findings establish upward flow from influent to effluent in this constructed wetland. Supplement 5 shows the greatest flow to be occuring along southern (AB) and effluent (BC) side of wetland. Analysis at 0.23m also identifies a fast moving horizontal flow path in the center of wetland. (Entingh, 2002; Lach, 2003; Corbin, 2008). Water flows vertically through each of the 3 layers in 75% of wetland.

Substrate variations cause restriction in flow from the Middle to Upper layer in 15% of wetland. Analysis of the 3 layers shows greatest variance in conductivities in the Middle layer (Supplement 5). Effluent flow changes head pressure at 0.23 m and 0.69 m depths, but only minimally. The Lower layer demonstrates greatest head pressures and a vertical flow up to 50 times greater than Upper and Middle layers.

Site Studies: 2001-2006

Between 2001 and 2006, AFIT and WSU researchers sampled 32 different chemical parameters within the wetland totaling approximately 32,500 data points, which detailed short term changes in PCE concentrations or chemical indicators of reductive dechlorination. AFIT researchers tested for organic or inorganic species, alternating yearly and WSU researchers sampled a variety of both classifications of species (Tables 1a and 1b). Findings suggest the amount of PCE degraded in each layer has changed over time (Table 2). Researchers documented reductive dechlorination of PCE and reported a concentration decrease of 74%-95% (Table 2). These individual studies indicated the wetland's efficiency in degrading PCE will increase until a steady state is reached.

Due to the length of study and multi-level sampling from a network of piezometers, the pilot scale wetland generated abundant data and provided a unique analysis opportunity. The goal of this study was to consolidate and standardize 2001-2006 datasets in order to analyze the rate and distribution of PCE degradation starting from initial construction to its mature and stable operation in 2006. Characterization of the spatial boundaries of PCE dechlorination has provided better insight into the influence of the chemical, physical, and geological parameters in the wetland on the fate of PCE in the wetland. Understanding how variations in hydraulic

conductivity and terminal electron accepting processes in the pilot-scale wetland affect CAH

destruction can be the key to its acceptance as an effective remediation technology. This study

attempts to establish the relationship between geochemical and physical attributes of the wetland

soil and PCE dechlorination at this site.

II. Methods

Statistical Analysis: Jenks Optimization

In this study, uniformly applied '*Jenks Optimization'* technique (goodness of variance fit;

Jenks, 1967) was uniformly applied to all water chemistry datasets collected from November

2001 through December 2006 in order to identify and remove outliers. As a result of instrument

error, detection limits too low to capture and null or missing sample values, WPAFB wetland

datasets contained a large number of zero concentration values for all parameters. From a

statistical point of view, it is unlikely that all of the zero values are accurate. Moreover, the large

number of zero and null values can suppress variations in geochemical activity. The *Jenks*

Optimization can solve this problem by minimizing the sum of squared deviations to establish

classes for data (Jenks, 1967). Jenks optimization was applied to each of the 3 sampling depths

separately as each chemical parameter varies with depth. Upper and lower classes contain

outliers in dataset, including a percentage of excessive zero data for each species. Results

identified problematic data sets, which led to evaluation of possible computation, or method

errors, for each sampling event. Identified errors were corrected and the revised data was

reprocessed using *Jenks Optimization*. Upper and lower classes from second optimization were

removed before initiating analysis of remaining data (Table 3). All inorganic data for

July/November 2003 was above error limits, and was therefore removed from final dataset.

Additionally, a large number of high values were removed from 2006 trans-DCE data. Due to this fact, remaining data in this sampling event may be in error. The resulting amalgamated, Jenks optimized dataset presumably contained more accurate ranges of values for each geochemical parameters from 2001-2006, and which was used for additional analysis.

2001-2006 Individual Piezometer Subsets

This study used Microsoft Access to consolidate and reorganize 2001-2006 data into 66 subsets grouped by sampling location (piezometer). Graphs of PCE vs. time for each of the 66 piezometers were compared to 2008 hydraulic conductivity data to determine how short circuits (faster flow-paths) of water flowing upward through the wetland may have affected CAH degradation. Each sampling depth, 0.23 m, 0.69 m and 1.14 m, was considered separately. The analytical results from piezometers located in the areas with faster flow path (short-circuit) were then compared to those in areas of low flow.

DCE/VC scatter plots constructed from piezometer subsets were employed to explore wetland efficiency. The DCE/VC datasets from 2003 and 2006 were selected for this analysis as these datasets included all 66 piezometers and were sampled in the same season. DCE/VC was not detected in influent for these datasets. The formation of DCE and VC compounds as daughter products may indicate biogeochemical processes of PCE degradation occurring within wetlands. Formation of DCE and VC as degradation products can occur in a strongly reducing environment by reductive dechlorination of PCE and TCE. The absence of DCE and VC, however, coupled with low PCE and TCE concentrations in strongly reducing wetland soil may either indicate their complete reduction by hydrogenolysis or by one of the alternative pathways, such as reductive elimination. TCE can also degrade by co-metabolic oxidation to CO_2;

therefore high concentrations of DCE and VC in aerobic wetland soils may indicate the migration/flux of these daughter products from adjoining anaerobic environments (Bradley and Chappelle, 1998; Lorah and Olsen, 1999). The presence of DCEs and VC concentrations in samples from each of the 66 piezometers may indicate biogeochemically active zones the wetland.

Influent to Effluent Transects

This study constructed six horizontal influent to effluent transects across the treatment wetland site by integrating piezometer subsets and 6 x 11 sampling grid (Figure 2). All data from 2001-2006 (Jenks Optimization applied) from each piezometer were integrated into transects. These transects describe the relationship between concentration and distance from the source, which can aid in interpreting the wetland's efficiency (Kadlec, 2000). Because distance is constant for each transect, concentration differences in north, south and central sections of the wetland (Figure 17) can provide insights into variations in flow rates and residence time. The regulatory guidelines (U.S. EPA, 1999) have approved using decrease in aqueous contaminant concentrations along the water flow-path from source as means to evaluate CAH attenuation. Using trends over several monitoring points, researchers can assess overall attenuation of CAHs in a constructed wetland (Aziz et al., 2000). In 2000, the USEPA Office of Research and Development released BIOCHLOR "Natural Attenuation Decision Support System" -an Excel based program to evaluate natural attenuation in aquifers using field data and distance from source. Though geophysical parameters in an aquifer may differ from those in a constructed wetland, most shallow subsurface environments will likely possess biogeochemical processes and similarly affect biotransformation reactions of CAH species. This study used transects prepared from water chemistry data from the WPAFB constructed wetland, and the data analysis

approach using BIOCHLOR to document CAH attenuation at Cape Canaveral Air Force Base (Aziz et al., 2000) for evaluating the efficiency of the constructed wetland at WPAFB.

ArcGIS Maps

This study employed ArcGIS software to process and map data thus relating CAH and redox-active species to geographical co-ordinates in the constructed wetland. Maps (Figures 4-6,8,9,11-15,19) were constructed by applying natural neighbor interpolation to subsets of winter data, which was collected annually (Table 4). Examining data collected in cold months, independent of additional data, reduced temperature related variations in geochemical processes and provided a more accurate analysis of wetland processes through years. For example, data collected in January 2006 and December 2006 were previously combined into yearly averages, but they may represent 2 separate stages in the biogeochemical evolution of the wetland. Both stages are displayed in maps of winter data. Maps describe these 2 sampling events as winter 2005/2006 and winter 2006/2007 to distinguish both stages. Maps were constructed from raw data and data with Jenks Optimization and then compared. Only upper classes of Jenks Optimization were removed from data for map construction, as all low outliers occurred adjacent to the lowest concentrations in wetlands and did not affect interpolation. Species analysis included PCE, TCE, cis-DCE, trans-DCE, VC, ethane, sulfate, nitrate, nitrite, ferrous iron and methane. Winter data was not available for iron and methane. Additional maps were constructed from July 2003 data (for Fe^{2+}) and July/September data (for methane). Analyses of maps reveal patterns in the rates and spatial distribution of PCE degradation and redox-active species, thereby highlighting the biogeochemical processes in the constructed wetland site.

III. Results and Discussion

Terminal Electron Accepting Processes (TEAPs) in the Wetland

Multiple terminal electron acceptors were present at all depths in the wetland, allowing different processes of reduction or oxidation to proceed simultaneously at different depth intervals and zones. The results indicate that the dominant TEAP changed with time throughout the wetland. For example, while nitrate reduction was dominant in 2002, sulfate reduction and iron (III) reduction became dominant in 2003, and nitrate reduction increased in 2005 and 2006. Methanogenesis was confirmed in 2003, which likely continued through 2006, as evident from continued attenuation in PCE (Lorah and Voytek, 2004; Waldron, 2007) (Figures 3-10).

Nitrate Reduction in the Wetland: Variations in nitrate and nitrite concentrations suggest that nitrate reduction began after 2002 and continued through 2006 (Figures 3, 4 a-c). Modest to high nitrate concentrations were observed in January 2002, which declined significantly in 2003, indicating active nitrate reduction (Figures 4 a,b). In 2002, nitrate was produced in Middle and Upper layers in the wetland (Figure 4a). At this stage in development, plants are well established and the organic matter in the amended hydric soil may be decaying. Anaerobic zones, however, may not have been sufficiently established in 2002, thus allowing ammonification of soil organic matter and subsequent nitrification to form nitrate in upper 2 layers (Figure 4a). By winter 2005/2006, nitrate depletion was widespread across the wetland. Nitrite maps show the opposite pattern with near zero concentrations in winter 2002/ 2003 and high concentrations in winter 2005/2006, which suggests nitrate reduction at all depths (Figures 5a-5b). A corresponding increase in nitrite in 2005 and 2006 confirms ongoing nitrate reduction (Figure 3). Sulfate

reducing and methanogenic environments, which can more completely dechlorinate PCE, generally require a stronger reducing condition past nitrate reduction.

Sulfate and nitrate decrease simultaneously by December 2002, which indicates a change in wetland chemistry. Though oxic water enters the wetland, these decreases in average sulfate and nitrate concentrations indicate a reducing chemistry capable of partially dechlorinating PCE. Widespread exhaustion of nitrate suggests iron III or sulfate reduction is probable in the wetland.

Fe(III) Reduction in the Wetland: Figure 6a shows elevated Fe^{2+}(aq) concentrations at (0.23 m) and (0.69 m) suggesting that microbial iron (III) reduction was well established in the Middle and Upper layers in 2003. However, Fe^{2+}(aq) concentrations decreased in 2005 (Figure 6b), suggesting a decline in iron III reduction possibly due to a shift in local biogeochemistry due possibly to changes in ORP of the groundwater entering the wetland or depletion of Fe(III) bearing mineral phases. Since the water samples collected in 2006 were not analyzed for Fe^{2+}(aq), it remains unclear if Fe(III) reduction resumed immediately after 2005. As sulfate reduction follows iron (III) reduction, sulfate analysis has shown competing terminal electron accepting processes in the wetland.

Sulfate Reduction in the Wetland: The wetland exhibits some variations in the sulfate reducing conditions between December 2002 and 2005 (Figure 3). In January 2002, mean sulfate concentration in the Lower layer is only 0.028 mM, but increases in the Middle and the Upper layers throughout the wetland indicate sulfate production presumably due to oxidation of reduced sulfur species in the hydric soil during the early stages of wetland development. It is possible that sulfate was produced in the Middle and Upper layers in winter 2001/2002 by oxidation of reduced sulfur species at root zones. Beginning in 2003, however, and continuing through the

14

summer of 2005, sulfate concentrations showed a decline along the water flow path from Lower to Middle and Upper layers (Figures 3, 8b-d). Such widespread declines in sulfate concentrations independent of season during this period may suggest bacterially mediated sulfate reduction (Wiedemeier et al., 1999). Higher sulfate concentrations in the Lower layer (1.14 m) in 2002/2003, and 2005/2006 correspond to elevated influent concentrations (Figures 3, 8b,d). During these years, sulfate concentrations showed a significant decrease in Middle and Upper layers (0.69 m and 0.23 m), despite high sulfate concentration in the influent water entering the wetland. However, higher sulfate concentrations are expressed in isolated areas/patches 1-8 meters in width in Middle and Upper layers in 2002/2003, and 2005/2006 (Figures 8b,d). These areas showed elevated levels of sulfate (average ~0.4 mM) indicating patches of fluidized soil that may reduce residence time due to faster water flow, while remaining areas of Middle and Upper layers show near complete sulfate depletion. Higher sulfate levels in the Lower layer in winter of 2002/2003 and 2005/2006 may reflect increased influent concentrations or possibly a slowing sulfate reduction (Figures 8b,d). The winter 2003/2004 map shows sulfate depletion throughout the wetland, perhaps indicating a strongly reducing environment for the life of the wetland (Figure 8c).

Methanogenesis in the Wetland: The sulfate concentration maps of 2002-2006 and the methane concentration map of 2003 suggest that sulfate reduction and methanogenesis probably occurred simultaneously from winter 2002 to 2005 (8a-d and 9). Methanogenesis should generally occur in areas where sulfate was depleted (Figures 8 b-d). Methane map of 2003 shows elevated methane concentrations in at least one geographic location at all depths in the wetland (Figure 9). Methane levels in the Upper layer are below atmospheric background of 1750 ppb, which may have been influenced by volatilization, acetate fermentation and methane oxidation (Conrad,

15

1999). Methane levels in Middle and Lower layers (Figure 9) may be attributed to microbial methanogenesis (Wuebbles and Hayhoe, 2002). A modest decrease in methane concentrations in the Upper layer in comparison to the Middle layer may suggest bacterially-mediated methane oxidation or plant-mediated transpiration in the Upper layer.

Throughout the study period, the Middle layer exhibited a strongly reducing condition. The sulfate maps of winter 2002/2003 and 2005/2006 show reducing conditions in the Upper and the Middle layers (Figures 8 b,d). The maps showing Fe^{2+}(aq) (Figures 6 a,b) and methane of 2003 (Figure 9) indicate that the strongest reducing conditions may occur in the Middle layer. CAH data analysis (discussed below, in the following section) also indicates that Upper and Middle layers are primary locations for reductive dechlorination.

CAH Degradation in the Wetland

The fluctuations in PCE and daughter product concentrations can describe wetland efficiency and chemical pathways occurring over time. Low PCE and TCE concentrations in the Middle and Upper layers coupled with documented upward flow (Entingh, 2002), indicated reductive dechlorination as early as January 2002 (Figure 10). PCE concentrations decreased to low levels quickly in the Middle layer by November 2003 (Figure 10). The PCE concentration entering the wetland showed some variations in the study period, with a modest decline during 2003-'05, but the PCE level increased again gradually in 2006 (Figure 10). A significant decline in PCE concentration was observed along the water flow path from Lower layer to Middle layer through 2001-'06 (Figures 11 a-e), which may be attributed to degradation, presumably due to reductive dechlorination. Based on the mean influent and effluent concentrations during October-December 2006, the PCE removal efficiency from the contaminated water passing

through the wetland is ~82%-93% (Mohamud, 2007; Waldron, 2007). The removal efficiency showed some fluctuation during the study period, however, perhaps due to changing influent PCE concentration, and spatial variations in hydraulic conductivity and terminal electron acceptors.

The variations in PCE concentration show degradation at all depths, but the greatest decline in PCE concentrations and largest concentrations of daughter products occur in the Middle layer (Figures 10, 13b, 14a,b, 15). The spikes showing on TCE, trans-DCE, VC and ethane concentration maps of 2001-2006 occur in the Middle layer (Figures 12-15). Such spikes in TCE, trans-DCE, VC and ethane maps may be located in the areas affected by decrease in water residence time due to soil fluidization (Figures 13, 14).

A modest decline in PCE concentration from the Middle layer to the Upper layer (Figures 11a-e) may indicate that its degradation continues along the water flow in the wetland. During the winters of 2002/2003, and 2005/2006, isolated PCE concentrations, which are not depleted in Middle layer (0.69 m), decline to zero in Upper layer (0.23 m), (Figures 11b,d). This depletion is greatest farthest from influent, suggesting residence time increases PCE declorination for Upper and Middle layer. Residence time also affects any reductive dechlorination, which occurs at greater depth in wetland.

Reductive dechlorination in soils at 1.14 m begins in 2003 with high influent concentrations, temperature and residence time affecting rate of decrease. Figure 10 shows declines in PCE even in less reducing soils at this depth. Sorption, upward flow or reductive dechlorination, may cause the consistent 7-19- ppb loss of PCE from influent to Lower layer (1.14 m). The difference between influent and concentrations in Lower layer increases with

time, which indicates PCE loss increases this layer (1.14 m) as the wetland ages.(Figure 10). This fact along with spatial changes in distribution in central and effluent the end of the wetland during 2001/2002 - 2005/2005 suggest that the decline in PCE concentration at 1.14 m may be the result of reductive dechlorination (Figures 10, 11a-d).

CAHs in the wetland break down at different depths and redox environments. TCE, trans-DCE and VC species above highest influent concentrations of 2.4 ppb, 3.13 ppb and 0.57 ppb, respectively are present in wetland soils at all depths (Figures 12c, 13b, 14a,b). 2003 data shows daughter products; trans-DCE, cis-DCE or VC, at 63 of the 66 sampling locations (Figure 16). Occurance of DCE and VC in the Middle layer, which appears to be the strongly reducing interval, indicates hydrogenolysis of PCE and TCE in sulfate reducing and methanogenic soils (Lorah and Olsen, 1999). Low/no DCE and VC concentrations at 0.23 m suggest degradation via oxidative processes (Figures 13 and 14). Decreases in methane concentrations coupled with disappearance of VC at 0.23 m depth in 2003 supports VC destruction via oxidative co-metabolic processes (Figures 9, 14a). TEAP environment and availability of chlorinated hydrocarbon dictates pathways and the multitude of available pathways ensure continued dechlorination

Analysis of Wetland Transects

Transects constructed from 2005-2006 data show-horizontal distribution and describe the relationship between PCE concentrations and distance from its source. Although flow rate changes dramatically due to soil heterogeneity in wetland, distance from influent to effluent remains constant. PCE decreases to near 0 for all 3 transects in Upper (0.23 m) and Middle (0.69 m) layers. This suggests size of the wetland is sufficient to accommodate existing variations in

flow rate in upper two layers. Trend line slopes for Lower layer (1.14 m) are positive or near zero, which suggests significantly less reductive dechlorination at this depth during the life of the wetland and elucidates the importance of upward flow in a constructed wetland (Figure 17).

Though multiple forms of analysis establish PCE loss via reductive dechlorination at the WPAFB site, the diversity of biogeochemical activity, and chemical exchanges in an open wetland system make quantifying rate of reduction a considerable challenge (Baez-Cazul et al., 2008; Kadlec, 2000). A study completed in 1999 by Parson's Engineering Science Inc, confirmed ongoing reductive dechlorination in an aquifer containing a CAH plume at Cape Canaveral Air Force Base (Aziz et al., 2000). Biochlor analysis of the Cape Canaveral plume, adjusted to a period of 6 years, yields a biotransformation rate of 75% for PCE reaching zero mM 116 m from source at a flow rate of 1.55 m/day. Calculated intercepts from WPAFB transect data suggest PCE concentrations can reach zero mM 21 m to 45 m from source at depths of 0.23 m and 0.69 m and a PCE remediation rate of 75% over the lifetime of the wetland. Given the 37 m length of wetland, and multiple flow paths, PCE concentrations above 0 will reach effluent. The calculated percent loss from average influent/effluent samples from 2001-2006 also yields a 75% PCE loss. Variations from 82%-93% degradation rate calculated by individual researchers from influent/effluent may be caused by differences in monthly or seasonal datasets and layer sampled.

Effects of Hydraulic conductivity

Ideal flow rate in a wetland constructed to remediate CAH's is fast enough to mix water of varying densities and temperatures, and slow enough to maintain a residence time for PCE sufficient for reduction to ethane and carbon dioxide (Kadlec, 2000; Koskiaho, 2003; Amon et al., 2007; Austin, 2009; Giraldi et al., 2009; Lightbody et al., 2009). As constructed wetlands

19

with subsurface horizontal and vertical flow are most efficient (Imfeld et al., 2009), it is important to validate these flow patterns in the wetland at WPAFB. PCE peaks in upper two layers which correspond to depressions at basement of wetland show effects of vertical flow (Figures 11 a,b). The southeast drift of PCE peaks/depressions in all layers from winter 2001/2002 to winter 2002/2003 validate horizontal flow from influent to effluent as does the eastern drift of PCE depression from winter 2005/2006 to winter 2006/2007 (Figures 11a-b, d-e).

Flow rate for this wetland was estimated from changes in physical features on PCE concentration maps. The influent PCE decrease measured in July 2003 (Figure 10) produces a 6 meter depression 29 months later at 1.14 m on 2005 map (Figure 11d). The corresponding rate of flow equals 0.0068 m/day and an analogues residence time at this depth of 0.25 days. By December 2006, the depression has traveled 9 m in 41 months giving an analogous flow rate of 0.0072 m/day and residence time of 0.26 days (Figure20). The predominantly uniform physical attribute on winter 2005/2006 and winter 2006/2007 PCE concentration map, and 0.04 m/day change in value from 2005 to 2006 suggests a more uniform horizontal flow at 1.14 m depths. These rates of flow are sufficient to maintain complete reductive dechlorination of PCE.

Paths of increased flow, or short circuits undermine the process of reductive dechlorination at other constructed wetland sites (Lightbody, 2009). Short circuits, or accelerated flow paths were identified in central regions of the wetland at WPAFB (Entinigh, 2002; Corbin, 2008) (Supplements 4 and 5). Effects of these short circuits on PCE degradation at this wetland were evaluated by comparing PCE concentrations in areas of greatest and least vertical and horizontal flow (Figure 18). Analysis of PCE/TCE concentrations in Middle, most reducing layer, which also included greatest variations in head pressures, should elucidate the influence of flow rate on degradation. Plots show very similar behavior in non-adjacent areas of

similar flow suggesting biogeochemical activity is similar in areas of similar hydraulic conductivity. PCE/TCE concentrations of zero in 2005 in all 4 locations indicate PCE dechlorination regardless of flow rate (Figure 18). In areas of high flow, PCE/TCE concentrations fluctuate more than in areas of low flow and exhibit a net PCE decrease of 96.7% from concentrations at 1.14 m. PCE/TCE concentrations exhibit less fluctuation in areas of low flow, and a 99% decrease in PCE from the level at 1.14 m. Reductive dechlorination occurs at a high rate in Middle layer regardless of hydraulic conductivity.

Elevated chemical concentrations in Upper layer (0.23 m), adjacent to boundaries of wetland are the result of physical, rather than chemical processes. Though necessary to isolate contamination, the wetland's liner decreases friction and increases vertical flow. CAH concentration changes at 0.23 m, which can be attributed to increased transmissivity at wetland's liner are evident at piezometers 24, 37, 42 and 49 (Figure 19). Figure 19 also illustrates high VC and trans-DCE concentrations at mid-depth at these piezometers. Corresponding VC and DCE concentrations at 0.23 m at these same piezometers are not consistently expressed due to oxic conditions. Concentrations in excess of 100 ppb at the edges of the wetland at mid depth in these areas may not degrade to maximum concentration limits of 2 ppb and should be closely monitored. Constancy in position of peaks during longevity of wetland suggests transmissivity along liner will continue to decreases the wetland's efficiency.

Due to lateral flow at effluent, higher hydraulic gradient draws CAH species from depth as shown on 0.23 m depth maps at piezometers 63, 64 and 65 (Figure 19). This process raised PCE effluent concentrations above maximum concentration limit of 5 ppb multiple times within the study period (Table 5). All other effluent CAH concentrations present in Upper layer were below MCLs, which indicates soils directly beneath effluent are the origin of elevated PCE. This

21

quick vertical transport limited residence time of PCE and curtailed reductive dechlorination, despite chemically mature remediation wetland (Figure 19). Even if effluent samples were below MCLs, documented existence of areas of elevated concentrations in Upper layer (0.23 m) throughout lifetime of wetland dictates monitoring effluent regularly.

IV. Conclusions

Analysis of consolidated 2001-2006 datasets illuminates the genesis of PCE treatment wetland from initial concept to a functioning wetland with strongly reducing geochemical conditions and flow patterns capable of PCE destruction within 18-24 months. Dechlorination of PCE occurs at every depth and at every sampled location despite significant differences in hydraulic conductivity and available electron acceptors. Rate of dechlorination varies with depth and hydraulic conductivity. Mid-depth areas of highest hydraulic conductivity demonstrate the highest rates of PCE's dechlorination. Maximum VC and DCE dechlorination occurs between Middle (0.69 m) Upper layer (0.23 m) where conditions are less reducing.

Size of pilot scale treatment wetland insures adequate residence time despite short circuits. Two exceptions to this occur. At effluent, increases in head pressure, due to laminar flow bring higher concentrations from gravel layer to surface quickly. In several areas at boundary of wetland, chemicals are transmitted quickly along the liner. Despite these processes, effluent concentrations for all species of chlorinated aliphatic hydrocarbons remain below maximum concentration limits for all sampling events between January 2003 and September 2006. 2006 effluent concentrations above MCL may be the result additional contaminant sources in intersecting aquifer, rebound or changes in flowpaths in wetland.

After an initial stage extending for ~18-24 month, the pilot-scale wetland responds to changes in influent concentrations. Declining PCE influent concentrations late 2005 coincide with 2005/2006 increases in sulfate, PCE and TCE in the wetland. This may be due to a decline in bacterially mediated dechlorination, a rebound effect, which drives sorbed PCE/TCE into pore water or sampling error. Implications to construction of wetland for treating PCE contaminated water include establishing and employing a grid monitoring system to ascertain geographical boundaries for problem areas, frequent sampling in initial 24 months and establishing controls on influent pumping system to adjust residence time as needed.

V. References

Agrawal, A. 2007. Validation of Engineered Wetlands as a Groundwater Treatment Technology for Chlorinated Solvents. ESTCP Proposal (unpublished).

Amon, J., A. Agrawal, M.L. Shelley, B.C. Opperman, M.P. Enright, N.D. Clemmer, T. Slusser, J. Lach, T. Sobolewski, W. Gruner, A.C. Entingh. 2007. Development of a Wetland Constructed for the Treatment of Groundwater Contaminated by Chlorinated Ethenes. Ecol. Eng. 30: 51-56.

Arnold, W.,P. Winget, C. Cramer. 2002. Reductive Dechorination of 1,1,2,2,Tetrachloroethane. Environ. Sci. Technol. 36: 3536-3541.

Austin, D.C., J. Nivala. 2009. Energy Requirements for Nitrification and Biological Nitrogen Removal in Engineered Wetlands. Ecol. Eng. 35: 184-192.

Aziz, C.E., C.J. Newell, J.R. Gonzales, P.E. Haas, T.P. Clement, Y. Sun. 2001. BIOCHLOR Natural Attenuation Decision Support System, User's Manual Version 1.1, U.S. EPA, Office of Research and Development, EP A/600/R-00/008,Washington D.C. www.epa.gov/ada/csmos/models.html. 46 p.

Baez-Cazull, S.E., J.Y. McGuire, I.M. Cozzarelli, M.A. Voytek. 2008. Determination of Dominant Biogeochemical Processes in a Contaminated Aquifer-Wetland System Using Multivariate Statistical Analysis. J. Environ. Qual. 37: 30-46.

Bankston, J.L., D.L. Sola, A.T. Komor, D.F. Dwyer. 2002. Degradation of Trichloroethylene in Wetland Microcosms Containing Broad-Leaved Cattail and Eastern Cottonwood. Water Res. 36: 1539–1546.

Becker, J.G. 2006. A Modeling Study and Implications of Competition Between Dehalococcoides Ethenogenes and Other Tetrachloroethene-Respiring Bacteria. Eviron. Sci. Technol. 40: 4473-4480.

BonDurant, C., Capt. 2004. Characterization of Microbial Processes that Degrade Chlorinated Solvents in a Constructed Wetland Using Organic Acid and Inorganic Anion Concentration Profiles. Air force Institute of Technology Thesis. 113 p.

Bradley, P.M.,F.H. Chapelle. 1998. Microbial Degradation of Chloroethenes in Groundwater Systems. Anerobe, Clinical Microbiology. 4: 81-87.

Bradley, P.M. F.H. Chapelle. 1996. Anaerobic Mineralization of Vinyl Chloride in Fe(III)-Reducing, Aquifer Sediments. Eviron. Sci. Technol. 30: 2084-2086.

Bugg, Capt., B. 2002. An Anion Characterization of a Constructed Wetland Used for Chlorinated Ethene Remediation. Air Force Institute of Technology Thesis. 266 p.

Chang, H., L. Alverez-Cohen. 1996. Biodegradation of Individual and Multiple Chlorinated Aliphatic Hydrocarbons by Methane-Oxdizing Cultures. Appl. Environ. Microb. 62: 3371-3377.

Chanton, J.P., L.C. Chasar., P. Glaser, D. Siegel. 2005. Chapter 6: Carbon and HydrogenIsotopic Effects in Microbial Methane From Terrestrial Environments, in: L.B. Flanagan, J.R. Ehleringer, D.E. Pataki (Eds.). Stable Isotopes and Biosphere-Atmosphere Interactions,Physiological Ecology Series, Elsevier-Academic Press, Amsterdam. 85-105.

Chappellaz, J.A.,I.Y. Fung, A.M. Thompson. 1993. The Atmospheric CH4 Increase Since the Last Glacial Minimum. Tellus. 45B: 228-240.

Clemmer, Capt., N. 2003. Characterization of Chlorinated Solvent Degradation in a Constructed Wetland. Air force Institute of Technology Thesis. 99 p.

Conrad, R. 1999. Contribution of Hydrogen to Methane Production and Control of Hydrogen Concentrations in Methanogenic Soils and Sediments. FEMS Microb. Ecol. 28: 193-202.

Corbin, Capt. R. 2008. An Analysis of Groundwater Flow Paterns in a Constructed Treatment Wetland Cell. Air Force Institute of Technology Thesis. 104 p.

D'Angelo, E.M., K.R. Reddy. 1999. Regulators of Heterotrophic Microbial Potentials in Wetland Soils. Soil Biol. Biochem. 31: 815-830.

Entingh, Capt. A.C. 2002. Groundwater Flow Through a Constructed Treatment Wetland. Graduate School of Engineering and Management, Air Force Institute of Technology Thesis. 1-182 p.

Gilliam, J.W. 1994. Riparian Wetlands and Water Quality. J. Environ. Qual. 23: 896-900.

Giraldi, D.,M. de'Michieli, M. Zaramella, A. Marion, R. Iannelli. 2009. Hydrodynamics of Vertical Subsurface Flow Constructed Wetlands: Tracer Tests with Rhodamine WT and Numerical Modeling. Ecol. Eng. 35: 265-273.

Golterman, H.L. 1995. The Labyrinth of Nutrient Cycles and Buffers in Wetlands: Results Based on Research in the Camargue (southern France). Hydrobiologia. 315: 39-58.

Imfeld, G., M. Braeckevelt, P. Kuschk, H. Richnow. 2009. Monitering and Assessing Processes of Organic Chemicals Removal in Constructed Wetlands. Chemosphere. 74: 349-362.

Imfeld, G.,C. Zeiger, S. Aragones, C. Vitzthum von Eckstadt, H. Paschk, R. Trabitzsch, H. Weiss, H. Richnow. 2008. Tracking in situ Biodegradation of 1,2-Dichloroethenes in a Model Wetland. Eviron. Sci. Technol. 42: 7924-7930.

Jenks, G.F. 1967. The Data Model Concept in Statistical Mapping, International Yearbook of Cartography. 7: 186-190.

Kadlec, R.H. 2009. Comparison of Free Water and Horizontal Subsurface Treatment Wetlands. Ecol. Eng. 35: 159-174.

Kadlec, R.H. 2000. Inadequacy of First Order Treatment Wetland Models. Ecol. Eng. 15: 105-119.

Kadlec, R.H., D.L. Hey. 1994. Constructed Wetlands for River Water-Quality Improvement.Water Sci. Technol. 29: 159-168.

Kassenga, G.R., J.H. Pardue. 2006. Effect of Competitive Terminal Electron Acceptor Processes on Dechlorination of cis- 1,2-dichloroethene and 1,2-dichloroethane in Constructed Wetland Soils. Fems Microbiol. Ecol. 57: 331-323.

Kassenga, G.R., J.H. Pardue, S. Blair, T. Ferraro. 2003. Treatment of Chlorinated Volatile Organic Compounds in Upflow Wetland Mesocosms. Ecol. Eng. 19: 305-323.

Kassenga, G.R., J.H. Pardue, W.M. Moe, K.S. Bowman. 2004. Hydrogen Thresholds as Indicators of Dehalorespiration in Constructed Treatment Wetlands. Environ. Sci. Technol. 38: 1024-1030.

Kenneke, J.F., E.J. Weber. 2005. Reductive Dechlorination of Halomethanes in Iron and Sulfate-Reducing Sediments. 1 Reactivity Pattern Analysis. Environ. Sci. Technol. 37: 713-720.

Keppler, F., J.T.G. Hamilton, W.C. McRoberts, I. Vigano, M. Braß, T. Röckmann. 2008. Methoxyl Groups of Plant Pectin as a Precursor of Atmospheric Methane: Evidence from Deuterium Labelling Studies. New Phytologist. 174: 808-814.

Keppler, F., J.T.G. Hamilton, M. Brab, T. Rockmann. 2006. Methane Emissions From Terrestrial Plants Under Aerobic Conditions. Nature. 439: 187-191.

Khan, M.S., F.H. Haas, A.A. Samami, A.M. Gholami, A. Bauer, K. Fellenberg, M. Reichelt, R. Hansch, R.R. Mendel, A.J. Meyer, M. Wirtz, R. Hell. 2010. Sulfite Reductase Defines a Newly Discovered Bottleneck for Assimilatory Sulfate Reduction and Is Essential for Growth and Development in Aravidopsis thaliana. Plant Cell. 22: 1216-1231.

Koskiaho, J. 2003. Flow Velocity Retardation and Sediment Retention in Two Constructed Wetland Ponds. Ecol. Eng. 19: 325-337.

Kostka, J.E.,A. Roychoudhury, P. Van Cappellen. 2002. Rates and Controls of Anaerobic Microbial Respiration Across Spatial and Temporal Gradients in Saltmarsh Sediments. Biogeochemistry. 60: 49-76.

Kovacic, Leut.,J. 2003. Analysis of Anion Distributions in the Developing Strata of a Constructed Wetland Used for Chlorinated Ethene Remediation, Air Force Institute of Technology Thesis. 160 p.

Krairapanond, N., R.D. Delaune, W.H. Patrick Jr. 1992. Distribution of Organic and Reduced Sulfur Forms in Marsh Soils of Coastal Louisiana. Org. Geochem. 18: 489-500.

Lach, J. 2004. Treatment of Contaminated Groundwater in a Constructed Wetland: A Biogeochemical Analysis, Wright State University Thesis. 118 p.

Lee, M.D., J.M. Odom, R.J. Buchanan Jr. 1998. New Perspecitives on Microbial Dehologenation of Chlorinated Solvents, Insights from the Field. Annual Rev. 52: 423-452.

Lendvay, J.M., F.E. Loffler, M. Dollhopf, M.R. Aiello, C. Daniels, B.Z. Fathepure, M. Gebhard, R. Heine, R. Helton, J. Shi, R. Krajmalnik-Brown, C.L. Major, M.J. Barcelona, E. Petrovskis, R. Hickey, J.M. Tiedje, P. Adriaens. 2003. Bioreactive Barriers: A Comparison of Bioaugmentation and Biostimulation for Chlorinated Solvent Remediation. Environ. Sci. Technol. 37: 1422-1431.

Li, J.W. 1997. A Comparative Study of Hydrogeochemistry in a Constructed Wetland With and Without the Hydric Soil.Wright State University Thesis. 60p.

Lightbody, A.F., H.M. Nepf, J.S. Bays. 2009. Modeling the Hydraulic Effect of Tranverse Deep Zones On the Performance of Short-Circuiting Constructed Treatment Wetlands. Ecol. Eng. 35: 754-768.

Little, C.D., A.V. Palumbo , S.E. Herbes, M.E. Lidstrom, R.L. Tyndall, P.J. Gilmer. 1988. Trichloroethylene Biodegradion By a Methane-oxydizing Bacterium. Appl. Environ. Microbiol. 52: 951-956.

Lollar, S., G.F. Slater. 2001. Stable Carbon Isotope Evidence for Intrinsic Bioremediation of Tetrachloroethene and Trichloroethene at Area 6, Dover Air Force Base. Environ. Sci. Technol. 35: 261-269.

Lorah, M.M., D.R. Burris, L.J. Dyer. 2004. Natural Attenuation of Chlorinated Solvent Ground-Water Plumes Discharging Into Wetlands. USGS Scientific Investigations Report.

Lorah, M.M., E.M. Majcher, E.J. Jones, M.A. Voytek. 2007. Microbial Consortia Development and Microcosm and Column Experiments for Enhanced Bioremediation of Chlorinated Volatile Organic Compounds, West Branch Canal Creek Wetland Area, Aberdeen Proving Ground, Maryland. USGS Scientific Investigations Report.

Lorah, M., L.D. Olsen. 1999. Degradation of 1,1,2,2-Tetrachloroethane in a Freshwater Tidal Wetland: Field and Laboratory Evidence, Environ. Sci. and Technol. 33: 227-234.

Lorah, M., M. Voytek. 2004. Degradation of 1,12,2-tetrachloroethane and Accumulation of Vinyl Chloride in Wetland Sediment Microcosms and In Situ Porewater: Biogeochemical Controls and Associations with Microbial Communities, Contaminant Hydrology. 70: 117-145.

Manahan, S.E. 2004. Environmental Chemistry. 8th ed. CRC Press. Boca Raton FL: 87-105.

Mander, U., W. Mitsch. 2009. Pollution Control By Wetlands. Ecol. Eng. 35: 153-158.

McCarty, P.L., L. Semprini. 1994. Ground-water Treatment for Chlorinated Solvents, in: R.D. Norris, R.E. Hinchee, R. Brown, et al (Eds.), Handbook of Bioremediation., Lewis Publishers, Boca Raton FL. 87-110.

McKetta, J. 1979. Encyclopedia of Chemical Processing and Design. 1st ed., Drekker, NY, NY. 40-67.

Mischler, J.A., T.A. Sowers, R.B. Alley, M. Battle, J.R. McConnell, L. Mitchell, T. Popp, E. Sofen, M.K. Spencer. 2009. Carbon and Hydrogen Isotopic Composition of Methane Over the Last 1000 Years Global Biogeochem. Cy. 23: GB4024, doi:10.1029/2009GB003460

Mohamud, Y. 2007. Seasonal Variation in the Redox Zones and Biogeochemical Processes within the Constructed Wetland, Wright State University Thesis. 189p.

Mugford, S.G., B.R. Lee, A. Koprivov, C. Matthewman, S. Kopriva. 2011. Control of Sulfur Partitioning Between Primary and Secondary Metabolism. The Plant Journal. 65: 96-105.

Opperman Capt.B. 2003. Determination of chlorinated Solvent contamination in an Upward Flow Constructed Wetland, Air force Institute of Technology Thesis. 133 p.

Pankow, J.F., J.A. Cherry. 1996. Dense Chlorinated Solvents and Other DNAPLs in Groundwater, Waterloo Press, Portland, OR.

Parson's Engineering Science. 1999. Natural Attenuation of Chlorinated Solvents Performance and Cost Results From Multiple Air Force Demonstration Sites. Technology, Technology Demonstration Technical Summary Report. 4-1-4-12.

Powell, C., A. Agrawal, M.N. Goltz, M.L. Shelley, K.T. Krejny.2010. Natural Attenuation of Chlorinated Ethenes in an Upward-Flow Treatment Wetland: High-resolution Vertical Geochemical characterization by Novel Pore-Water Samplers, Wright State University Thesis. 68 p.

Reddy, K.R., R.D. Delaune.2008. Biogeochemistry of Wetlands Science and Application, CRC Press, Boca Raton, FL.: 40-46.

Rickard, D., G.W. 2007. Luther, Chemistry of Iron Sulfides. Chem. Rev. 107: 514-662.

Roden, E.E., R.G. Wetzel. 1996. Organic Carbon Oxidation and Suppression of Methane Production By Microbial FeIII Oxididation Reduction In Vegetated and Unvegetated Freshwater Wetland Sediments. Limnol. and Oceangr. 41: 1733-1748.

Schlater, P.2006. Seasonal Variation in VOC by the Constructed Wetland at WPAFB, Dayton OH Wright State University Presentation.(unpublished).

Shang, T.Q., S.L. Doty, A.M. Wilson, W.N. Howald, M.P. Gordon, Trichloroethylene Oxidative Metabolism In Plants: The Trichloroethoanol Pathway, Pytochemistry. 7 (2001) 1055-1065.

Sobolewski Capt.T. 2004. Characterization of Chlorinated Solvent Degradation Profile Due to Microbial and Chemical Processes in a Constructed Wetland, Air force Institute of Technology Thesis. 97 p.

Sutton-Grier, A.E., J.K. Keller, R. Koch, C. Gilmour, J.P. Megonigal. 2011. Electron Donors and Acceptors Influence Anaerobic Soil Organic Matter Mineralization In Tidal Marshes. Soil Biol. Biochem. 43: 1576-1583.

TOSC. 2001. Hazardous Substance Fact Sheet, http://tosc.orst.edu, Western Region Hazardous Substance Research Center.

United States. Environmental Protection Agency. C. Newell, S. Hanadi, J.T. Rifai, J. Wilson, A. Connor, J.A. Aziz, M.P. Suarez. 2002. Groundwater Issue: Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation. Gov. Pub.

United States. Office of Inspector General, EPA. 2003. Improving Nationwide Effectiveness of Pump-and-Treat Remedies Requires Sustained and Focused Action to Realize Benefits Gov. Pub.

United States. Office of Inspector General, EPA Technology Innovation and Field Services Division.2011. About Remediation Technologies, http://www.epa.gov/superfund/remedytech/remed.htm, 2012.

United States. Office of Inspector General, EPA Technology Innovation and Field Services Division, 1999. The Superfund Innovative Technology Evaluation (SITE) Program: Technology Profiles, Tenth Edition. Gov. Pub.

Valentine, D.E., E.A. Holland, D.S. Schimel. 1994. Ecosystem and Physiological Controls Over Methane Production In Northern Wetlands, J. Geophys. Res. 99: 1563-1571.

Verce, M.F.,C.K. Gunsch, A.S. Danko, D.L. Freedman. 2002. Cometabolism of cis-1,2-Dichloroethene by Aerobic Cultures Grown on Vinyl Chloride as the Primary Substrate . Environ. Sci. Technol. 36: 2171-2177.

Vymazal, J. 2007. Removal of Nutrients In Various Types of Constructed Wetlands, Sci. Total Environ. 380: 48-65.

Waldron Capt. J. 2007. Characterization of Chlorinated Ethene Degradation in a Vertical Flow Constructed Wetland, Air Force Institute of Technology Thesis. 132 p.

Wiedemeier, T.H., J.T. Wilson, D.H. D.H.Kampbell, R.N. R.N. Miller, J.E. Hansen. 1999. Technical Protocol for Implementing Intrinsic Remediation With Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater: U.S. Air Force Center for Environmental Excellence, v. 1 & 2, Gob. Pub. U. S. Air Force Center for Environmental Excellence,. A324248, A324247a, A32424 .

Wuebbles, D.J., K. Hayhoe. 2002. Atmospheric Methane and Global Change Earth Sci. Reviews. 57: 177-210.

FIGURES

Wetland Surface

Layer A: Plants, clay, sand, wetland soil

0.23m

0.69m

Layer B: Clay, sand ,wetland soil

1.14m

Layer C: Wetland soil and wood chips

Gravel
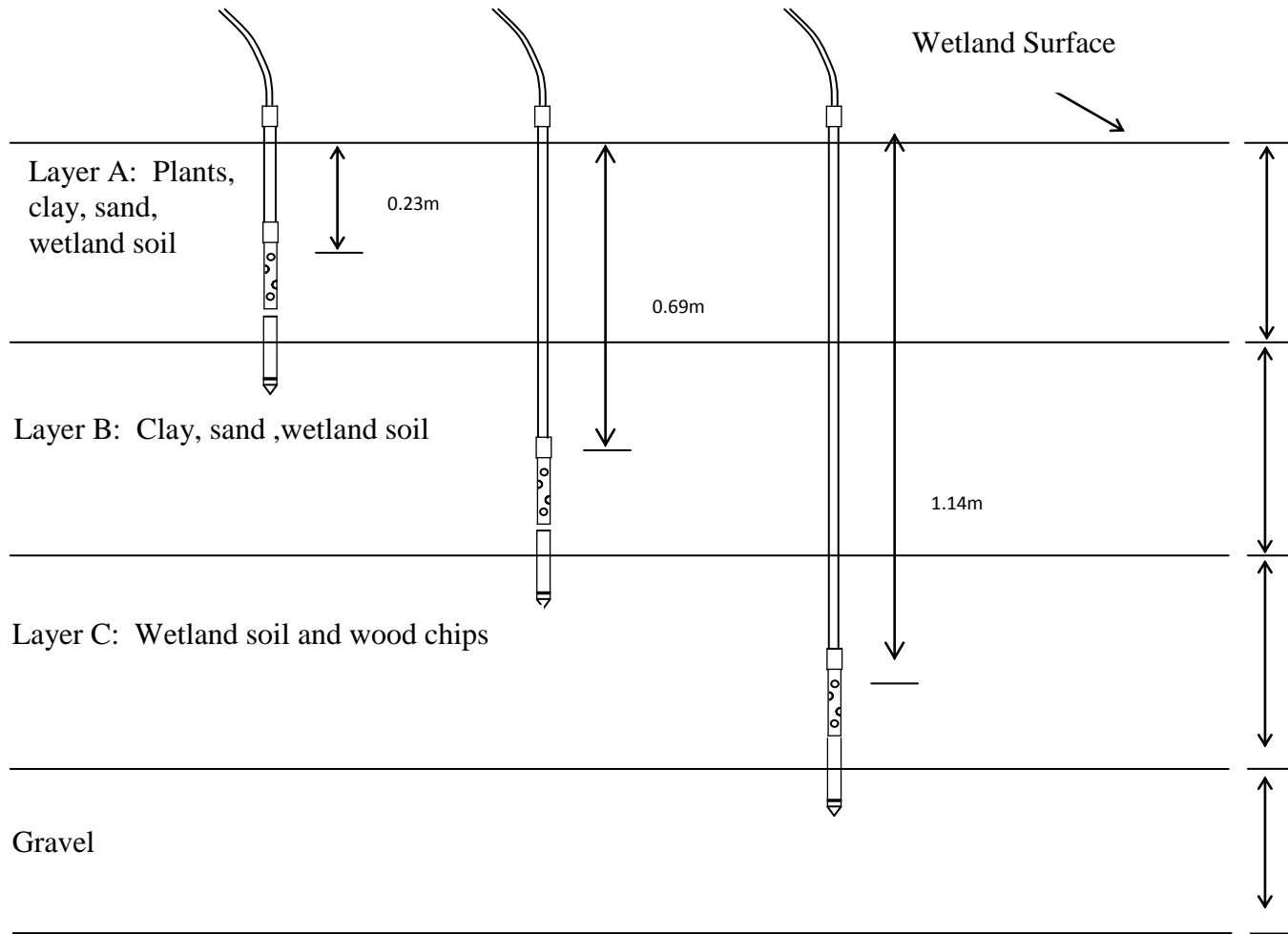
Figure 1: Wetland Layers- Opperman (2001)
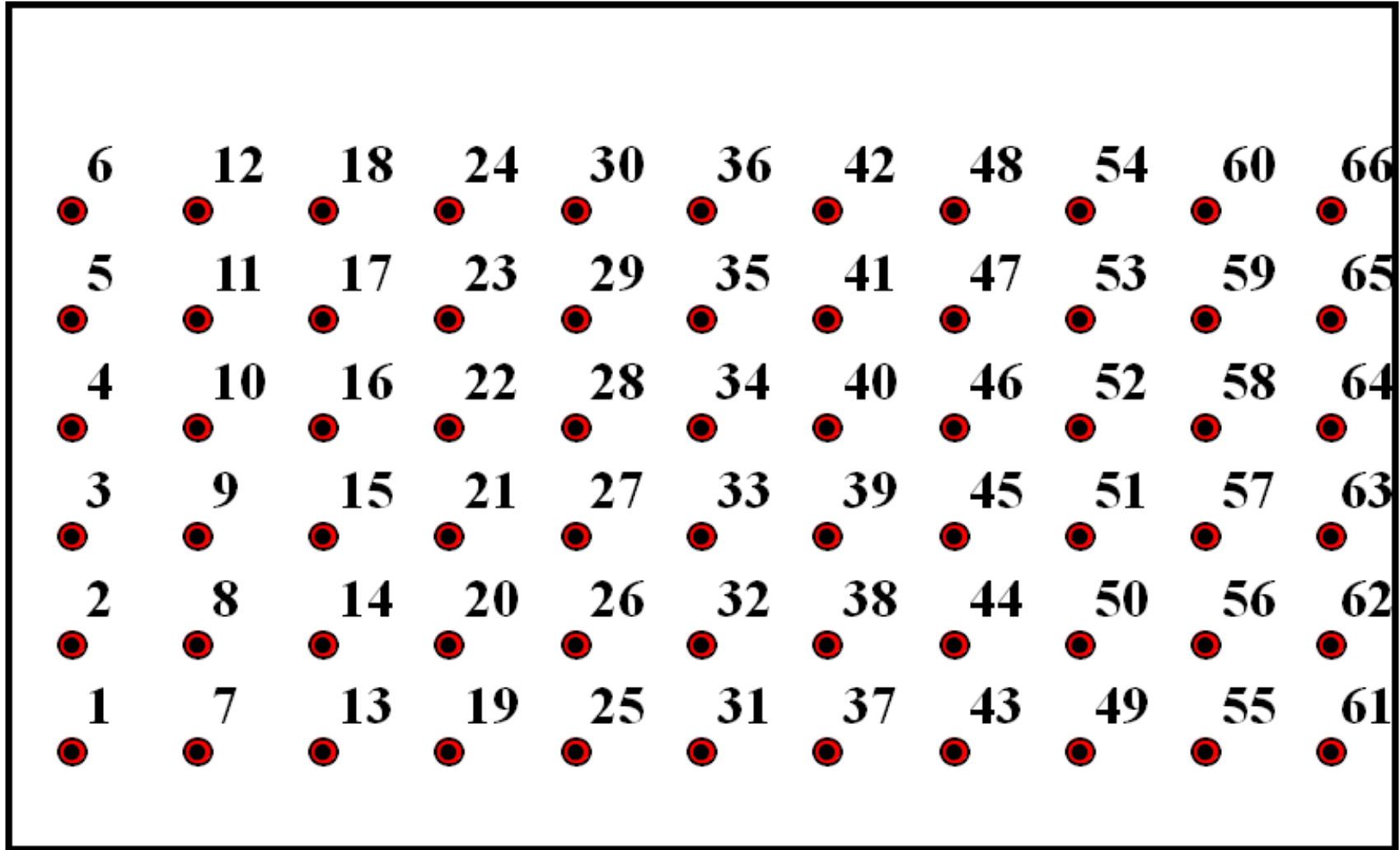
Figure 2: Sampling Layout
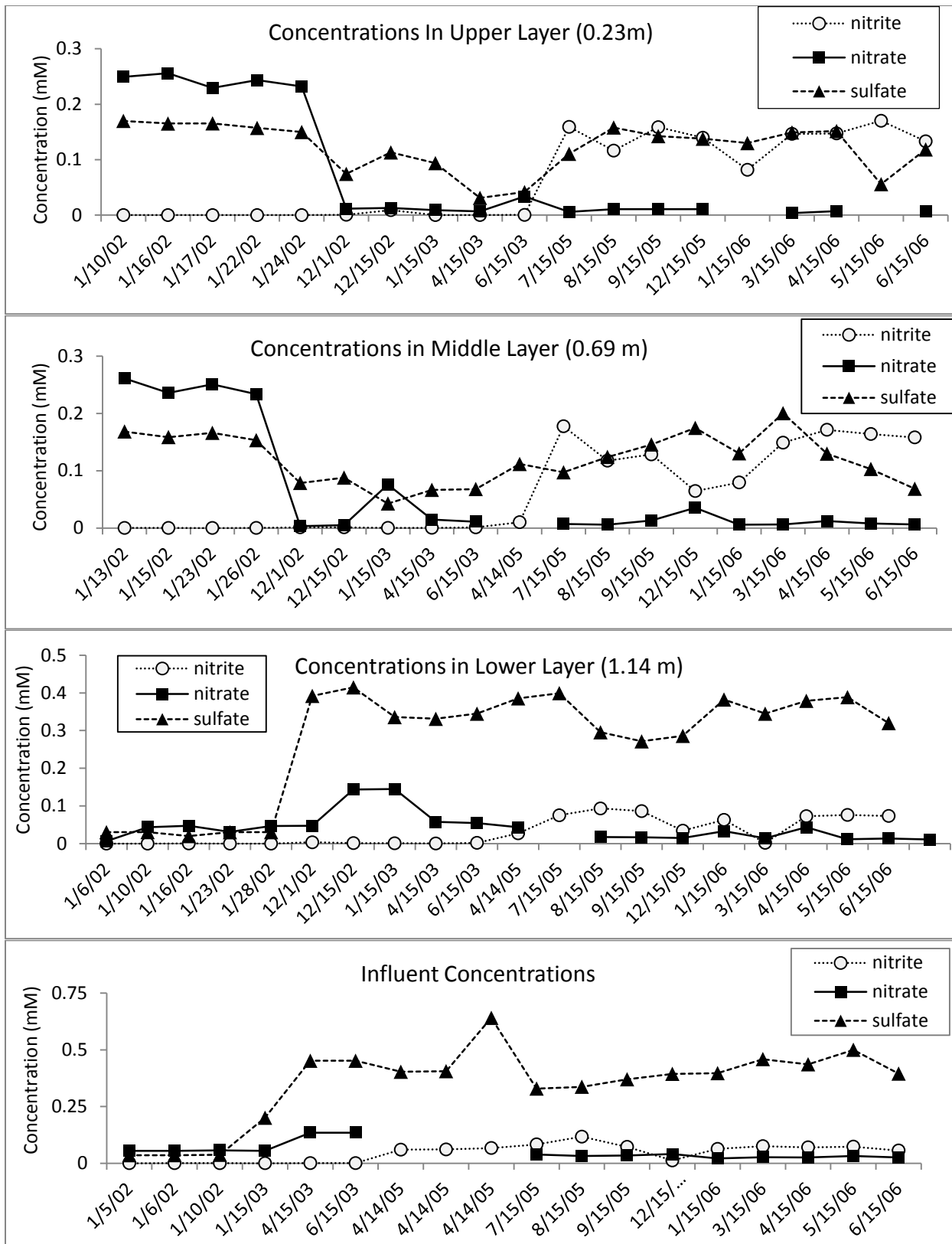
Figure 3: 2002-2006 nitrite, nitrate and sulfate in the groundwater: mean by sampling date.
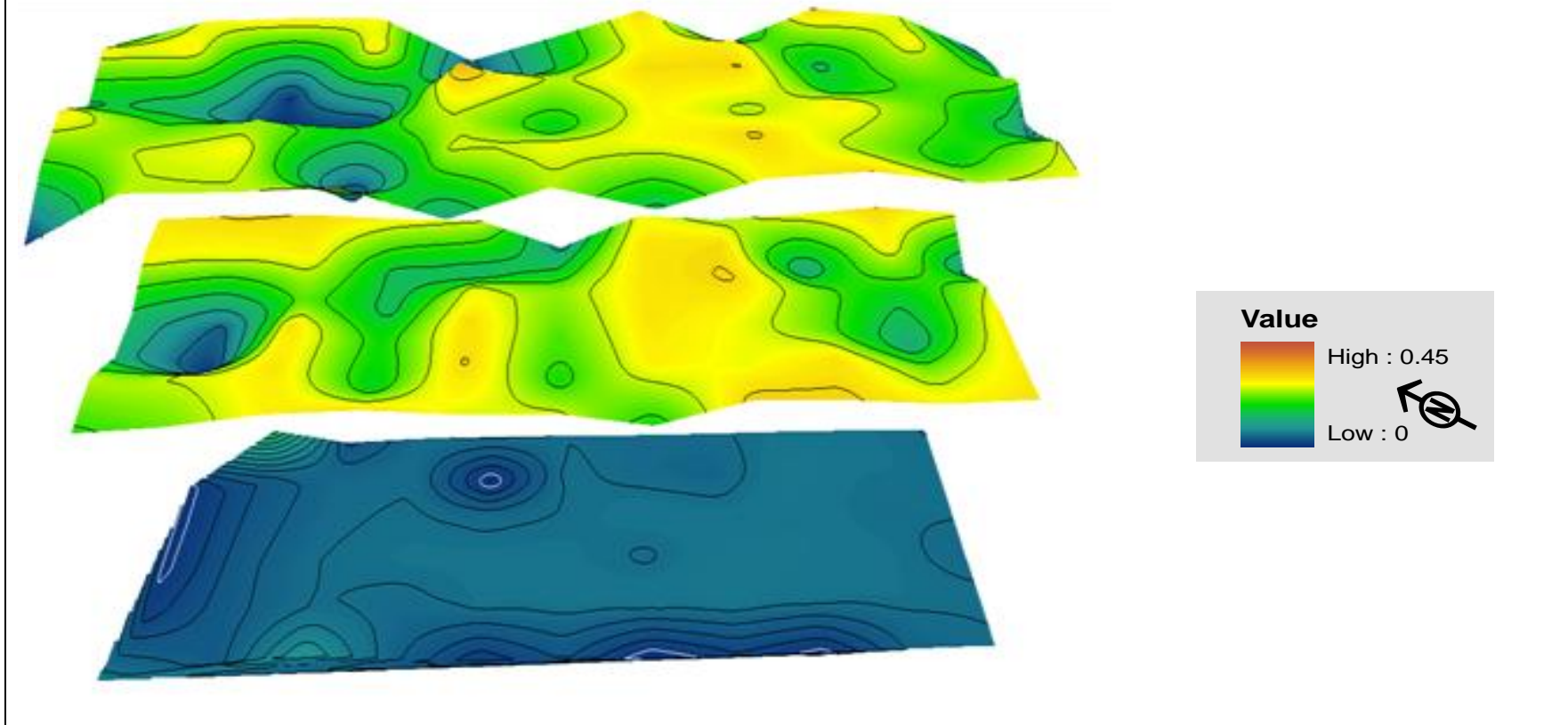
Nitrate: Winter 2001/2002

Figure 4a: Variations in nitrate concentration in the groundwater sampled at different depths in the wetland during Winter 2001/2002: contour maps at 0.23 m (Upper layer), .69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.05 mM.
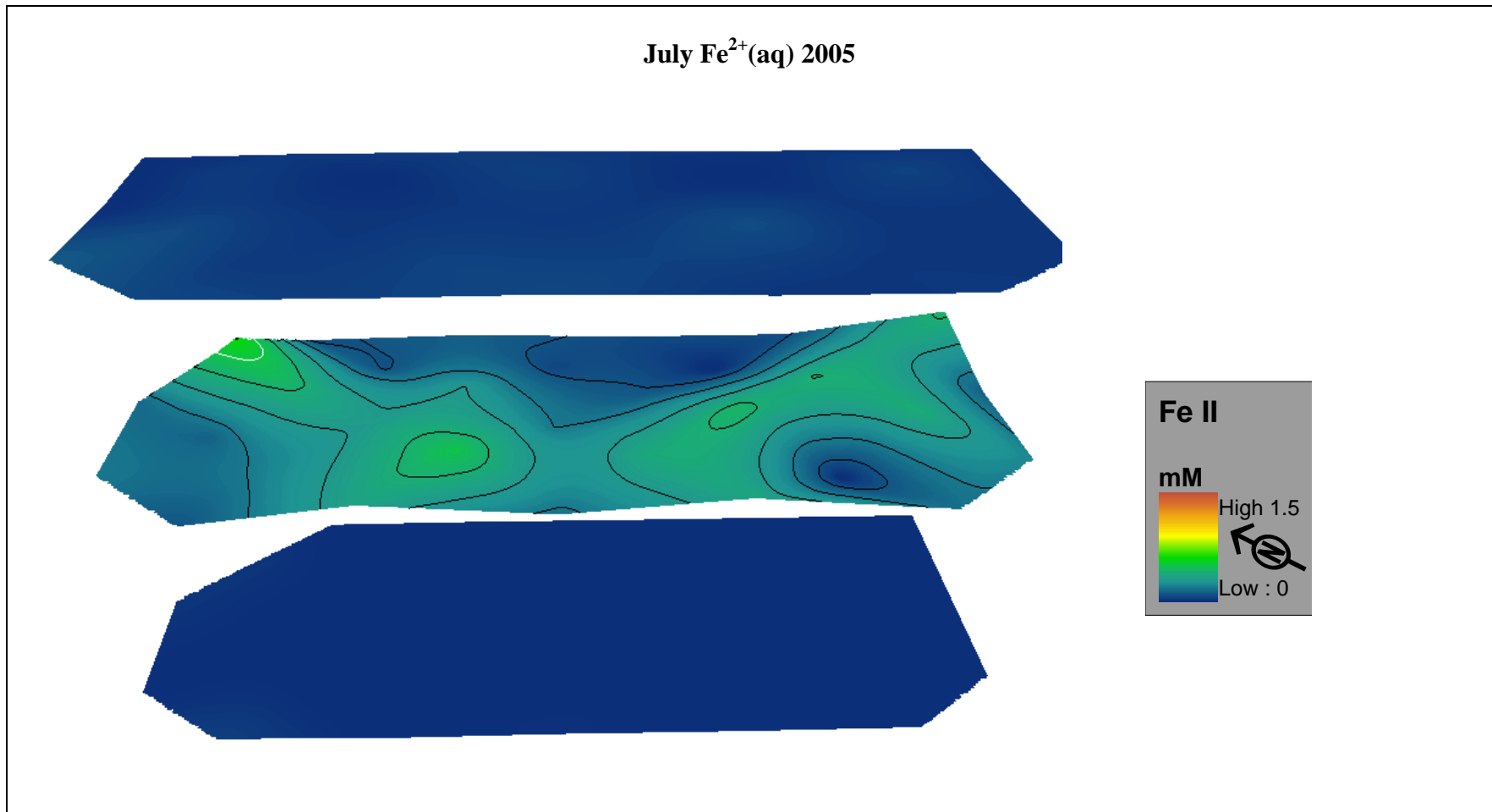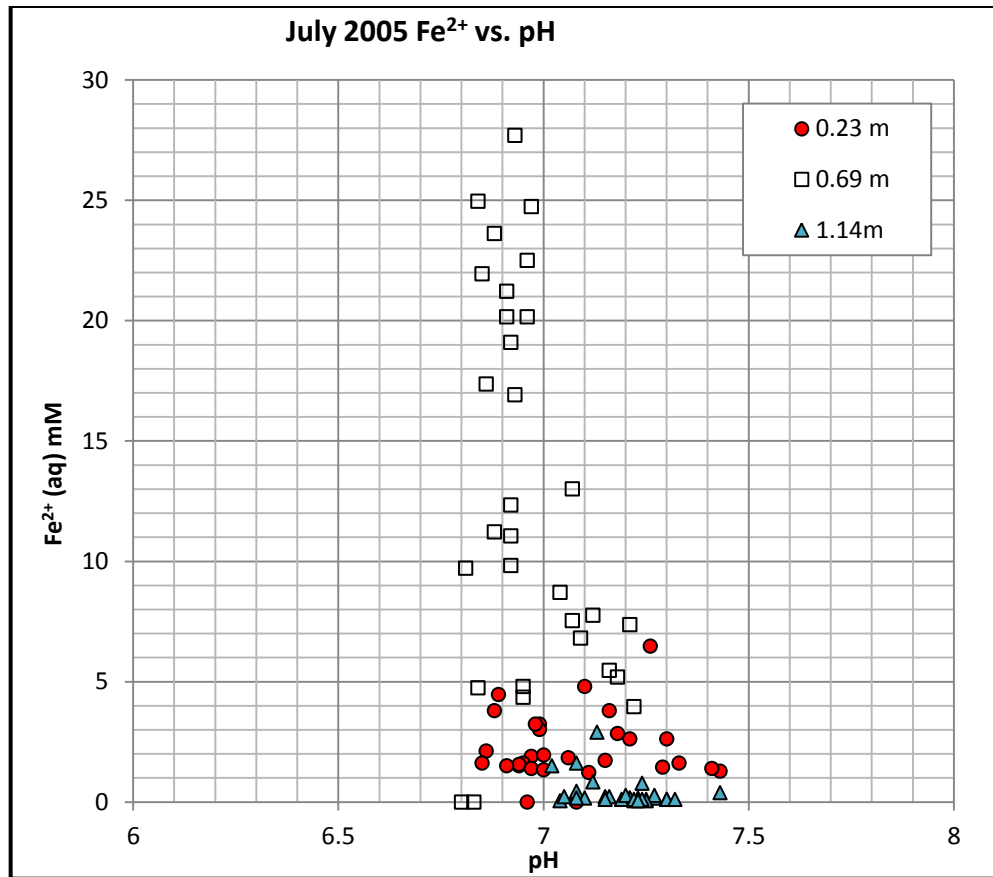
Nitrate Winter 2002/2003

Value
High : 0.45
Low : 0
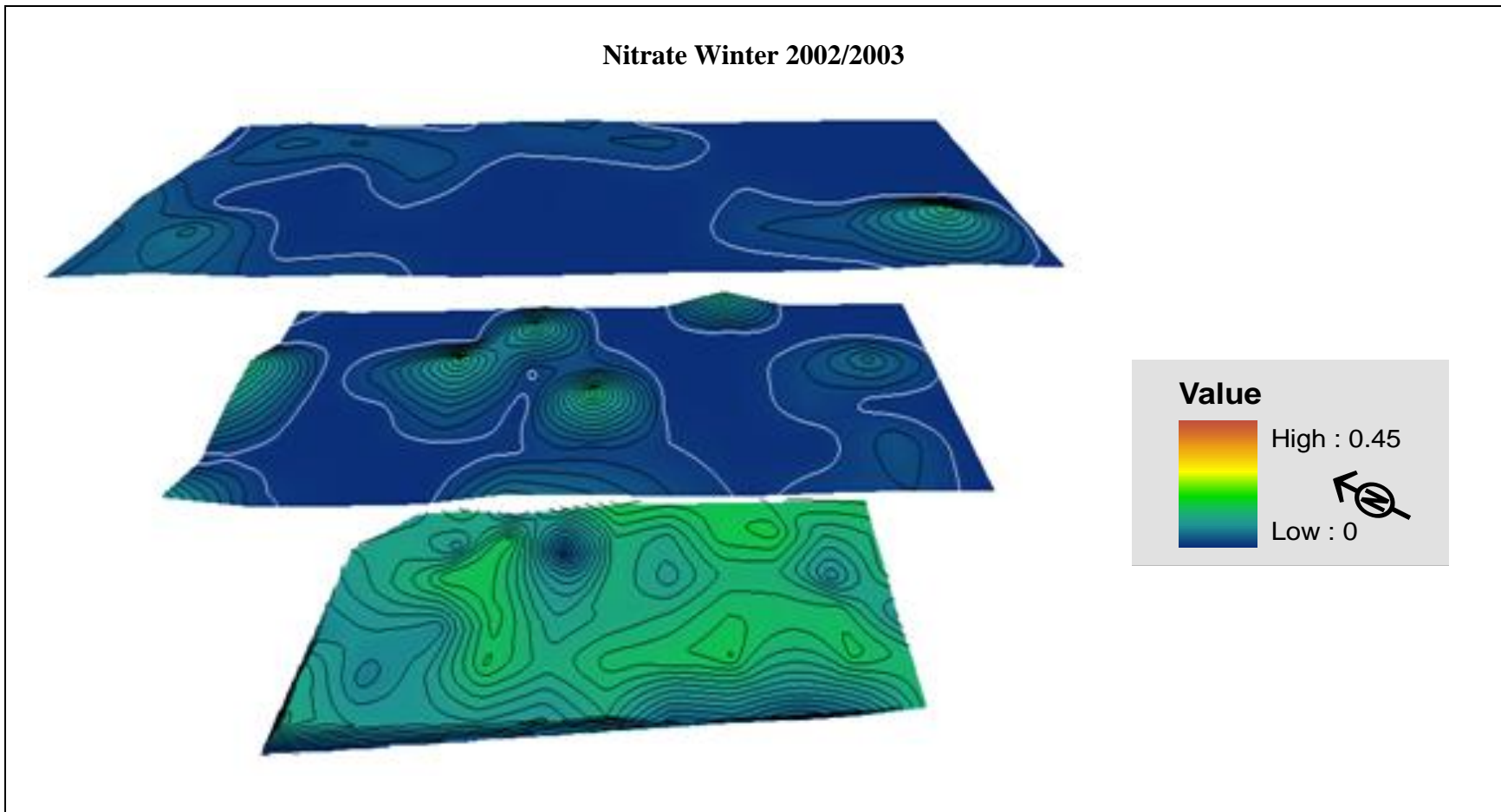
Figure 4b: Variations in nitrate concentration in the groundwater sampled at different depths in the wetland during Winter 2002/2003: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.05 mM.

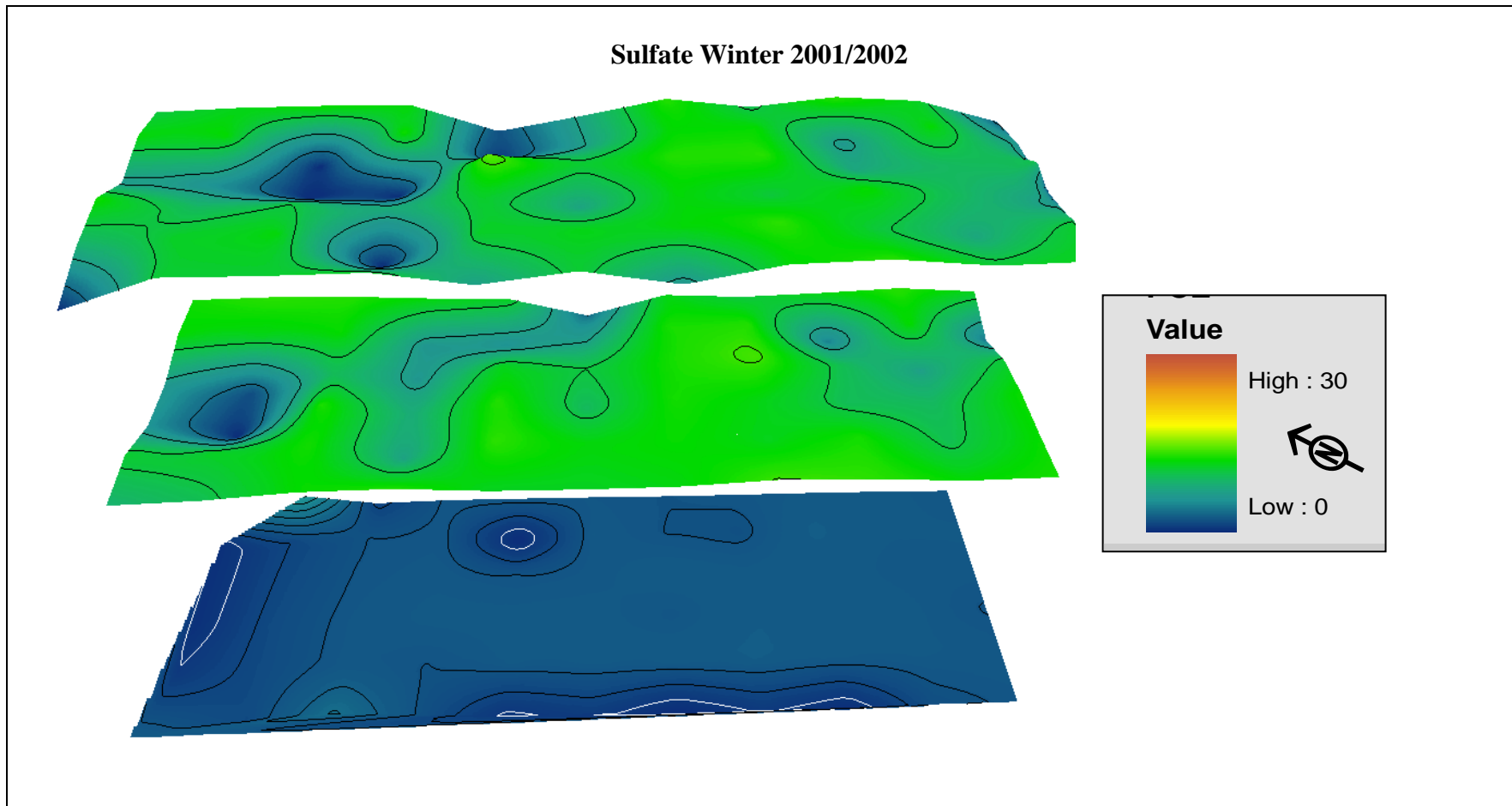**Nitrate Winter 2005/2006**

Value

High : 0.45

Low : 0
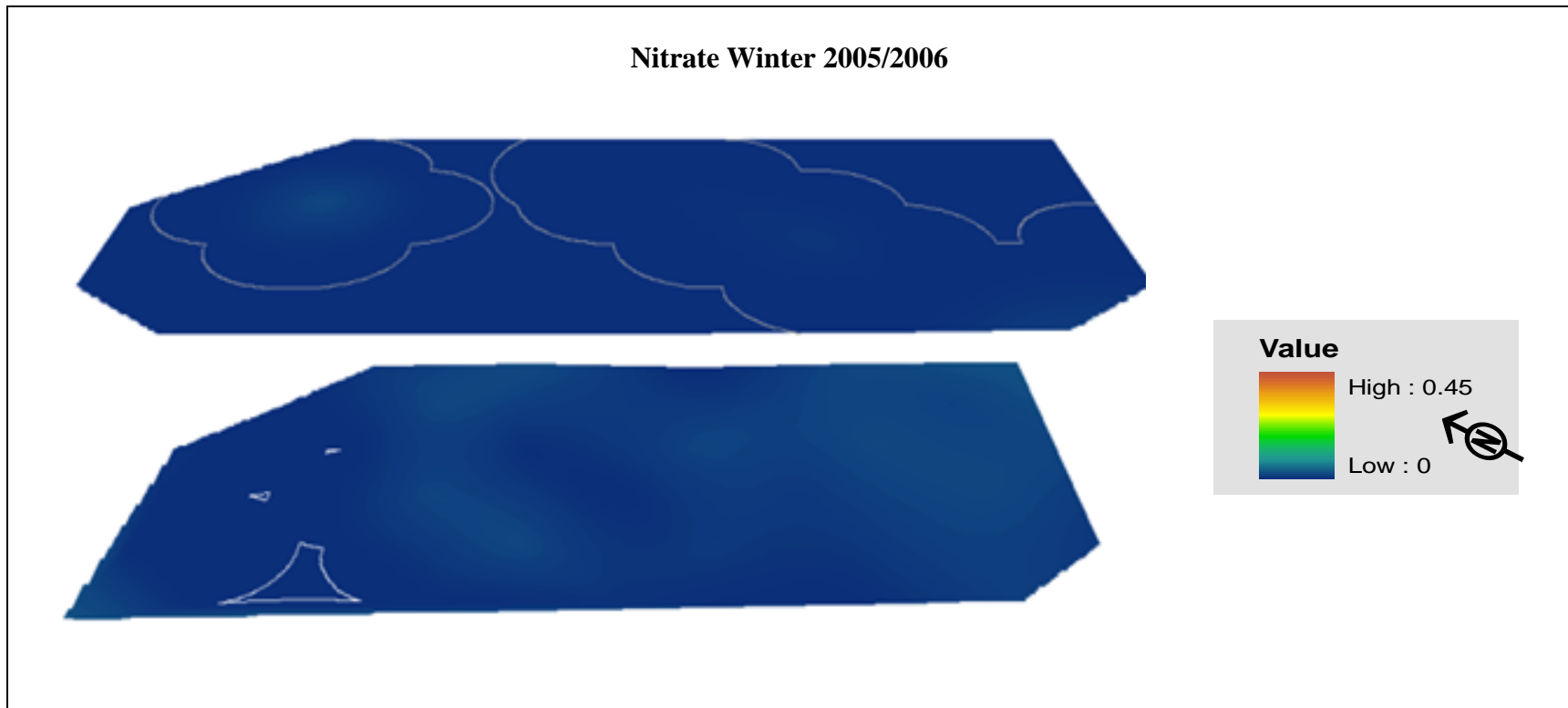
Figure 4c: Variations in nitrate concentration in the groundwater sampled at different depths in the wetland during Winter 2005/2006: contour maps at 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.01 mM.

Nitrite Winter 2002/2003

Value
High : 0.1
Low : 0
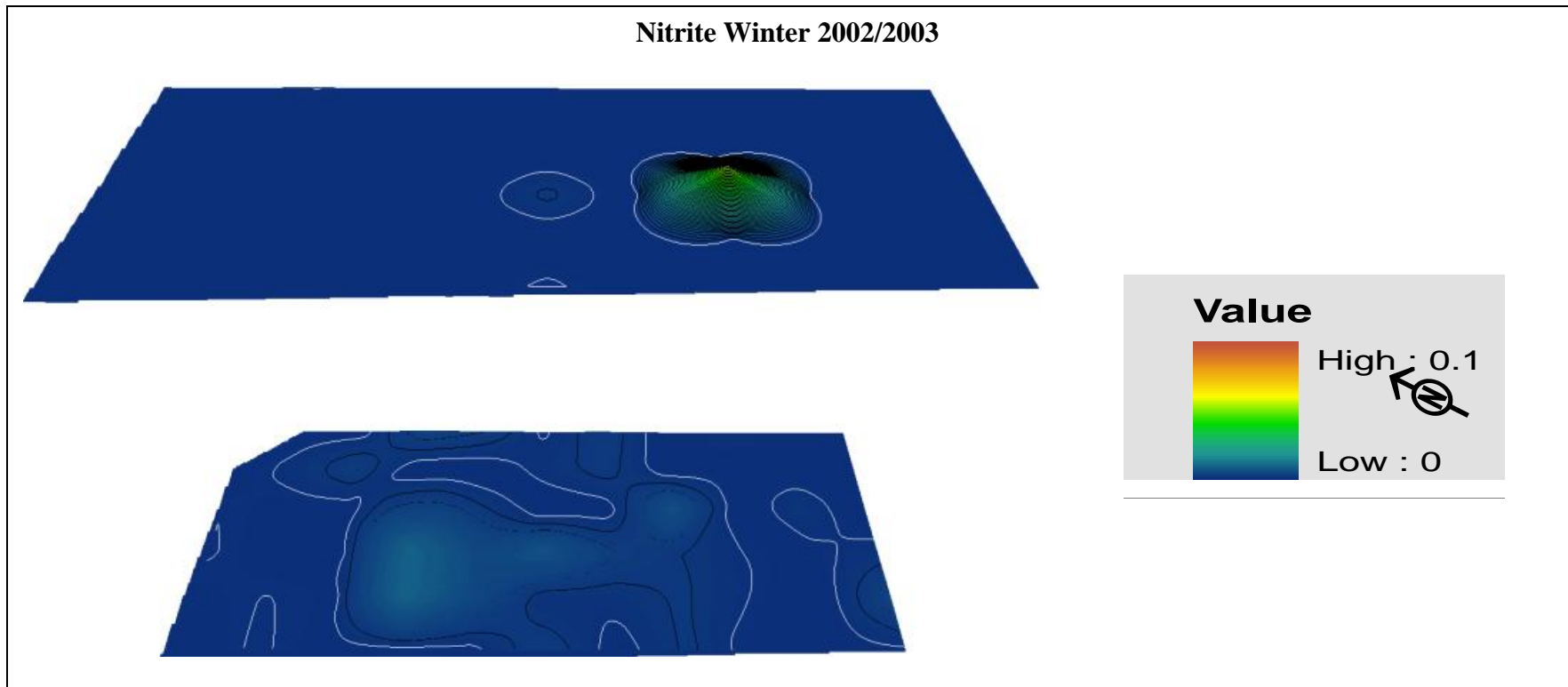
Figure 5a: Variations in nitrite concentration in the groundwater sampled at different depths in the wetland during Winter 2002/2003: contour maps at 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.001 mM. White contour: 0 mM.
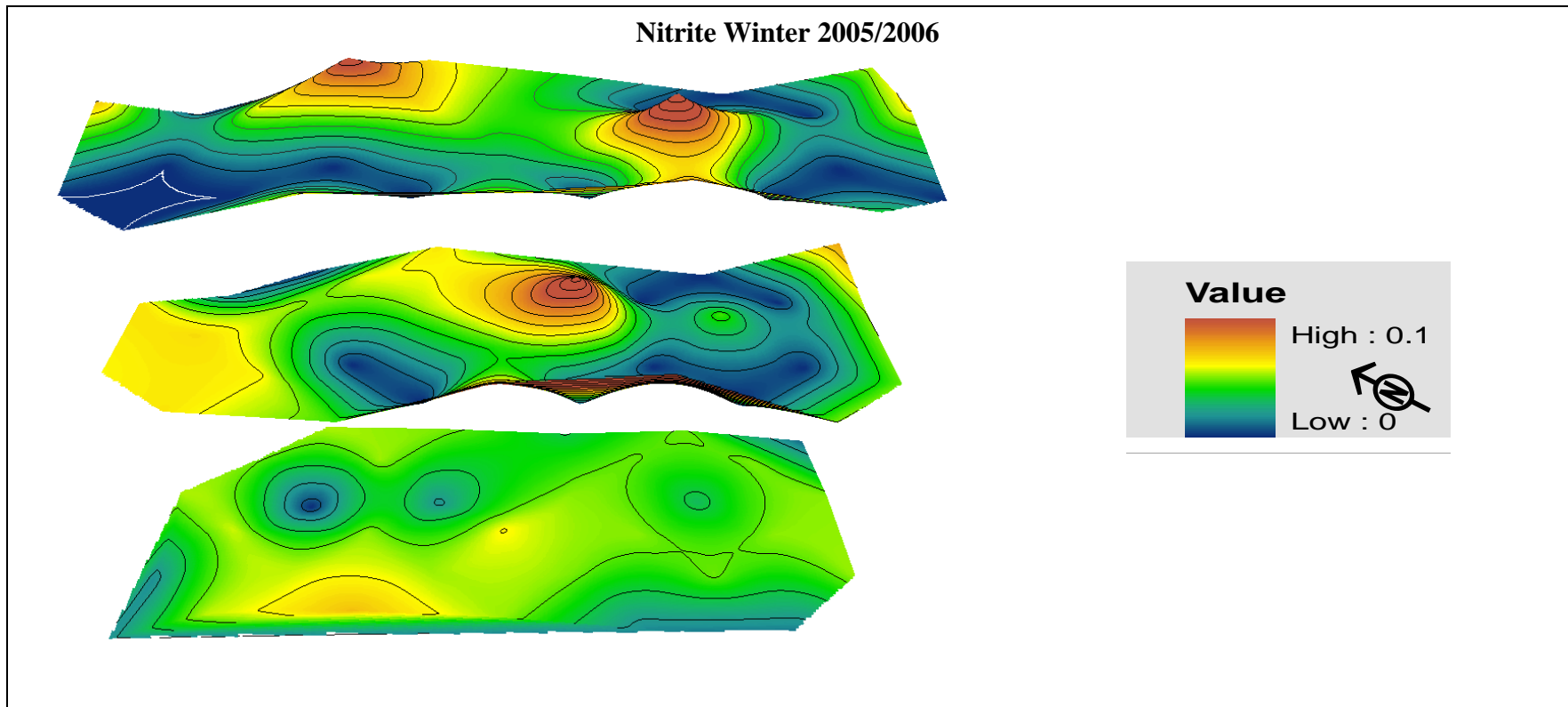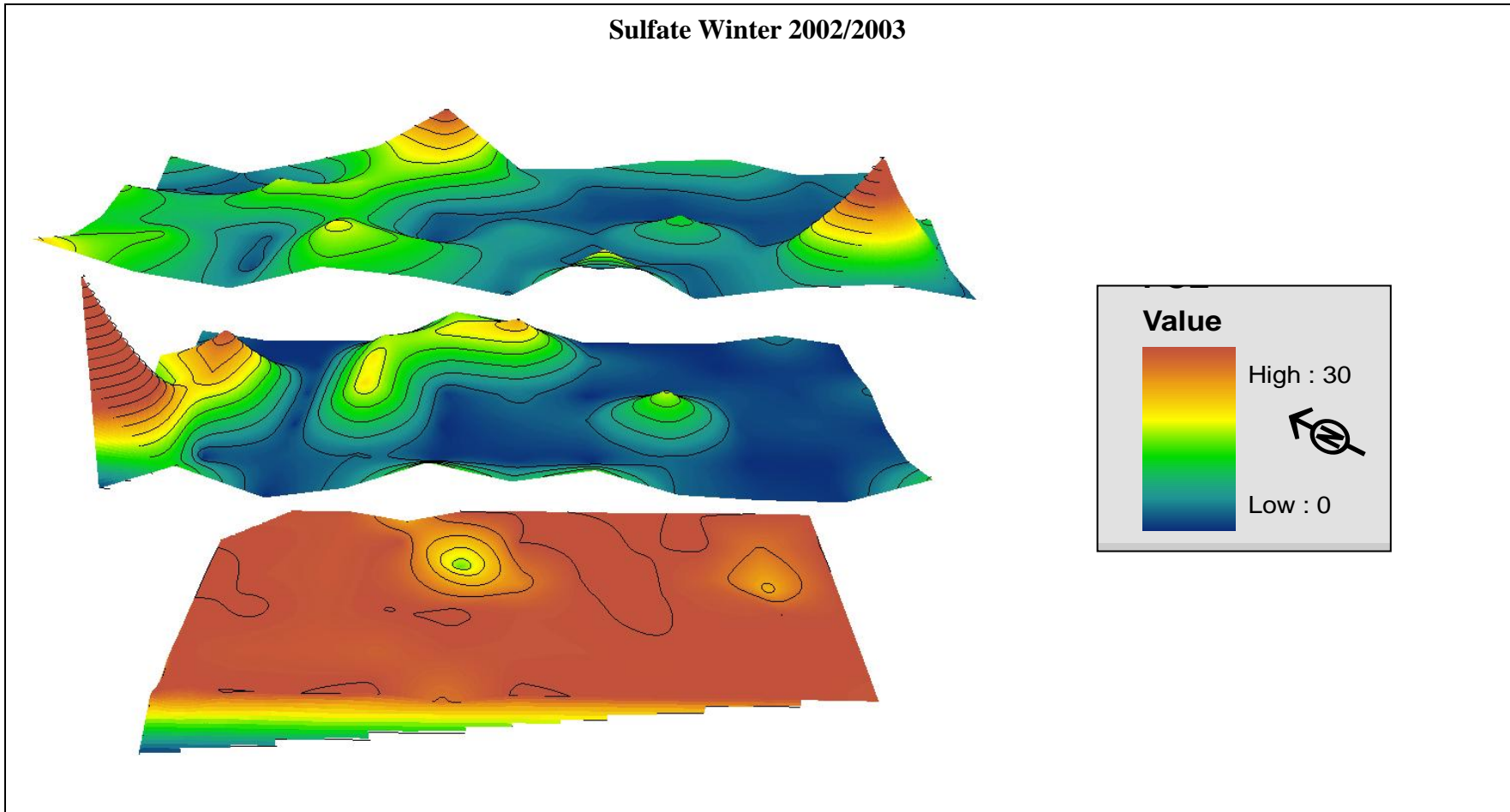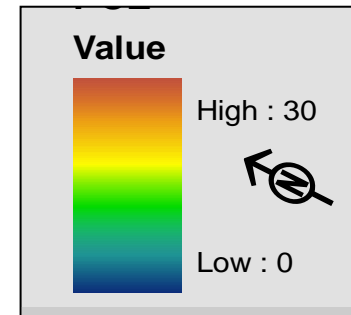
Figure 5b: Variations in nitrite concentration in the groundwater sampled at different depths in the wetland during Winter 2005/2006: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.01 mM.
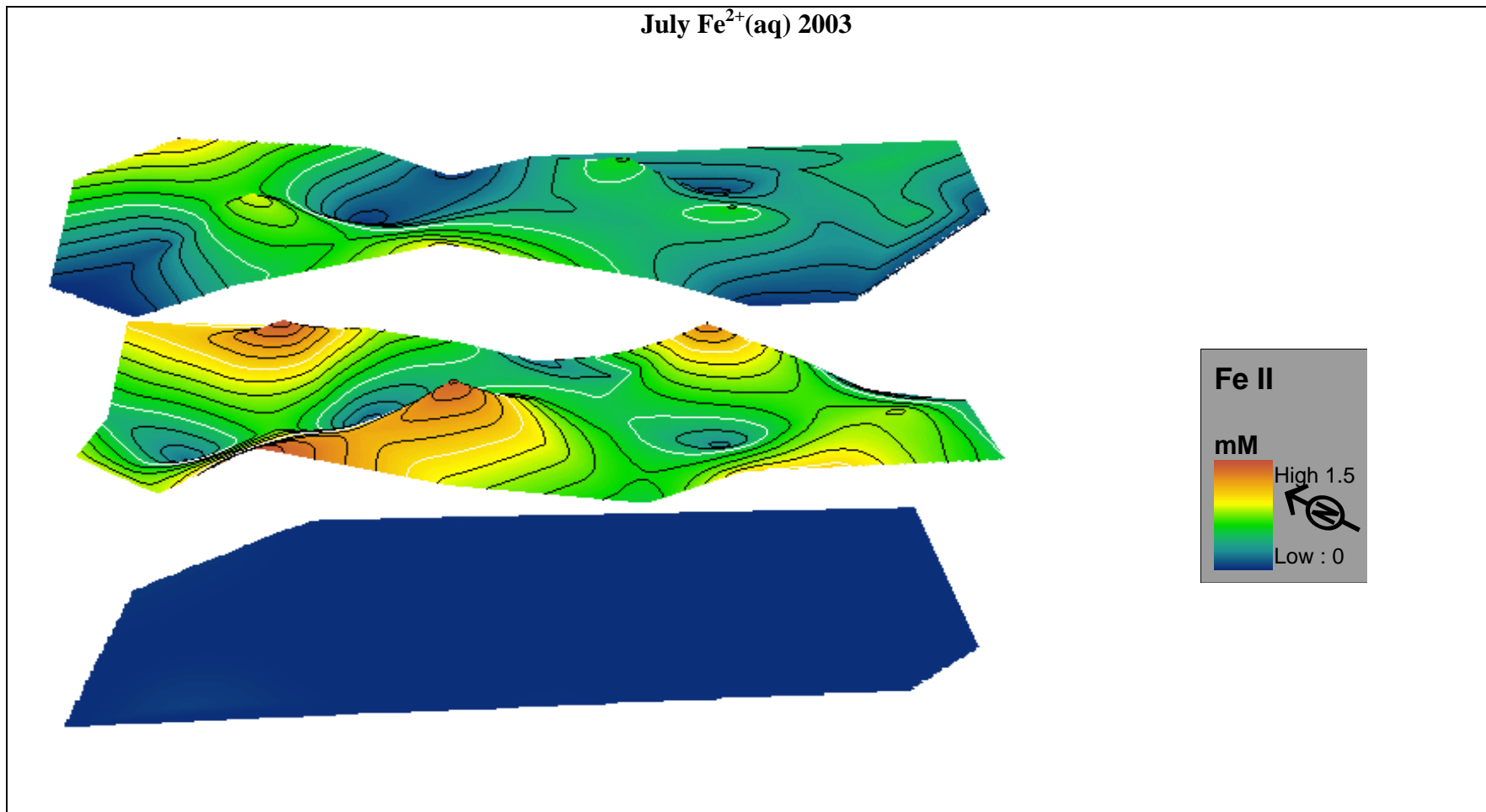
Figure 6a: Variations in Fe^{2+} (aq) concentration in the groundwater sampled at different depths in the wetland in July 2003: Fe^{2+}(aq) contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 mM**.

Figure 6b: Variations in Fe^{2+} (aq) concentration in the groundwater sampled at different depths in the wetland in July 2005: Fe^{2+}(aq) contour maps at 0.23 m.(Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 mM

Depth	Average pH
0.23 m	7.13
0.69 m	6.95
1.14 m	7.19

Figure 7: 2005 Variations in mean pH and mean Fe^{2+}(aq) mM at three representative depths in the wetland

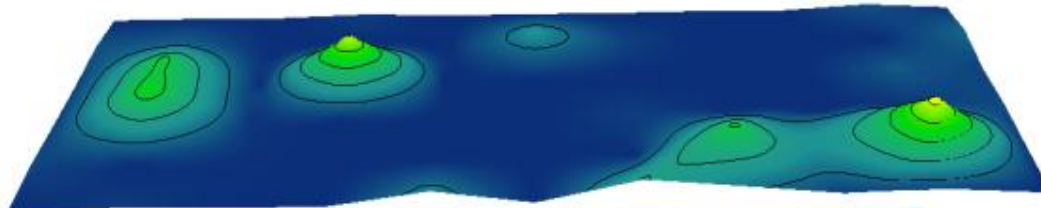**Sulfate Winter 2001/2002**

Value

High : 30

Low : 0

Figure 8a: Variations in sulfate concentration in the groundwater sampled at different depths in the wetlands during Winter 2001/2002: Contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.05 mM; white contour: 0.01 mM
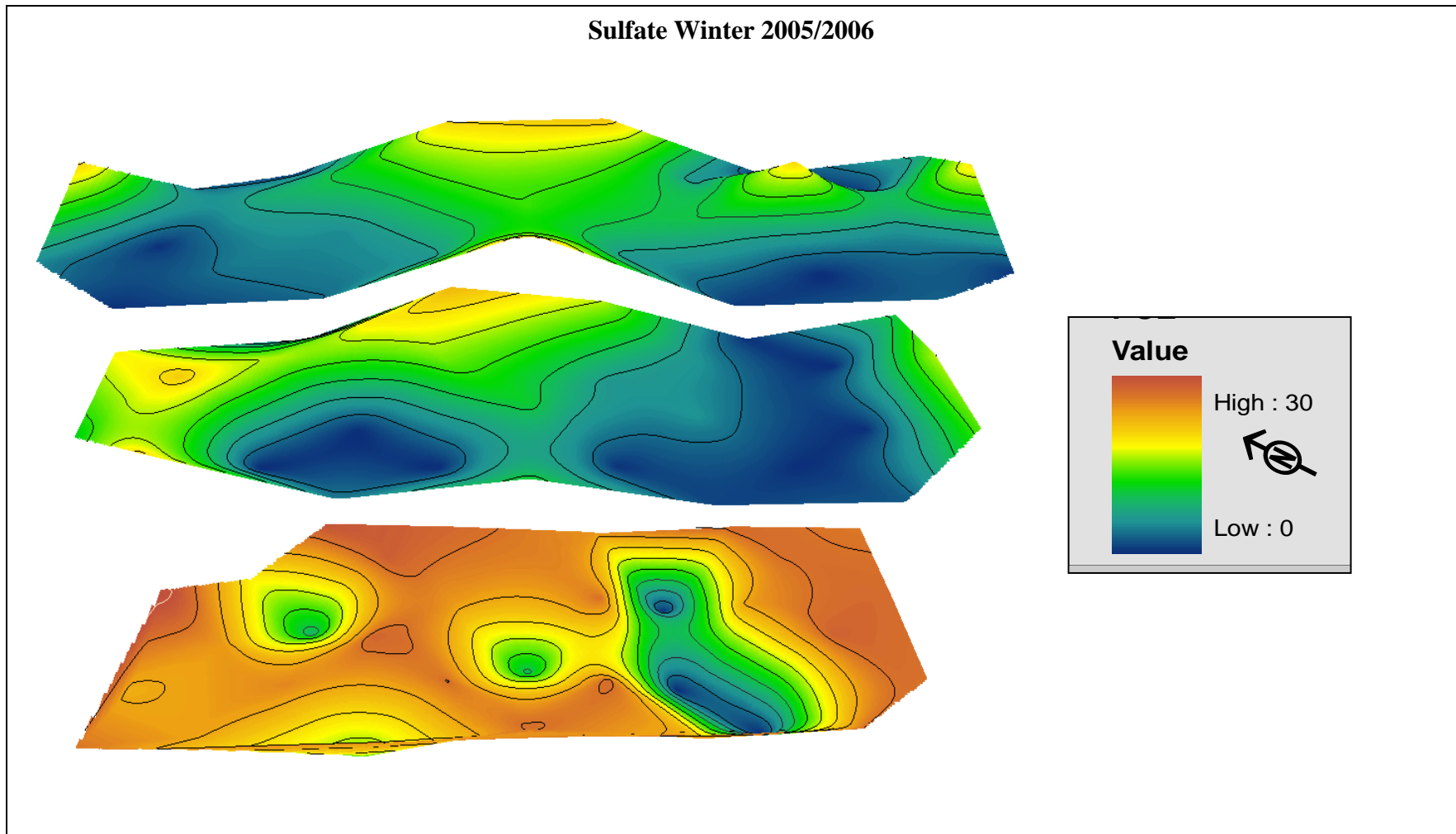
Figure 8b: Variations in sulfate concentration in the groundwater sampled at different depths in the wetlands during Winter 2002/2003: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.05 mM; white contour: 0.01mM
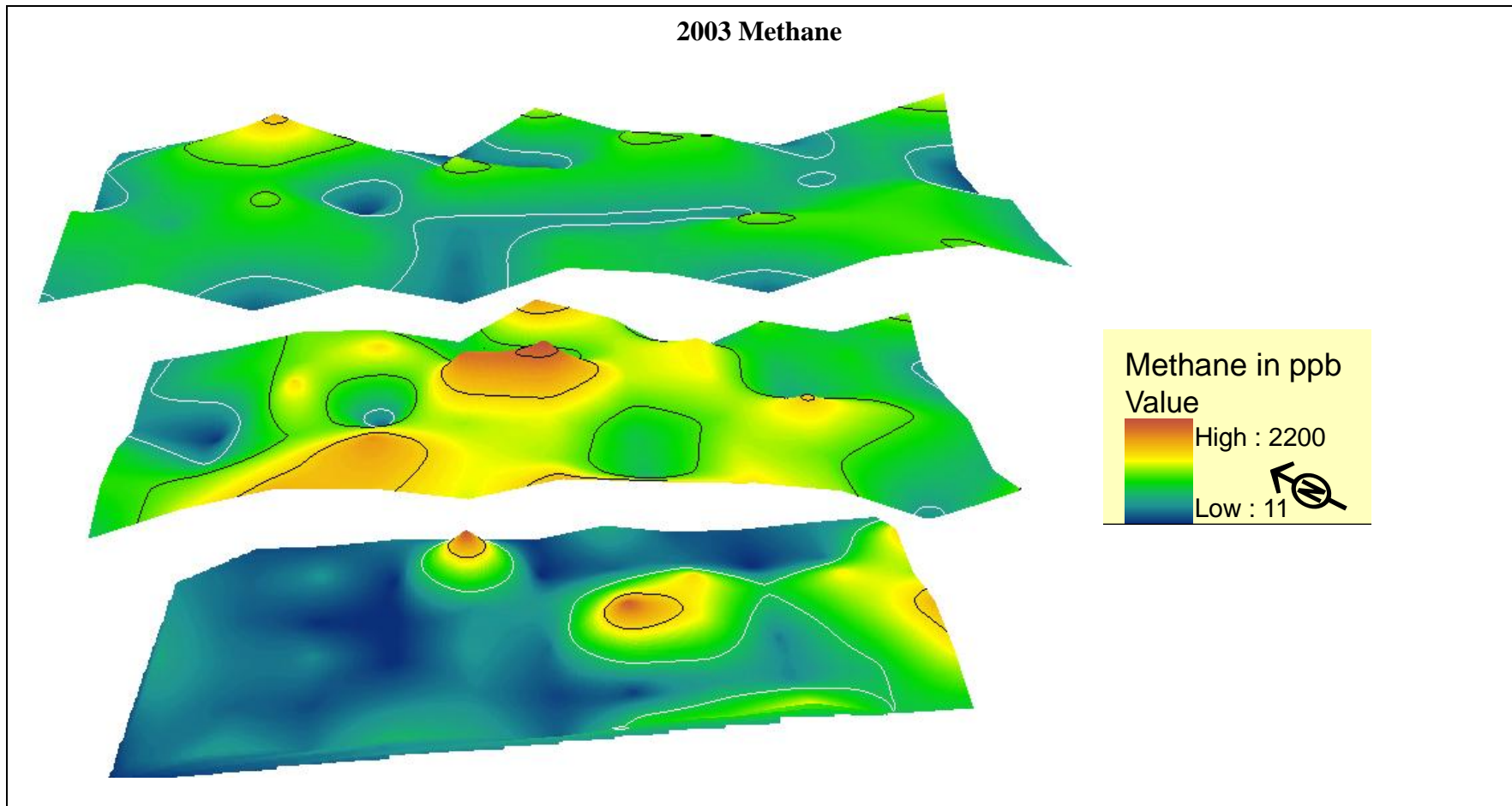
Figure 8c: Variations in sulfate concentration in the groundwater sampled at different depths in the wetlands during Winter 2003/2004: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.05 mM,

Figure 8d: Variations in sulfate concentration in the groundwater sampled at different depths in the wetlands during Winter 2005/2006: Sulfate surfaces at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.05 mM,
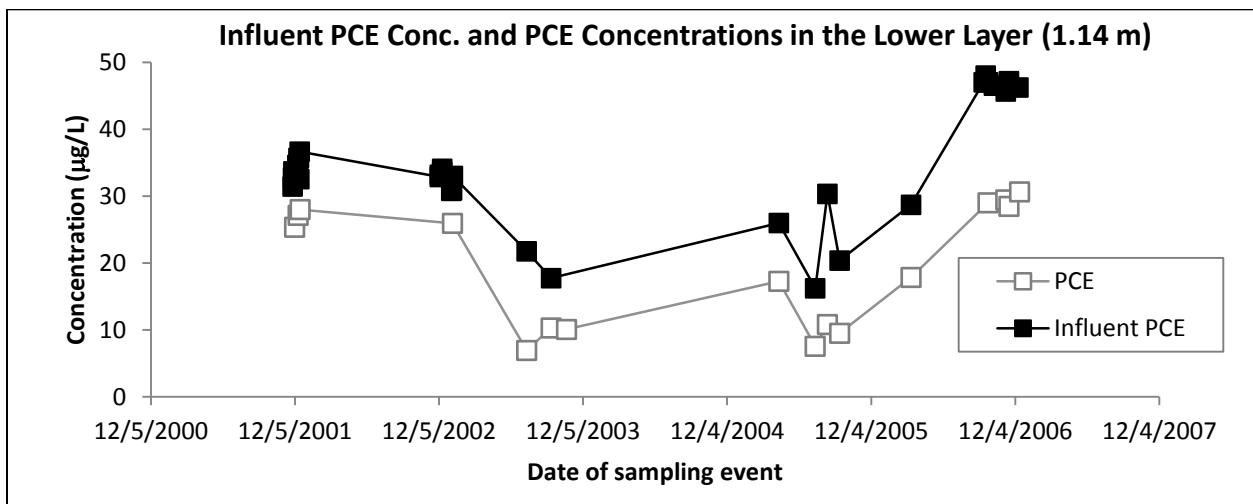
Figure 9: Variations in methane concentration in the groundwater sampled at different depths in the wetlands during July and September 2003: Methane surfaces at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 500 ppb
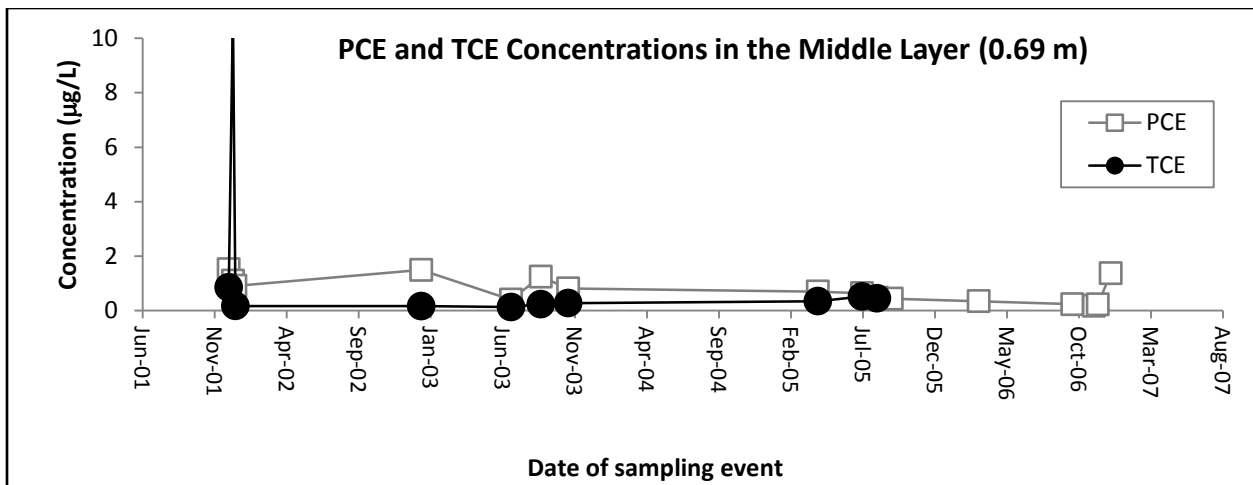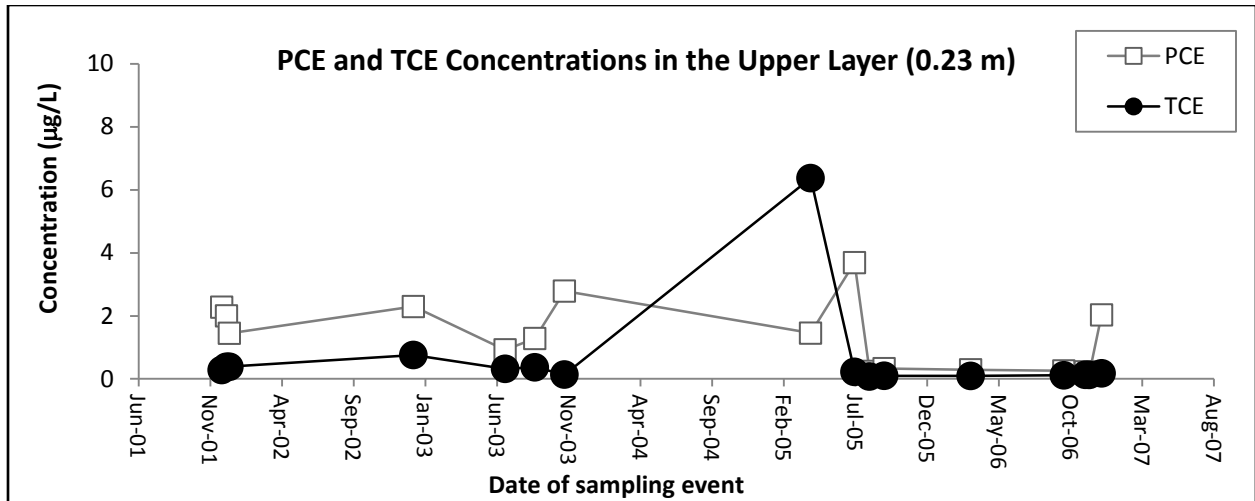
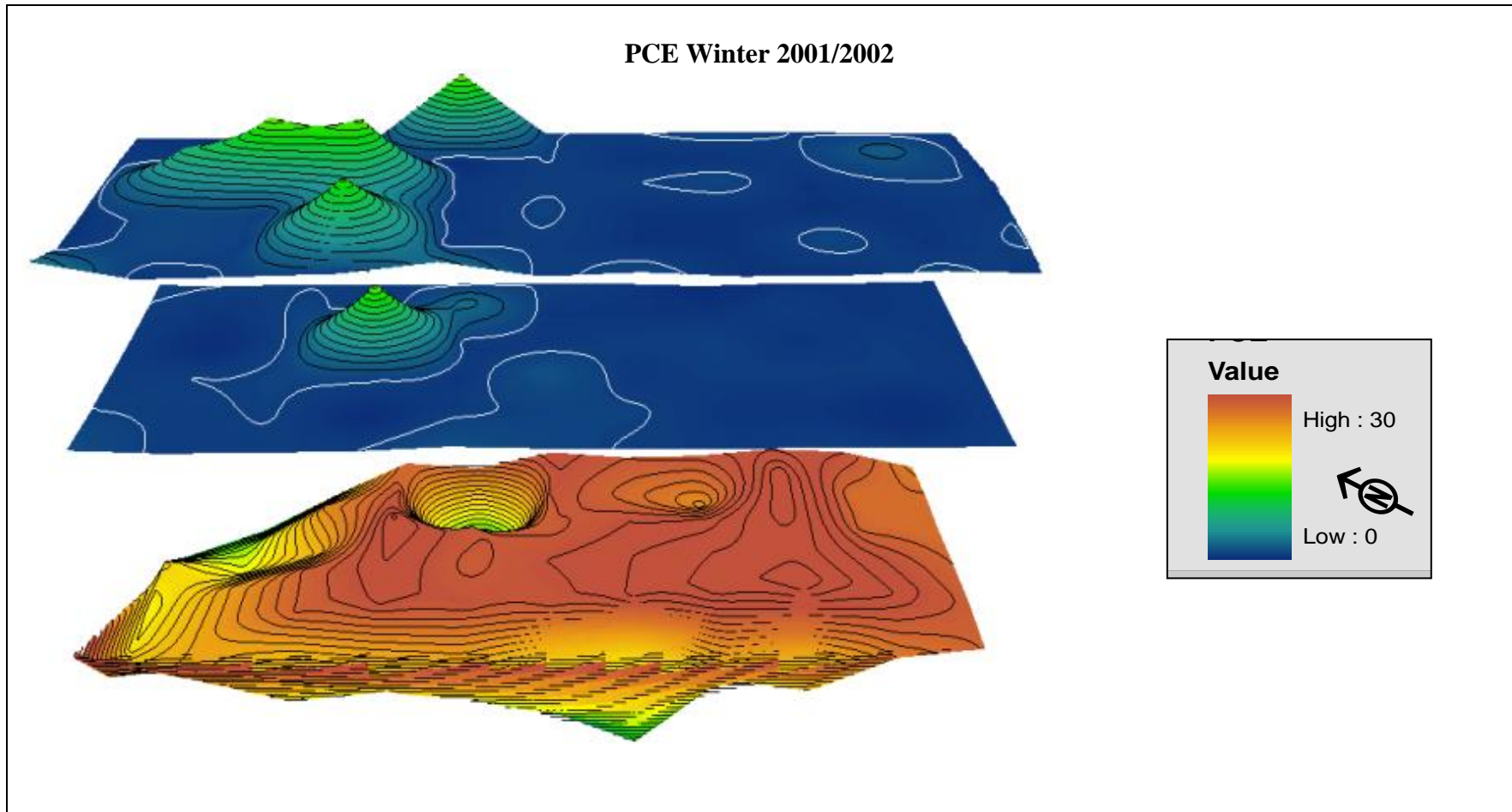Figure 10: Mean PCE concentrations in three layers by sampling event during 2001-'06

Figure 11a: Variations in PCE concentration in the groundwater sampled at different depths in the wetlands during winter 2001/2002: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb
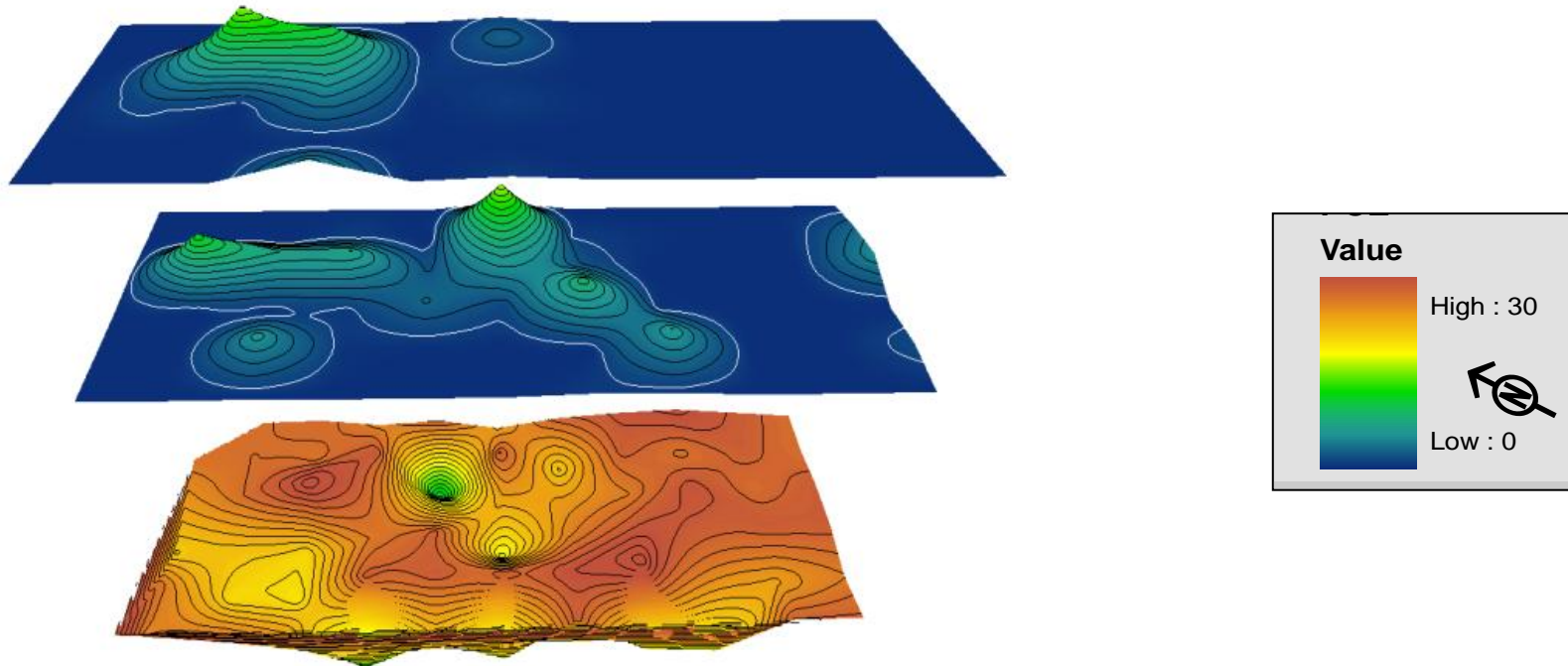
Figure 11b: Variations in PCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2002/2003: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb

Figure 11c: Variations in PCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2002/2003: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb
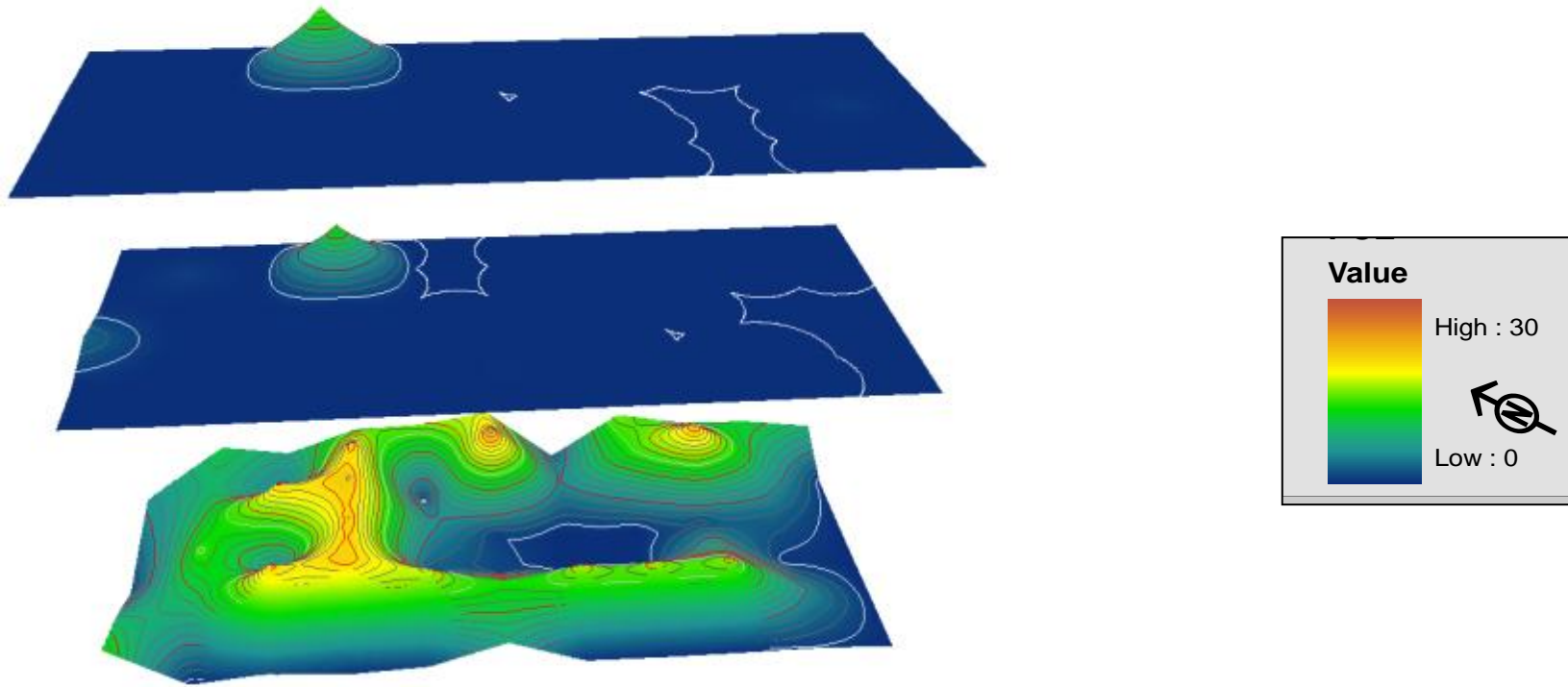
Figure 11d: Variations in PCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2005/2006 contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb
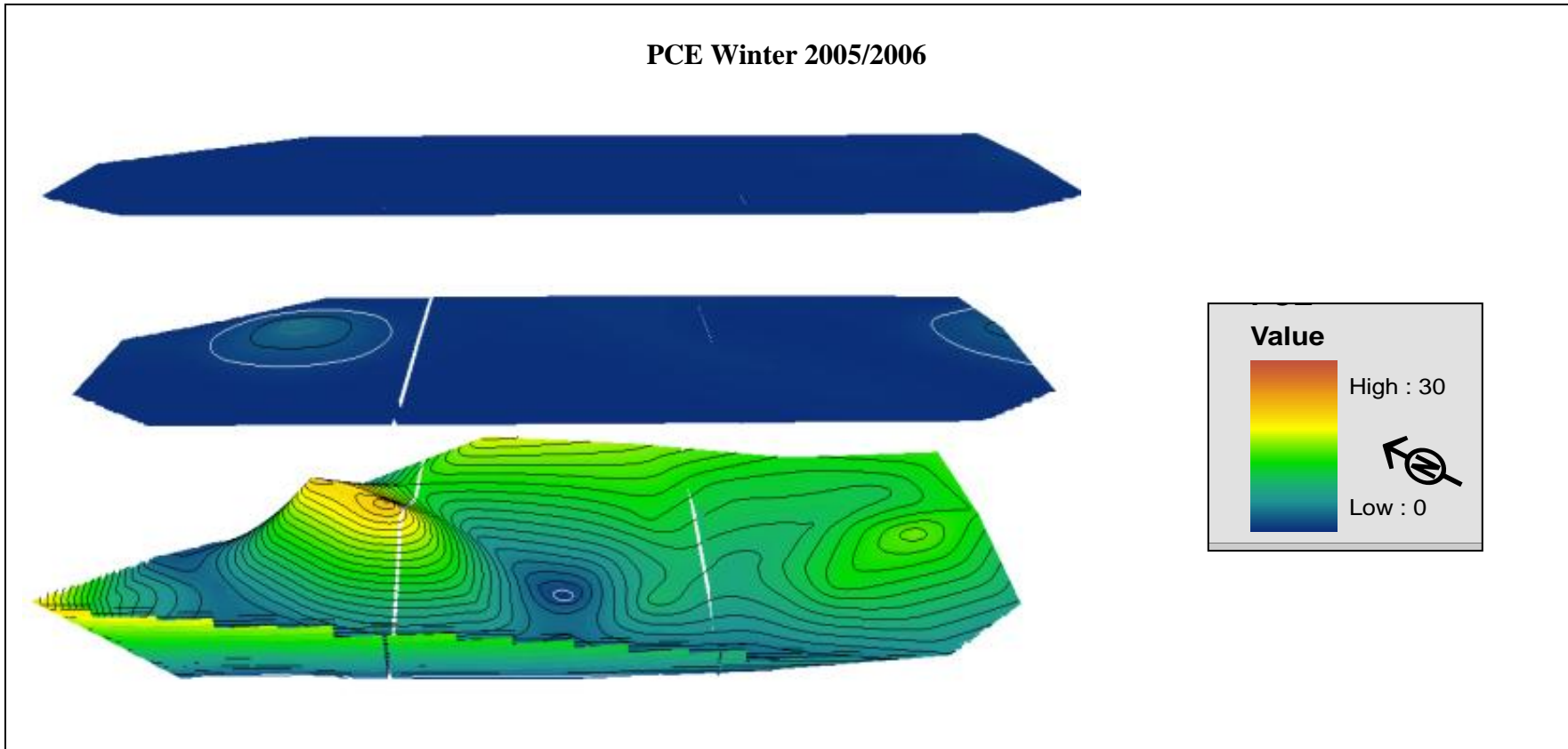
Figure 11e: Variations in PCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2006/2007: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb

Figure 12a: Variations in TCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2001/2002: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb
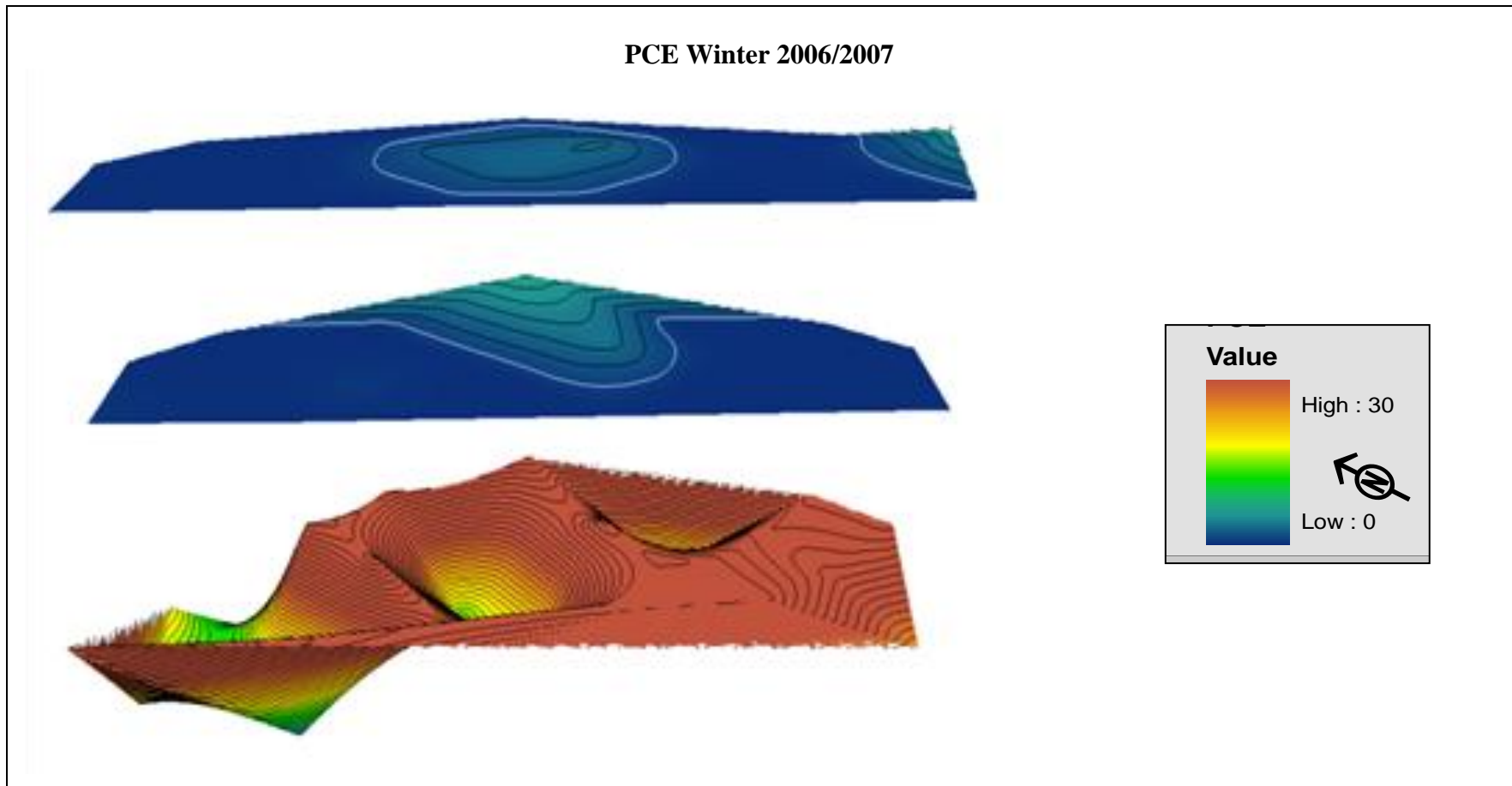
Figure 12b: Variations in TCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2002/2003 contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb

TCE Winter 2003/2004

Figure 12c: Variations in TCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2003/2004: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb
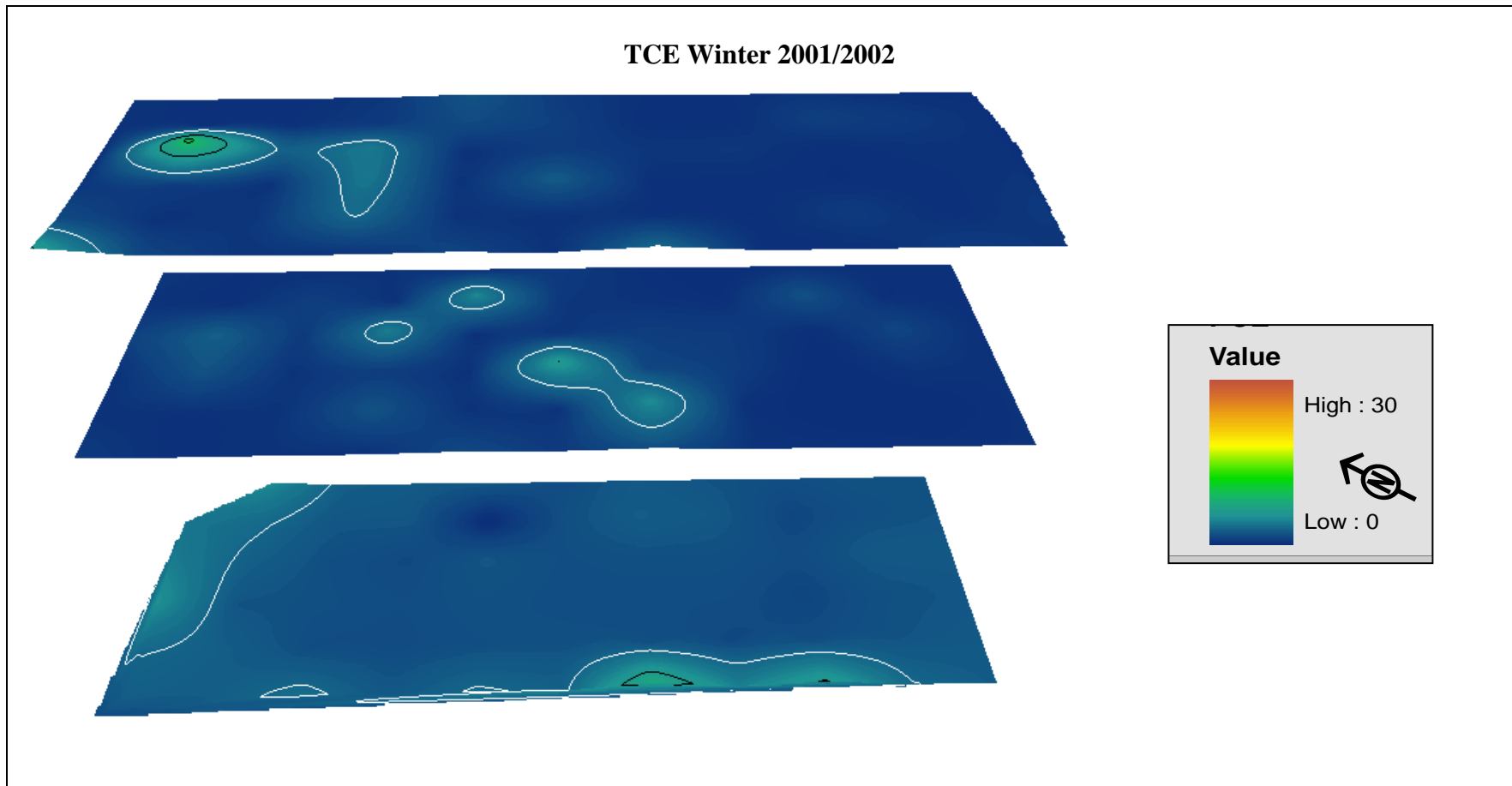
TCE Winter 2005/2006
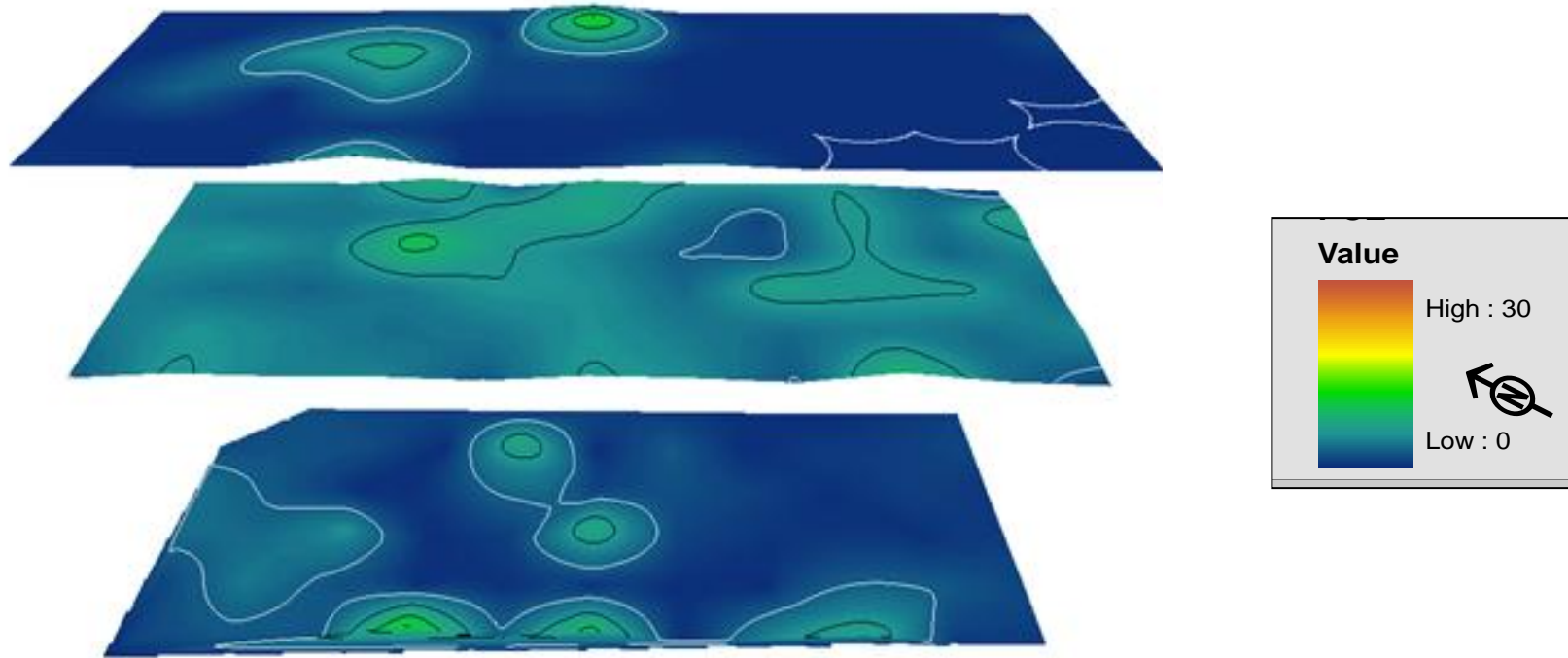
Value

High : 30

Low : 0

Figure 12d: Variations in TCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2004/2005: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb

TCE Winter 2006/2007

Value
High : 30
Low : 0

Figure: 12e Variations in TCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2006/2007: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 0.1 ppb, white=1 ppb

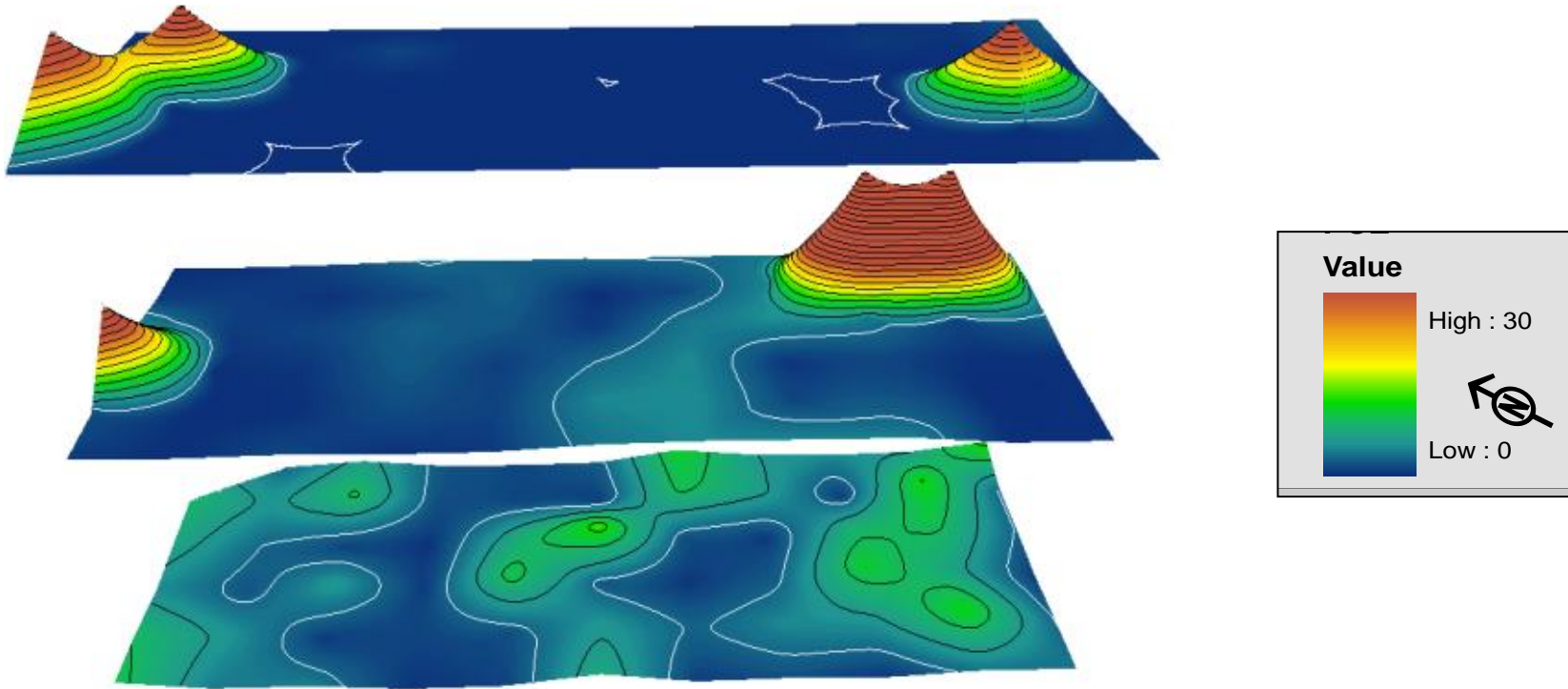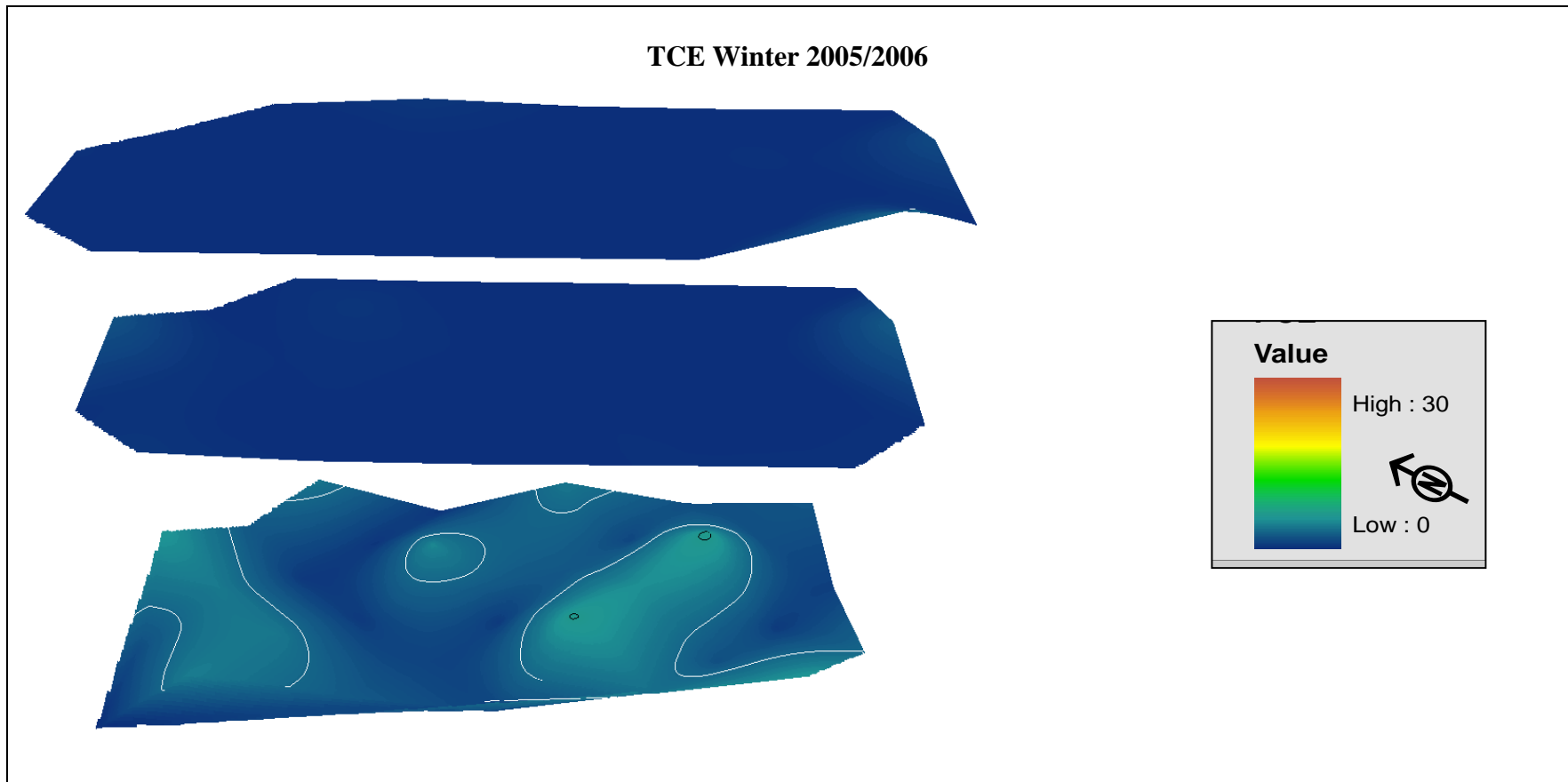**trans-DCE Winter 2003/2004**

Value

High : 50

Low : 0

Figure 13a: Variations in trans-DCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2003/2004: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 1 ppb, white=1 ppb

Figure 13b: Variations in trans-DCE concentration in the groundwater sampled at different depths in the wetlands during Winter 2006/2007: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 5 ppb, white= 5 ppb
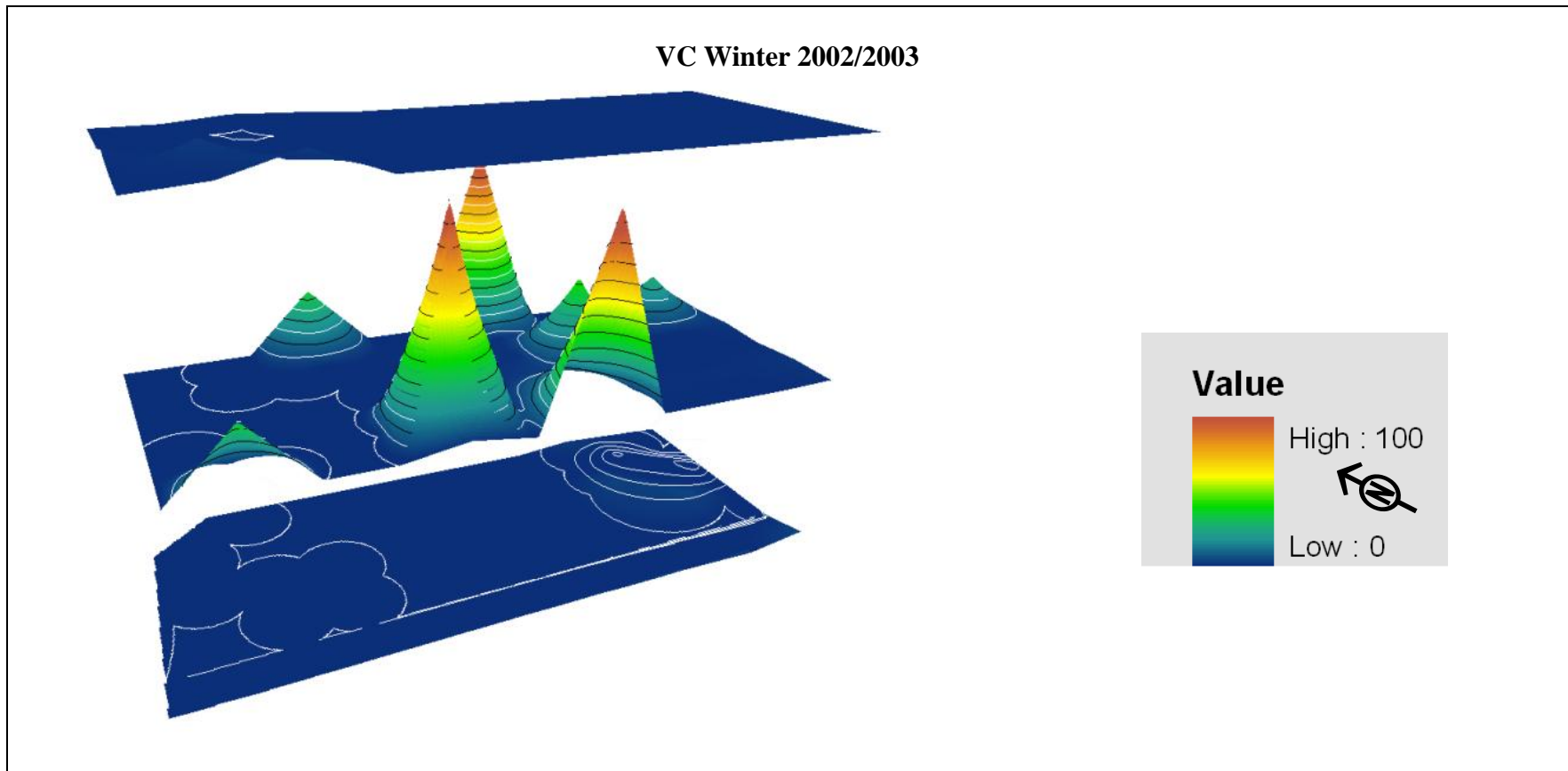
Figure 14a: Variations in VC concentration in the groundwater sampled at different depths in the wetlands Winter 2002/2003. contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 10 ppb, white= 0 ppb
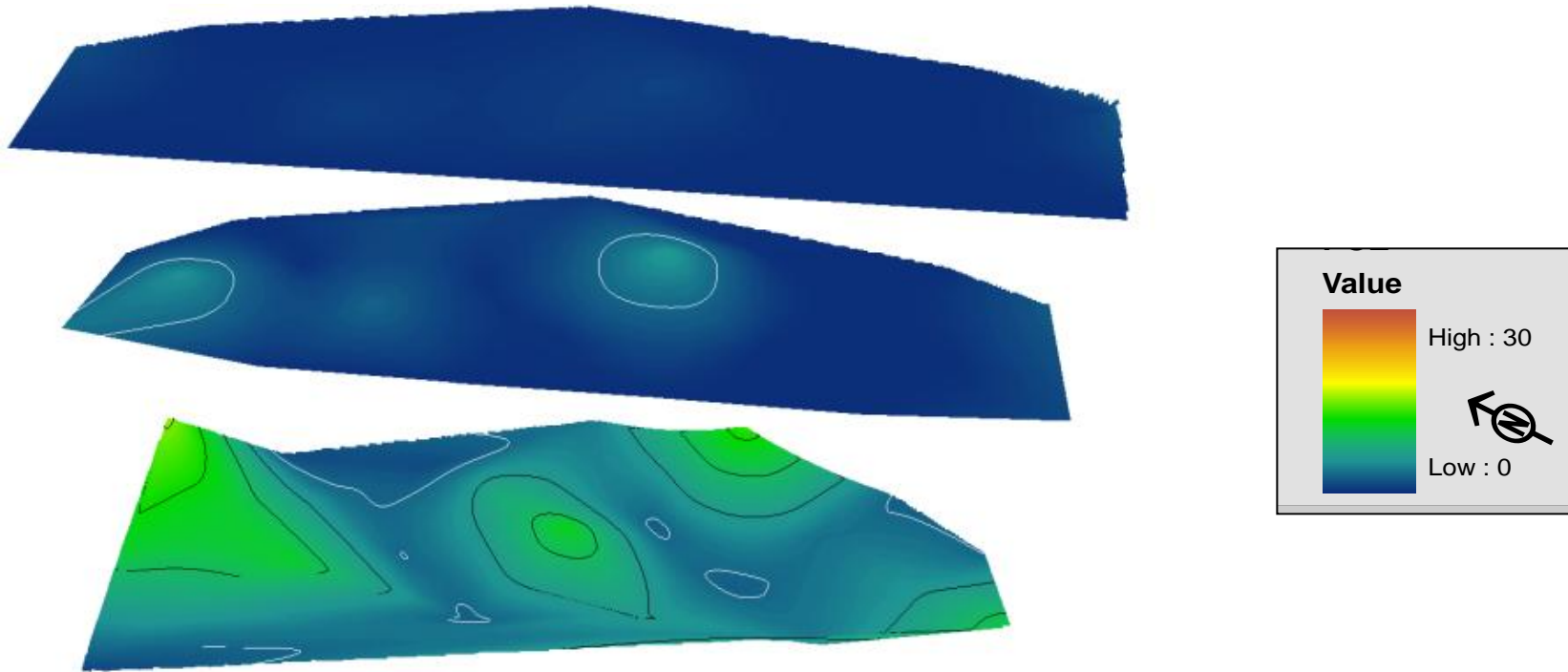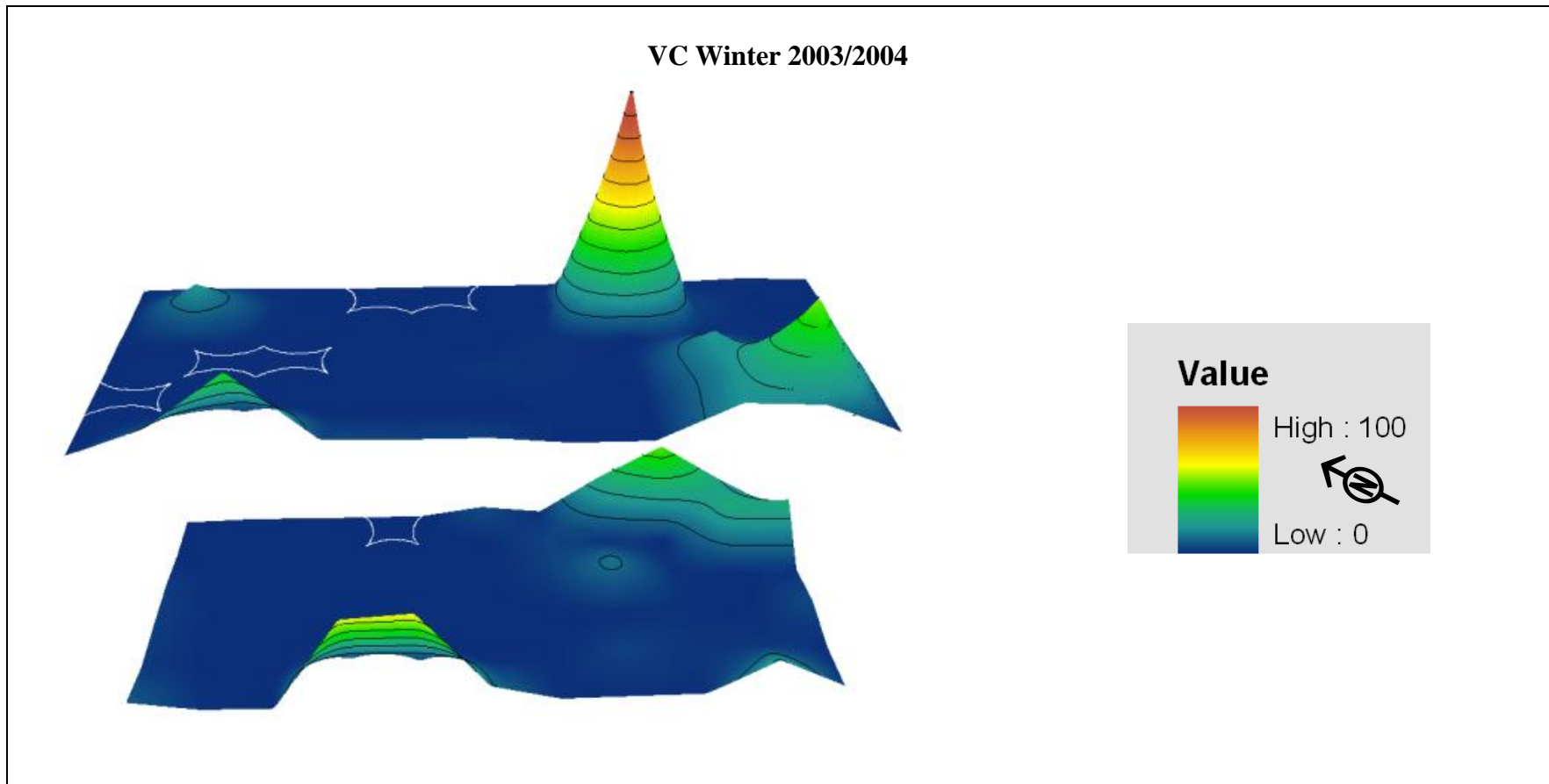
Figure 14b: Variations in VC concentration in the groundwater sampled at different depths in the wetlands during Winter 2003/2004 contour maps at 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 10 ppb, white= 0 ppb
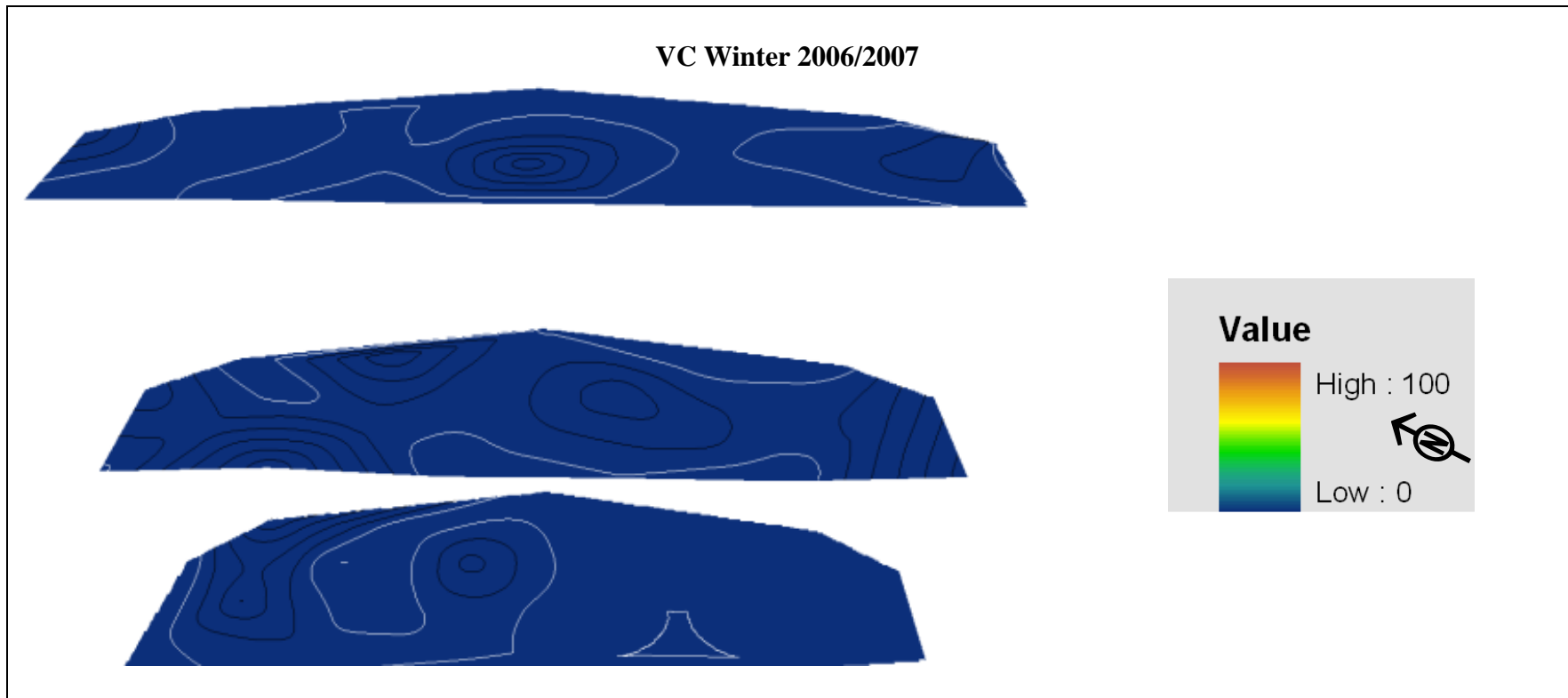
Figure 14c: Variations in VC concentration in the groundwater sampled at different depths in the wetlands during Winter 2006/2007: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer). Contour interval: 10 ppb, white= 0 ppb
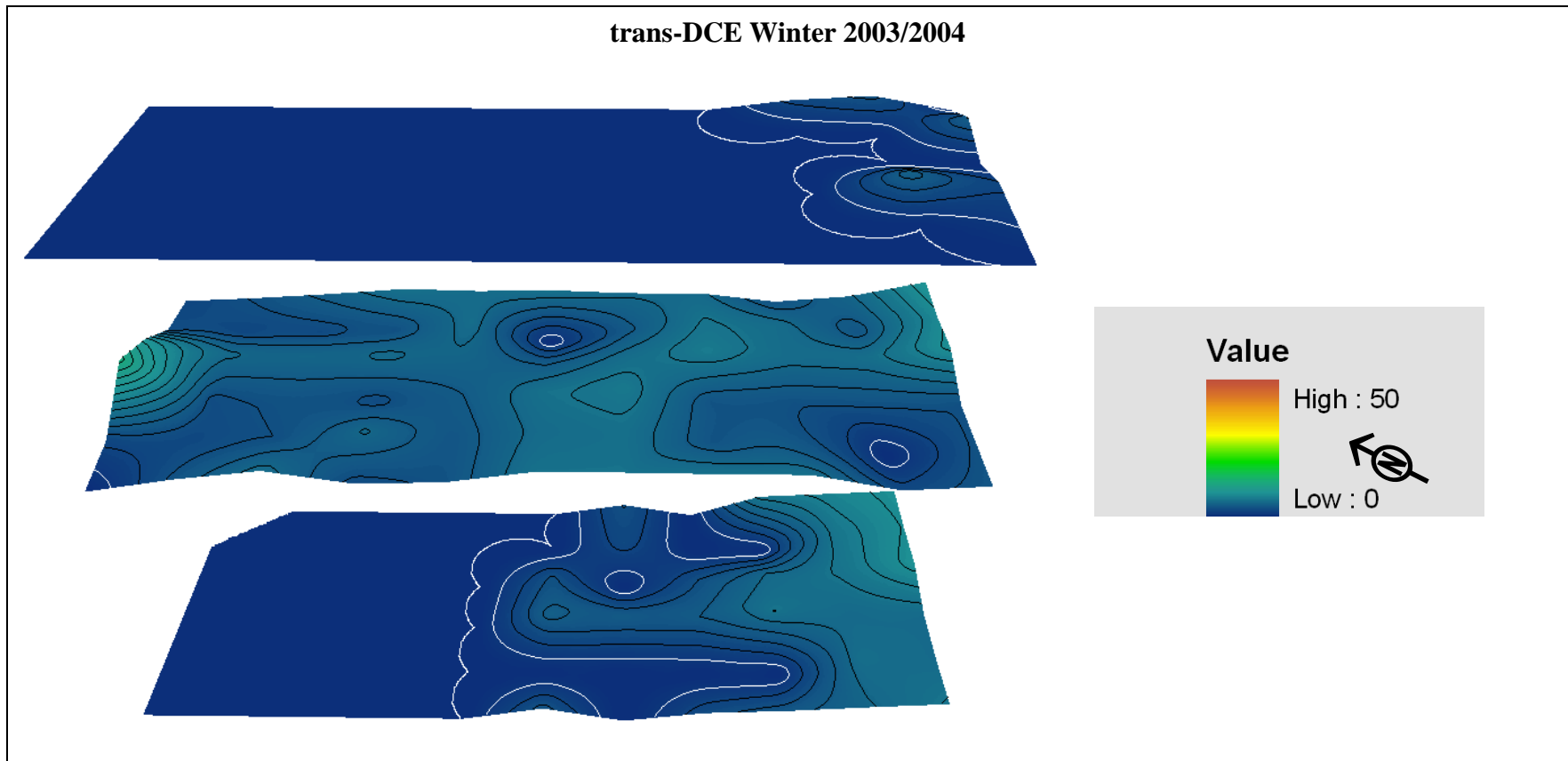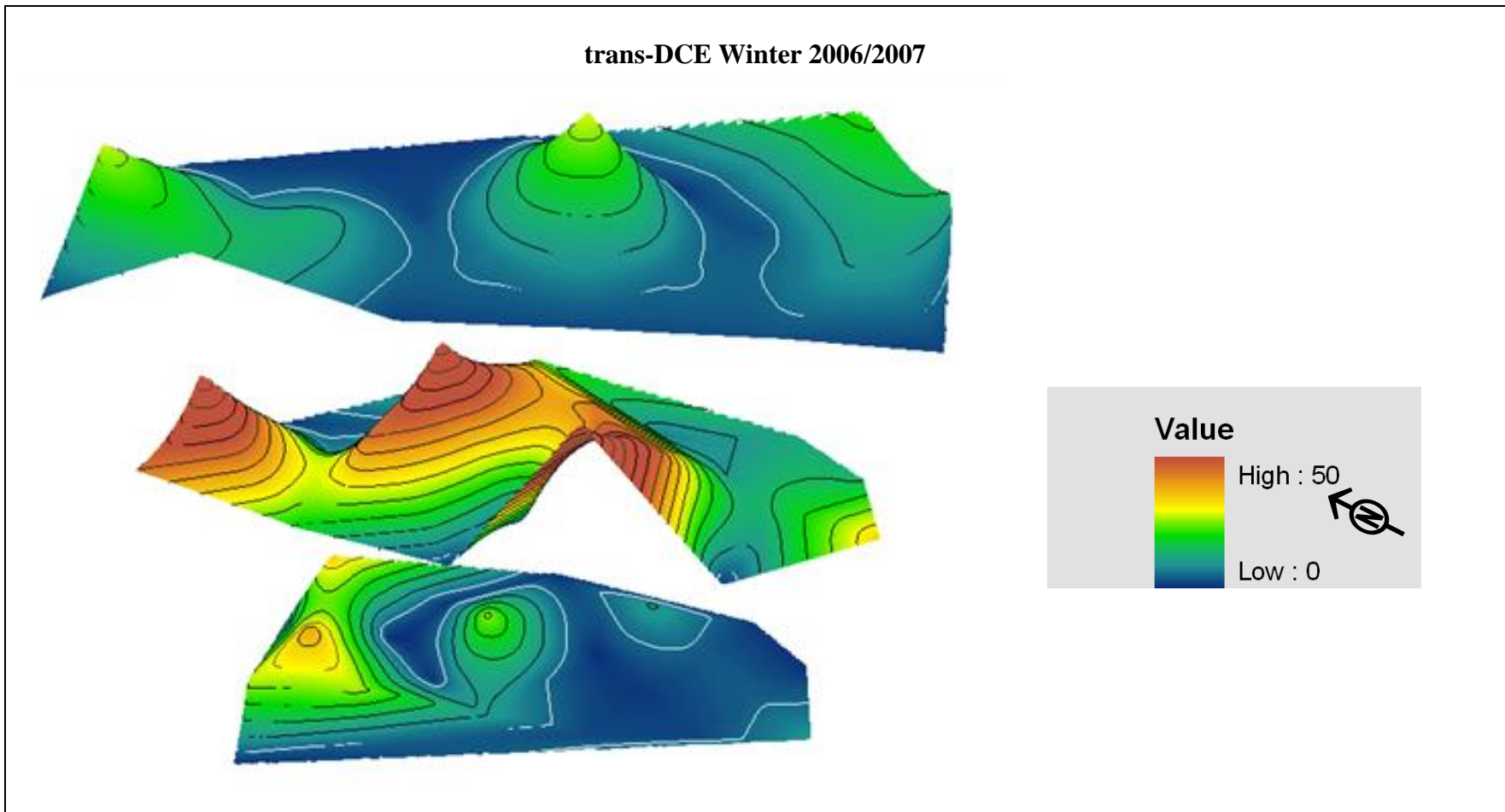
Ethane Winter 2006/2007

Ethane in ppb

Value

High : 0.0041

Low : 0
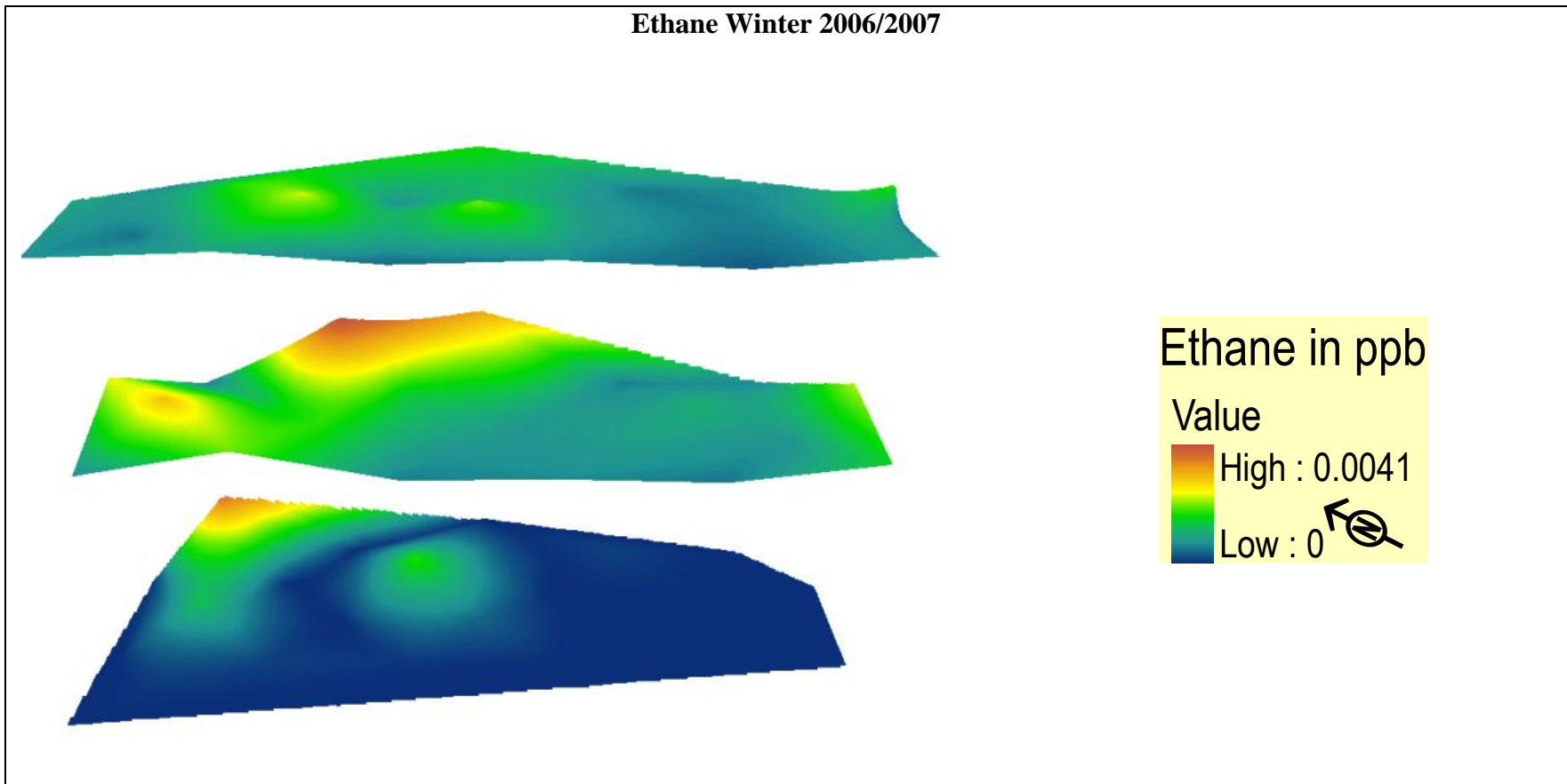
Figure 15: Ethane variations in ethane concentration in the groundwater sampled at different depths in the wetlands during Winter 2006/2007: contour maps at 0.23 m (Upper layer), 0.69 m (Middle layer) and 1.14 m (Lower layer).
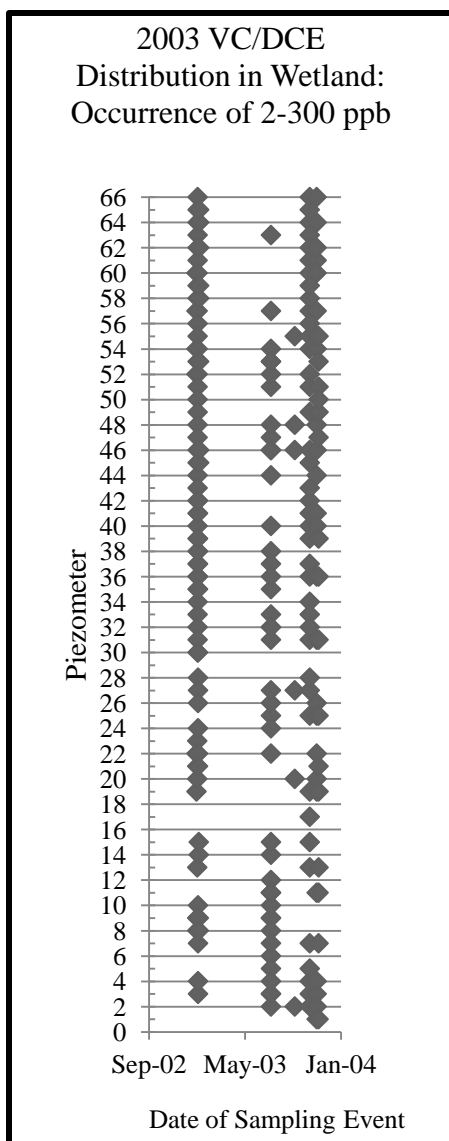
Figure 16: Occurrence of daughter products in wetland
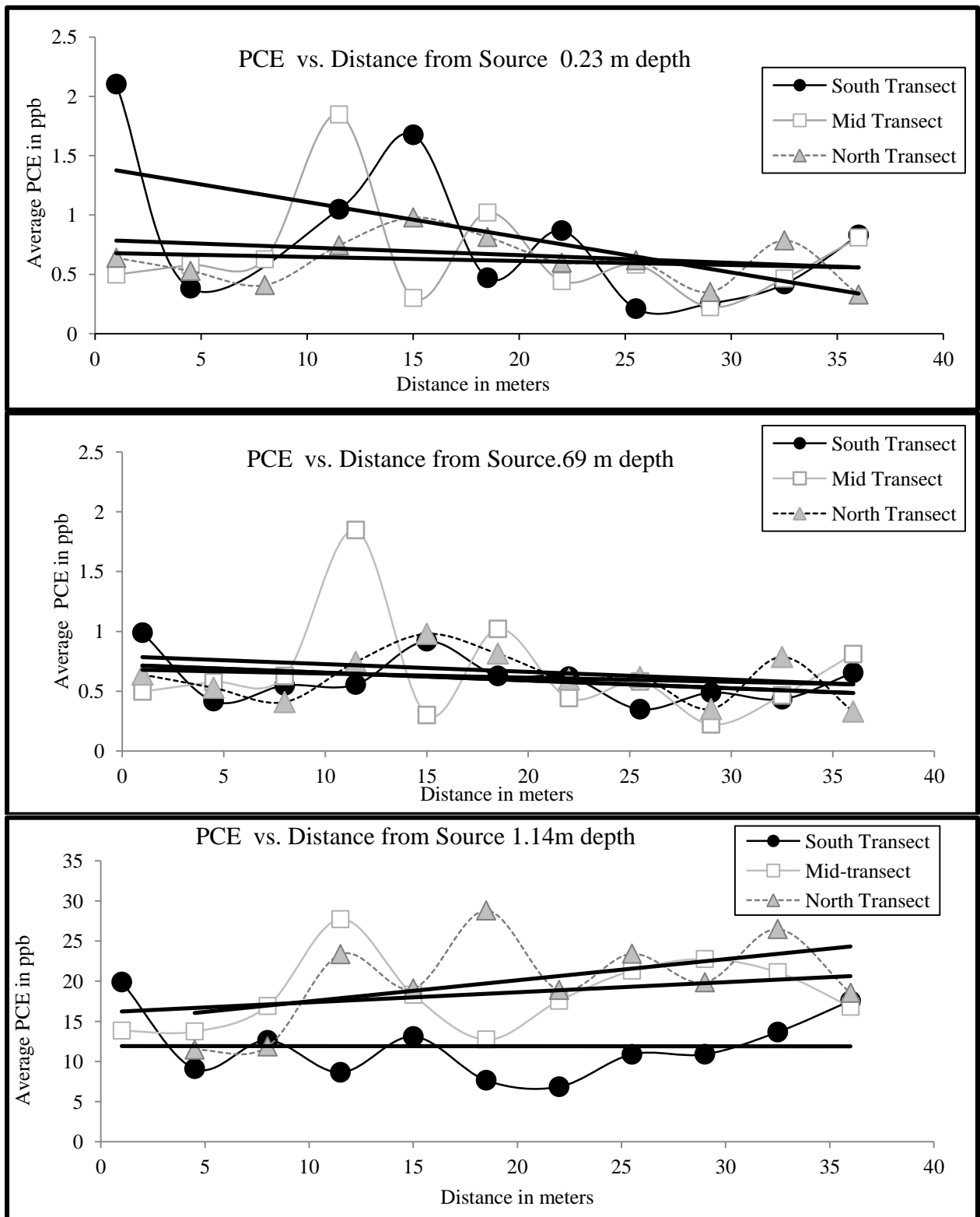
Figure 17: Horizontal PCE distribution across wetland (distance from source) and associated linear trend lines and distance from source at 0 PCE concentration.
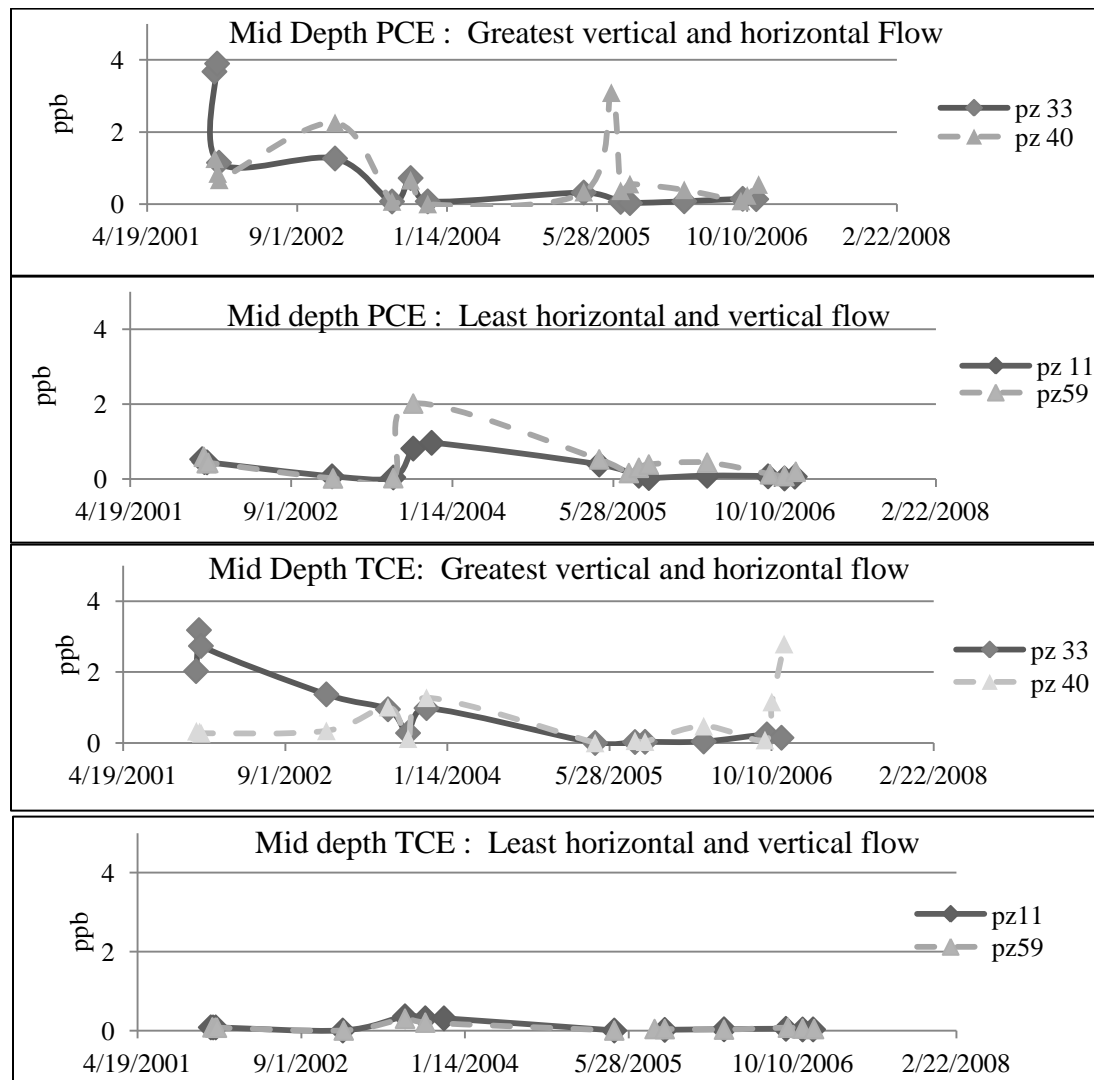
Figure 18: Hydraulic conductivity and PCE and TCE Concentrations during 2001-2006
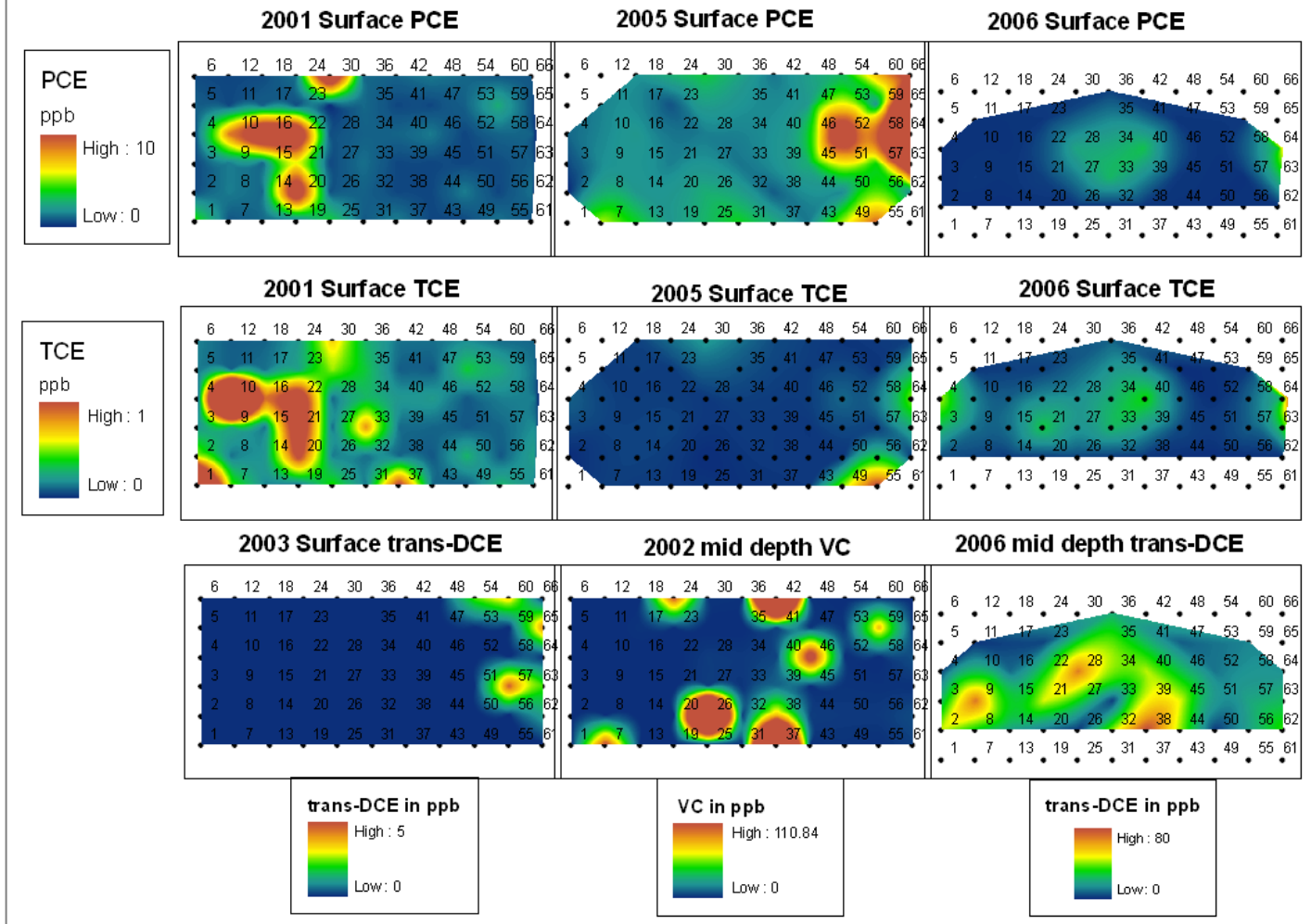
Figure 19: 0.23 m and 0.69 m depth CAH concentrations adjacent to wetland liner and effluent.

TABLES

Table 1a: 2001-2006 Sampling Events

| Author	Sampling Date	Temp	pH	Cond	PCE	TCE	cis-DCE	trans-DCE	VC	HCO3-	CO3-2	CT	Alk	Cl-	Fl-	S-	NO2-	NO3-	SO4-2	PO4-3	NH4+	Fe+2	Ca+2	K+	Na+2	Mg+2	CH4	C2H6	Butyrate	Lactate	Acetate	Propionate	Formate
Opperman	Nov/Dec, 2001				•	•																											
Bugg	Jan. 2002													•	•		•	•	•										•	•	•	•	•
Kovacic	Dec. 2002-Jan. 2003													•	•	•	•	•	•										•	•	•	•	•
Clemmer	Jan. 2003				•	•	•		•																								
Lach	Jan. 2003													•	•	•	•	•	•	•	•	•							•	•	•	•	•
Lach	April, June 2003										•			•	•	•	•	•	•	•	•	•	•	•	•	•			•	•	•	•	•
Lach/Bondurant	July, 2003	•	•		•	•	•							•	•		•	•	•							•		•	•	•	•	•
Lach	Sept. 2003				•	•	•																										
Sobolewski/ Bondurant	Oct. and Nov. 03	•	•	•	•	•	•	•	•					•					•														
Mohamud/ Schlater	April, 2005				•	•				•	•			•	•			•		•													

Table 1b: 2001-2006 Sampling Events

Author	Date	Temp	pH	Cond	PCE	TCE	cis-DCE	trans-DCE	VC	HCO3-	CO3-2	CT	Alk	Cl-	Fl-	S-	NO2-	NO3-	SO4-2	PO4-3	NH4+	Fe+2	Ca+2	K+	Na+2	Mg+2	CH4	C2H6	Butyrate	Lactate	Acetate	Propionate	Formate
Mo/ Schlater	July, 2005	•	•	•	•	•							•				•	•	•		•	•	•	•	•								
Schlater	Sept. 2005	•	•	•	•	•	•			•	•		•				•	•	•		•	•	•	•	•								
Mohamud	Dec. 2005	•	•	•						•	•	•		•			•	•	•	•	•		•	•	•								
Mohamud	Jan. 2006									•	•	•		•			•	•	•		•		•	•	•								
Moh/Schlater	March, 2006	•	•	•	•	•				•	•	•		•			•	•	•		•		•	•	•								
Mohamud	Apr/May/Jun 2006	•	•	•										•			•	•	•		•		•	•	•								
Waldron	Sept-Dec. 2006	•	•	•	•	•	•	•	•																			•					

68

Table 2: Studies and Findings

Author/ year	Analysis	Conclusions
Opperman (2001)	Hydraulic conductivity mapped	PCE degraded to TCE. No daughter products found-maybe due to analysis methods. Short circuiting occurring. HC greatest near effluent. Increase in PCE from mid to top layer
Bugg (2002)	Contour plots for organic acids, sulfate, nitrate, Cl,	Wetland less reducing with depth. Sulfate and Nitrate reduction.
BonDurant (2003)	Organic acids Some cation/anion data. Surfer maps,vertical profiles	Greatest reduction at least depth. Ethenes present. Organic acids present.
Clemmer (2003)	GC retention time eval., jump/excel statistical analysis, surfur plots.	Increase in cis-DCE/VC thouroughout wetland; not detected in inflow or outflow. PCE decreases at 1.14 m and 0.69 m depths. 74% removal rate-Inflow-outflow. 95% for top layer. Some water bypassed all 3 layers. Decrease in PCE from mid. to top layer. Increase PCE in effluent. Inverse correlation between PCE and all daughter products. Average effluent slightly above mcl.
Sobelewski (2003)	Surfur plots,cis-trans DCE, VC eval.	PCE retained in wetland. DCE in inflow and outflow. VC in inflow only. Inverse relationship between PCE/TCE concentrations and DCE/VC. Greater reduction in PCE at 1.14 m depth than can be accounted for by decrease in influent.
Kovacic (2002/03)	Retention, organic acids,DO, nitrate, sulfate maps, analysis with ecowatch software and jmp., multiple concentration maps.	Changes in organic acids and nitrate/sulfates suggest a changing geochemistry which is affected by seasons.
Lach (2003)	Core data and pz. data, evaluated ditches.	DCE detectable in all layers,none in effluent. VC and Ethene not detectable. Increasing methane suggests methanogenesis in all layers. Greatest amount of methane in layer B. Large fluctuation in methane with temperature noted.
Schlater (2005/06)	Degradation rates calculated for VOCs.	PCE and TCE concentrations spike in lower layer. Greatest percent decrease in lower layer. PCE/TCE may be accumulating in gravel.
Mohamud (2005/06)	anions/cations	Bacteria active year round though seasonal changes were noted.
Waldron (2005/06)	PCE,TCE,DCE(cis/trans) and VC averages compared to past	Improved reduction rate of PCE since intial data in 2001.
Corbin (2008)	Residence time tests, Hydraulic Conductivity compared to 2001. Modflow/modpath models.	Short circuiting occurs in paths similar to those noted by Opperman in 2001. Areas of little/no vertical flow in northwest. High flow shifted from north to south side of wetland. Increased flow vertically occurs on south and west(effluent) side of wetland. Average residence time in areas of high flow is 1-10 days(consistent with Entingh,2002); 425,000 days for areas of low flow. In all layers, residence time for distribution of chemicals within the layer averages .4-.5 days.

Table 3: Upper and lower class maximums/minimums from Jenks Optimization which established outliers

Jenks Optimization Results										
0m/0.23 m depth										
	PCE	**TCE**	**cis-DCE**	**trans-DCE**	**VC**	**Fe^{+2}**	**C$_2$H$_6$**	**NO$_2^-$**	**NO$_3^-$**	**SO$_4^{-2}$**
Maximum value of lower class below which data was removed	<0.1133	<0.01791	<0.0076	<0.667	<0.02071	<0.00487	<0.00014	<0.0000	<0.00018	<0.00064
Minimum value of upper class above which data was removed	>18.35	>=13.73	>=6.87	>=39.98	>=114.40	>=1.0059	>=219.6	>=0.261	>=0.341	>=0.5528
0.69 m depth										
Maximum value of lower class below which data was removed	<0.013	<0.02846	<0.0138	<1.116088	<0.01627	<0.00966	<0.00031	<0.0000	<0.0000	<0.00017
Minimum value of upper class above which data was removed	>=17.5904	>25.8925	>7.3650	>120.7086	>60.919	>1.31065	>0.00412	>2.2829	>0.3528	>0.53258
1.14 m/1.16 m depth										
Maximum value of lower class below which data was removed	<0.44	<0.08019	<0.020	<0.373299	<0.00861	<0.00214	<0.00006	<0.000012	<0.002	<0.00250
Minimum value of upper class above which data was removed	>=45.16	>=7.1893	>=19.48	>=38.6985	>=4.8466	>=0.1317	>=0.0039	>=0.266	>=0.2	>=0.5420

Table 4: Datasets averaged to construct ArcGIS maps

Inorganic Data	Sep	Oct	Nov	Dec	Jan
Winter 2001-2002					●
Winter 2002-2003				●	●
Winter 2003-2004			x		●
Winter 2005-2006				●	●
Organic Data	Sep	Oct	Nov	Dec	Jan
Winter 2001-2002			●	●	●
Winter 2002-2003				●	●
Winter 2003-2004	●	●	●		
Winter 2005-2006	●				
Winter 2006-2007	●	●	●	●	

Table 5: Effluent PCE Concentrations above MCL During 2001-2006

Occurrence of Effluent PCE above MCL (5 ppb)	
Date of Sample	PCE(ppb)
1/2/2002	5.92
12/7/2002	9.34
12/7/2002	8.96
12/8/2002	7.33
12/13/2002	9.38
12/13/2002	9.28
1/4/2003	6.16
1/5/2003	7.10
1/6/2003	5.44
1/7/2003	6.04
1/8/2003	7.33
1/9/2003	6.71
9/20/2006	10.30
9/26/2006	8.43
10/11/2006	8.34
11/10/2006	7.91
12/12/2006	5.58
12/15/2006	6.60

SUPPLEMENTAL INFORMATION
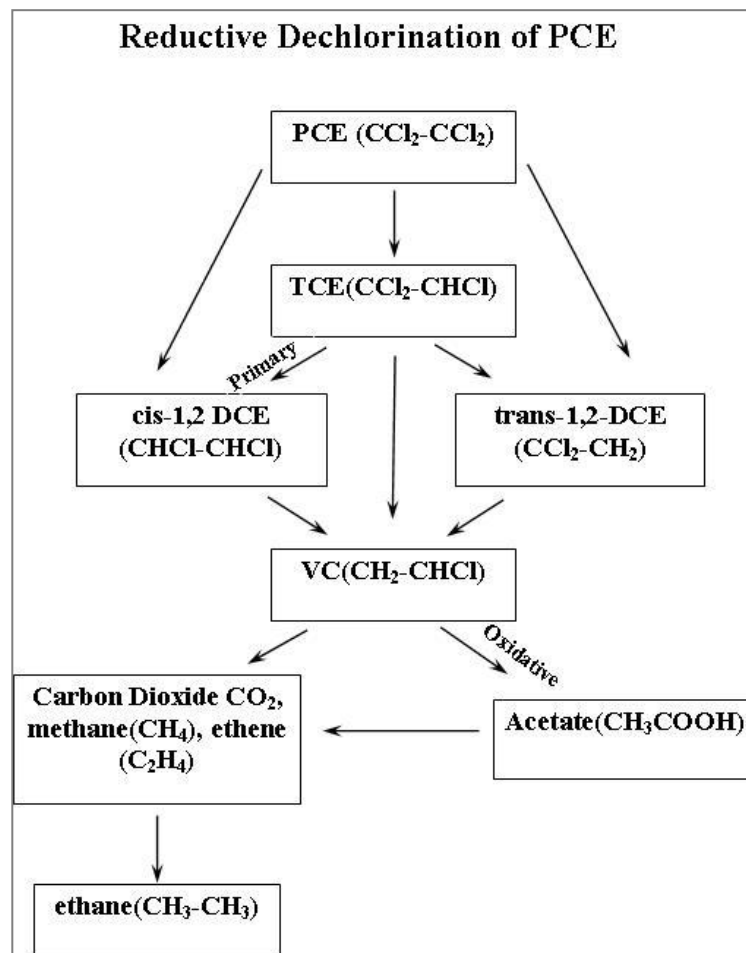
Supplement 1: CAH Pathways (adapted from McCarty and Semprini, 1994)

| Electron Acceptor	Reaction	ΔG °(kcal/mol e-)
Oxygen	$\frac{1}{2} O_2 + H_2 \rightarrow H_2O$	-28.5
Nitrate	$\frac{2}{5}NO_3^- + \frac{2}{5}H^+ \rightarrow \frac{1}{5}N_2 + 1\frac{1}{5}H_2O$	-27
PCE	$C_2Cl_4 + H_2 \rightarrow C_2HCl_3 + H^+ + Cl^-$	-19.7
Iron III	$2Fe_3+ + H_2 \rightarrow 2Fe^{2+} + 2H^+$	-19.6
TCE	$C_2HCl_3 + H_2 \rightarrow C_2H_2Cl_2 + H^+ + Cl^-$	-19.4
VC	$C_2H_3Cl + H_2 \rightarrow C_2H_4 + H^+ + Cl^-$	-18.7
DCE	$C_2H_2Cl_2 + H_2 \rightarrow C_2H_3Cl + H^+ + Cl^-$	-17.1
Sulfate	$\frac{1}{4} SO_4^{2-} + \frac{3}{8}H^+ + H_2 \rightarrow \frac{1}{8}HS^- + H_2O$	-4.8
Carbon Dioxide	$\frac{1}{4} CO_2 + H_2 \rightarrow CH_4 + \frac{1}{2}H_2O$	-4.1

Supplement 2: Common Reactions using H_2 as Donor (Adapted from Wiedemeier, 1999)
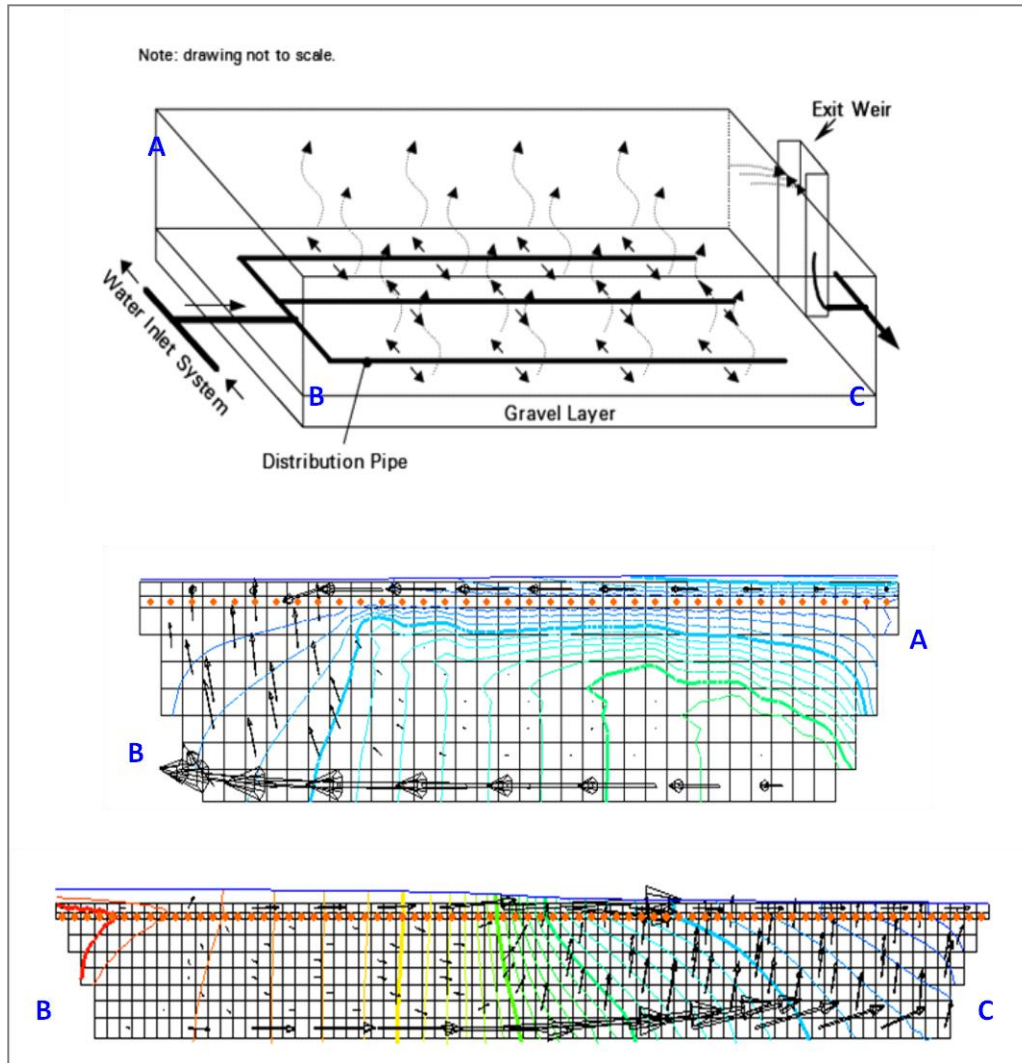
Supplement 3: Wetland Water Flow after Entingh (2002) and Corbin (2008)
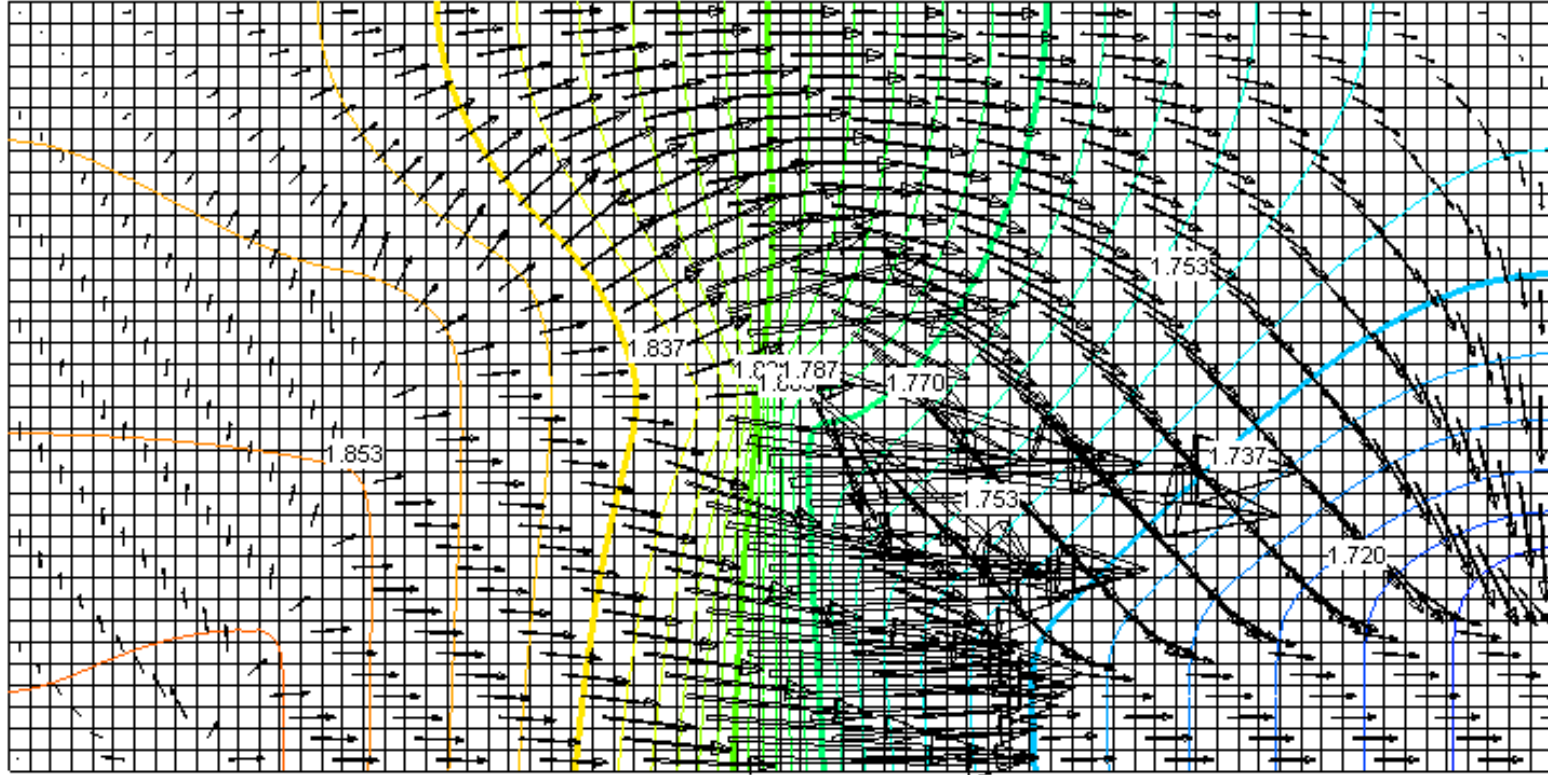
Supplement 4: Bird's Eye View of Hydraulic Conductivity (m/d) at 0. 23 m (after Corbin, 2008)
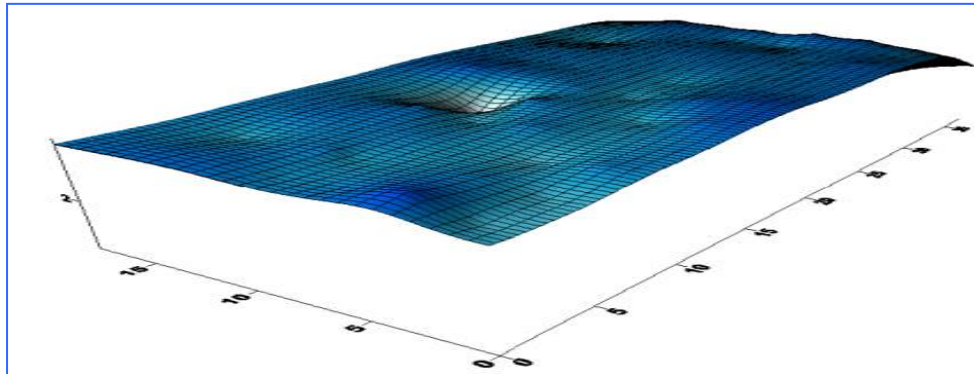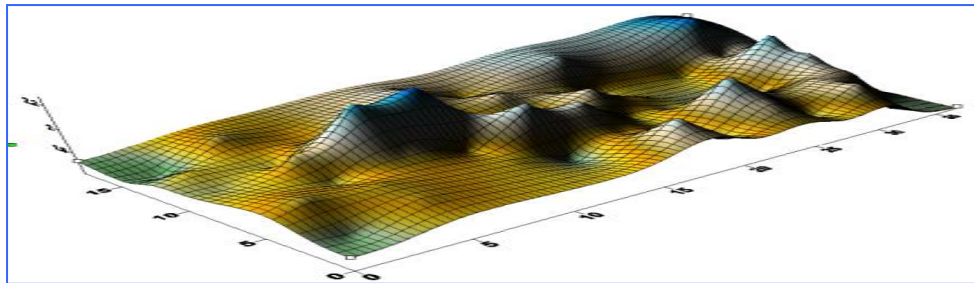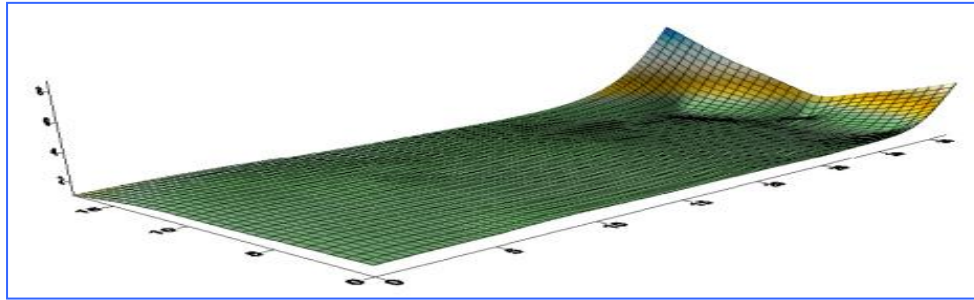
Supplement 5: Hydraulic Head in meters for 0.23 m, 0.69 m and 1.14 m, respectively (from Corbin, 2008)