Monitoring Environmental Effects at an Established Phytoremediation Site

Phase III

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PROJECT SUMMARY

Monitoring Environmental Effects at an Established Phytoremediation Site

Project I.D.: WR04R007

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This study is a continuation of groundwater monitoring (contaminants and elevation), along with examination of mortality and estimated biomass production of hybrid poplars at an established phytoremediation site in Bancroft, WI in southern Portage County.

Background - Phytoremediation offers the prospect of using a low-cost alternative to degrade or sequester contaminants from soil and groundwater, and/or slow the movement of shallow groundwater. Sequestration of heavy metals and degradation of petroleum hydrocarbons and volatile organic compounds is well documented; however, the fate of many pesticides is unclear. If groundwater movement can be slowed, possibly so will the movement of contaminants off-site, and therefore, a greater likelihood they will be degraded or sequestered by biotic or abiotic processes on site.

The study site is an active aerial agricultural chemical facility, located near Bancroft, Wisconsin, and has a history of soil and groundwater contamination. Dinoseb (2, sec-butyl-4,6-dinitrophenol) is the primary contaminant of concern. At the time this study was initiated, dinoseb-contaminated soil was unacceptable for conventional landfill disposal or landspreading. Sandy soil, shallow groundwater, and other factors make this a prime site to study the effects of phytoremediation.

Objectives - The objectives of this research were:

1) Assess mortality and biomass production of the established trees at the site in both the source area and downgradient area.
2) Investigate possible relationships between hydrologic response and transpiration rates at various times through the project duration (both daily and seasonal changes).
3) Monitor changes in the groundwater contaminant profile through the source and downgradient areas.

Methods - A total of 834 hybrid poplars and willows were planted in June 2000. An irrigation system and electric fence were installed to help establish the plantation. Mortality and estimated biomass production were measured following each growing season since 2000. A network of groundwater monitoring wells had been installed for contaminant testing and groundwater elevation monitoring using electronic data loggers. Contaminant monitoring occurred in the spring and fall of each year. Down-well data loggers provided continuous monitoring of groundwater elevation throughout the growing season. A complete weather station was located within 500 meters and all pertinent weather data was available for this project.

Previous studies have examined: transpiration rates of the hybrid poplars, groundwater response to transpiration, presence of contaminants in biological tissues, aquifer characteristics, hybrid poplar mortality rates, biomass production, and groundwater quality. This study examines mortality and biomass production, hydrologic response, and groundwater quality trends.

Mortality is assessed in the fall by visual inspection of the trees and evidence of viable leaves or leaf buds. Biomass is estimated through direct measurement of trunk diameter and height as recommended by U.S. Forest Service North Central Experimental Station. The equation for this estimation is d^2*h where d = diameter breast height, and h = total tree height. Groundwater quality trends are evaluated by comparing dinoseb concentrations in monitoring wells across the study area. Hydrologic response is monitored with the use of groundwater elevation dataloggers (Aquarod – Sequoia Scientific) in three areas of the property. Elevation is logged once every 30 minutes with 1 mm of accuracy. Weather data is gathered using a Davis Instruments weather station that logs data every 30 minutes.

Results and Discussion - Following six growing seasons, there were no significant differences in mortality of the two key poplar clones, NM-6 (39%) and DN-34 (40%) in the plot as a whole, nor in the contaminated (source) area of the plot (45% and 46%, respectively). There were, however, substantial differences in mortality between the source and downgradient areas (45% and 16%, respectively). Estimated biomass produced by the two clones was also significantly different, with 75% of the biomass produced by NM-6.

Groundwater was analyzed for dinoseb, which has historically been the main contaminant of concern at this site. Dinoseb concentrations in groundwater have fluctuated considerably, likely due to flushing actions from the soil associated with precipitation events. Samples from downgradient piezometers have steadily decreased in dinoseb concentration and have been recorded at less than detection limits (5.0 µg/L) since October 2004.

Groundwater elevation declined steadily throughout the summer months with a maximum decline of 807 mm measured between May and September 2004. The majority of drawdown is most likely due to regional and local irrigation pumping systems. Groundwater recharge correlated with rainfall events. Diurnal water table fluctuations from transpiration were not observed due to rapidly rising (rainfall) and falling (groundwater pumping) of the water table.

Conclusions/Implications/Recommendations - Biomass calculations show that hybrid poplar NM-6 is more prolific than DN-34 in soil and groundwater severely contaminated with dinoseb, although similar morality levels were observed. A hybrid poplar plantation appears to have effectively reduced off-site migration of dinoseb with the groundwater; however, assimilation or a mechanism of degradation of dissolved dinoseb in relation to the trees was not established. Hybrid poplars were found to influence water table elevations; however, this influence was often obscured during periods of extensive groundwater pumping and large rainfall events that resulted in a rapidly rising and dropping water table.

Key words - dinoseb, phytoremediation, hybrid poplars, groundwater

Funding - Water Resources Institute, University of Wisconsin

INTRODUCTION

Phytoremediation has received widespread attention for offering the prospect of a low cost alternative to restoration or containment of contaminated soils and groundwater. Its effectiveness has been demonstrated for the remediation of volatile organic compounds (1), metals (2), petroleum hydrocarbons (3), some pesticides (4), and a wide array of industrial compounds (5).

Contaminated groundwater is often remediated by expensive pump-and-treat methods. A dense stand of trees can offer similar benefits in shallow aquifers, without the capital expenditures of pumps, extraction wells, and disposal of treated water. Additionally, phytoremediation offers degradation of many contaminants through various biological and chemical routes. While many laboratory studies of phytoremediation potential have been conducted, application of this technology in field studies is limited. Sites contaminated with agricultural chemicals are widespread around Wisconsin and the United States.

At the time this study was initiated, dinoseb-contaminated soil was regulated to be disposed at hazardous waste approved landfills. Cost for disposing of the volume of soil at this site extended into millions of dollars. Since this site is located in an isolated area, with no sensitive receptors downgradient, a low-cost alternative was proposed.

The objectives of this study were to monitor survival rates and estimate biomass production of two hybrid poplar clones when exposed to contaminants in soil and groundwater, correlate hydrologic response to rain events at various times through the project duration (both daily and seasonal changes), and determine changes in groundwater dinoseb concentrations through the study area.

The study site is located in south-central Portage County, Wisconsin, in the township of Pine Grove. An aerial agricultural spraying service has operated on this site for approximately 25 years and is currently enrolled in the Wisconsin Department of Agriculture, Trade, and Consumer Protection (DATCP) administered Agricultural Chemical Cleanup Program (ACCP).

Knowledge of groundwater contamination at this site dates back to 1985. Testing of spraying equipment and disposal of pesticide containers resulted in groundwater contaminated with dinoseb (2-sec-butyl-4,6-dinitrophenol) and other pesticides of lesser concentrations and toxicological concern. Dinoseb had been reported as high as 2000 µg/L (6) in groundwater samples from this site. This study has focused on the presence of dinoseb because of its toxicity, cancellation of use by U.S. EPA in 1986, and cost of disposal of dinoseb-contaminated soil.

As required by DATCP, buried pesticide containers were located by magnetic testing and excavated in May 2000. The area that was excavated is defined as the “source area” of the site map (Figure 1). This activity likely resulted in a release of more contaminants into the subsurface environment from residual chemicals in discarded containers. During container removal, topsoil was disturbed and often buried, leaving very sandy and contaminated soils on the surface. Geologic material at this site was identified as outwash sand. The depth to groundwater is approximately 2 meters below ground surface (bgs).

PROCEDURES AND METHODS

In June 2000, trees were obtained from the U.S. Forest Service (USFS) through the U.S. Department of Energy Biofuels Feedstock Development Program. Trees were obtained as 20 cm cuttings and soaked in water for 5 days to promote root growth. Trees were planted in 12 rows in the main block (source area, clonal test plot, and downgradient plot) and 6 rows in the control plot. Rows were oriented in an east-west alignment. All trees were planted with 1.5 meter spacing between trees and 3 meters between rows. Prior to planting, 1 meter by 5 cm holes were augered into the soil to loosen the root zone. This approach was used to encourage root growth toward the water table. The hole was backfilled with native soil and cuttings were inserted into the loosened soil with the terminal bud just above the soil surface. A total of 834 trees were planted in this manner. Plots were divided as follows:

- Source area – 12 rows each consisting of 40 trees, planted in 3-row blocks of hybrid poplars DN-34 or NM-6.
- Clonal test plot – 12 rows each consisting of 11 trees, planted in 4-row blocks that were repeated three times randomly through the plot. One block consisted of DN-17 (hybrid poplar), D-105 (eastern cottonwood), SX-61 and SV-1 (both hybrid willows). Data from this clonal test plot are reported elsewhere (7, 8).
- Downgradient plot – 12 rows with 10 trees each, planted in 3-row blocks of DN-34 or NM-6.
- Control plot – 6 rows consisting of 17 trees, planted in 4 blocks. One block of 27 trees consisted of DN-34 that received two manure applications throughout the first year, while a second block of 27 DN-34 did not receive the manure treatment. A third block of 24 NM-6 received manure while the fourth block of 24 NM-6 did not. Results from manure application are reported elsewhere (7, 8).

Groundwater Monitoring Wells

A total of 27, 1.9 cm PVC monitoring wells with 30 cm screens were installed. Eight of these were nested wells consisting of two or three wells. Nested wells are identified on Figure 1 as having an “A, B, or C” letter designation. Monitoring wells identified in this manner as having a letter “A” were installed 30 cm below the water table, “B” were 60 cm below and “C” 90 cm below. Monitoring wells MW-3, 4 and 5 were installed with a 5-foot screen. Three wells (MW-14, 15, and 16) are 5 cm diameter observation wells with 1-meter screens. These wells contain groundwater elevation data loggers described later.

Monitoring wells DP-1 and DP-1P were installed during a previous ACCP investigation. DP-1 is a water table monitoring well with 0.75-meter screen and DP-1P is a piezometer with a 0.75-meter screen approximately 5.25 meters bgs. DP-1PP (6.75 meters bgs), and DP-1PPP (7.7 meters bgs) were installed with this study to ensure contaminated water was not exiting the site below the shallower wells. These wells, along with monitoring wells MW-1 through MW-12, were used to collect groundwater samples for pesticide analysis.

Groundwater sample collection

Groundwater elevation was measured before sample collection. A minimum of 30 cm of water in the well was required to insure that the surface of the water table was being sampled. If 30 cm of water was not available in “MW1-A”, for example, elevation of “MW1-B” would be

measured and if enough water was present, it was sampled. Wells were purged to insure a minimum of three volumes of water were flushed through the well before collection in a one-liter, amber, borosilicate glass bottle. Because of extremely high (> 1 mg/L) concentrations of dinoseb in some wells, sample tubing was dedicated to each well or well nest sampled.

Groundwater Analysis

Samples were analyzed by the Water and Environmental Analysis Laboratory at University of Wisconsin- Stevens Point using a modification to EPA Method 8270. This method employs high resolution gas chromatography with mass spectrometry. Initially, samples were analyzed for a wide variety of nitrogen and phosphorus containing pesticides. While other low levels (<2 µg/L) of pesticides were detected, this study focused on dinoseb at levels greater than 5 µg/L.

Groundwater Elevation Monitoring

Groundwater elevation monitoring was conducted on all monitoring wells by measuring the depths to water from the top of well casing to the nearest 3 mm using an electronic water level indicator. The well casing elevations were determined using a laser level accurate to 3 mm feet over a distance of 30 meters (100 feet).

Groundwater fluctuations were monitored in MW-14, MW-15 and MW-16 (5 cm diameter PVC monitoring wells with 1-meter screens) using AquaRods (Sequoia Scientific, Redmond, WA). This device measures capacitance (translated into groundwater elevation) at selected time intervals or changes in groundwater elevation. This study utilized 1-meter rods with accuracy of 1 mm. One data logger was located in the center of the main plot (MW-14), a second data logger was located on the north edge of the main plot (MW-15), and the third data logger was located south of and away from the control plot (MW-16).

Mortality and Estimated Biomass Production

Mortality and estimated biomass were determined concurrently at the end of each growing season. Mortality was determined by visual inspection of the tree and presence of buds. Estimated biomass was determined by the formula $d^2 * h$ where d = diameter and h = height. Initially, because of the small sizes of the trees, diameter was measured at the tree's base. However, for the duration of this study, diameter has been measured at breast height (dbh) as that is a more conventional forestry measurement. Biomass data from previous studies at this site should not be used as comparisons because measuring techniques were altered.

RESULTS AND DISCUSSION

Mortality and Estimated Biomass Production

Numerous variables will affect survival and estimated biomass production of these new trees. With the limited resources available, it is not reasonable to assess all possible variables. Differences in soil conditions (texture, nutrient content, and contaminant concentration) exist within the study site. Random differences also exist from weed growth, damage from deer browsing, girdling by rabbits/voles and damage from site maintenance equipment. Examination of the control plot as well as the downgradient plot facilitates the interpretation of mortality and estimated biomass production throughout the study site.

Total mortality of the NM-6 and DN-34 clones within the main study block (source area plus downgradient area) was 39%. Segregation of these areas reveals significant differences. Total mortality of the two poplar clones in the source area was 45%, while downgradient mortality was 16%. Total control plot mortality of 24% was also lower than the source area but similar to downgradient mortality. Differences in source area compared to downgradient and control plot mortality may indeed be due to contaminants present since other variables such as soil type exist across the entire site.

Differences between mortality of NM-6 and DN-34 in the source area were insignificant (39% versus 40% respectively) as was mortality in the downgradient area (13% versus 18% respectively). Closer examination of the source area reveals great differences in mortality across the study site (see Figures 3 and 4.) Numbering the rows from north (row 1) to south (row 12), it is evident that rows 3 through 8 experienced the greatest losses with row 5 demonstrating 83% mortality of the DN-34 clone. Rows 3 through 8 all experienced mortality of greater than 50% in the source area. This area, as noted on Figure 1, is considered the source area where buried containers were excavated and topsoil disturbed.

Mortality of clonal varieties DN-34 and NM-6 within the three plots they were planted (source, downgradient, and control) is illustrated in Figure 3. Greater mortality in the source area is evident when compared to the downgradient and control areas. It is uncertain whether mortality in the source area was due to toxic conditions in the soil or groundwater. Trees in the source area are exposed to dinoseb in groundwater (as evident by MW-3, 10 and 11) as are trees downgradient (MW-5, 6 and 7). Wells located in the middle of the site (MW-4 and 9) are also highly contaminated, yet trees downgradient of these wells have much higher survival rates. It is possible that soil in the source area remains as the key to mortality and trees are affected as their roots are exposed to pockets of highly contaminated soil, or as contaminants are mobilized from soil into the root zone. It may also be possible that once contaminants are mobilized to the saturated zone, they do not migrate back into the capillary fringe. Regardless, mortality of both the NM-6 and DN-34 clones was greater in the source area than either the downgradient and control plots.

Biomass is often evaluated through harvesting of the trees. This was not an option for continuation of this study, so biomass production was estimated by measuring tree diameter at breast height (d) and height (h), then calculated by taking diameter squared multiplied by the height of the tree ($d^2*h = cm^3$). If more than one shoot was present, then multiple measurements were made on each tree and summed to obtain estimated biomass. This method of biomass estimation has been utilized by U.S. Forest Service and measurements were taken in October of 2004 and 2005.

Figure 4 illustrates total estimated biomass production within the source area by rows numbered 1 through 12 from north to south. As illustrated by this graph, total estimated biomass reflects survival rate (Figure 4) in the NM-6 clone (rows 1-3, 7-9). However, the DN-34 clone, while experiencing similar survivability, portrays one-third the biomass. Nearly identical differences appear when considering the data as average estimated biomass per surviving tree.

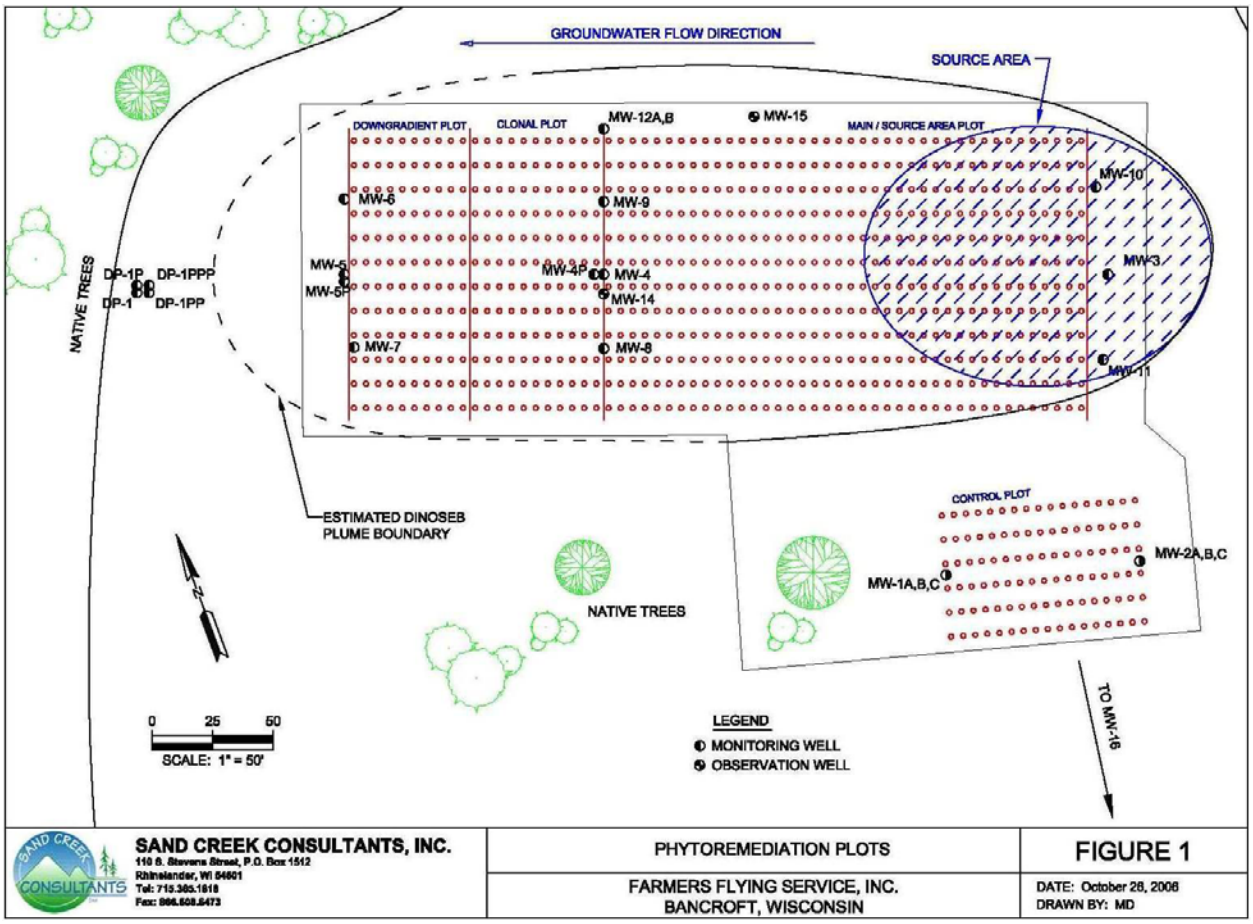

Figure 1. Site map with monitoring well locations.

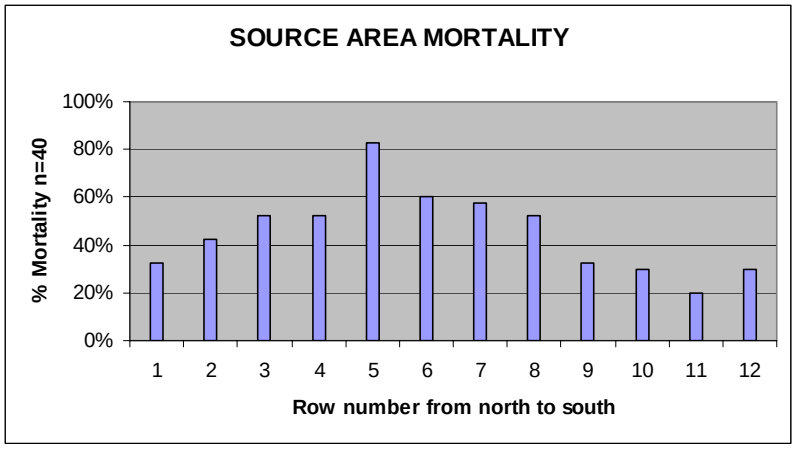

Figure 2. Source area mortality across rows

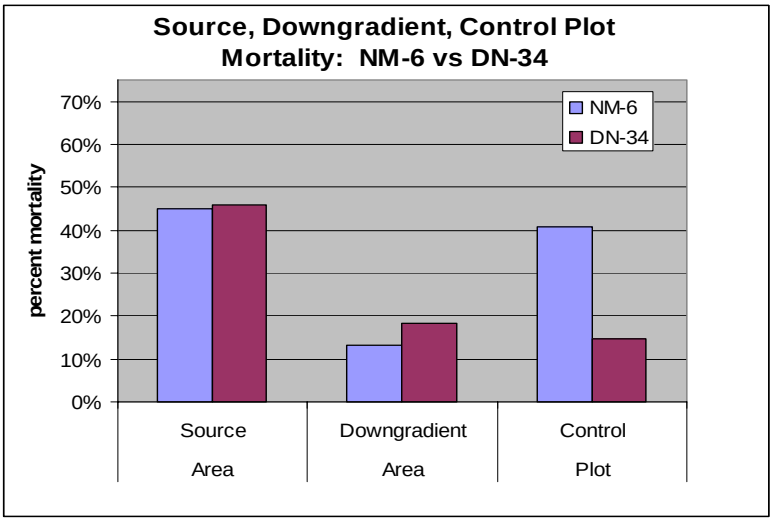

Figure 3. Downgradient, source and control plot mortality of DN-34 and NM-6 clones.

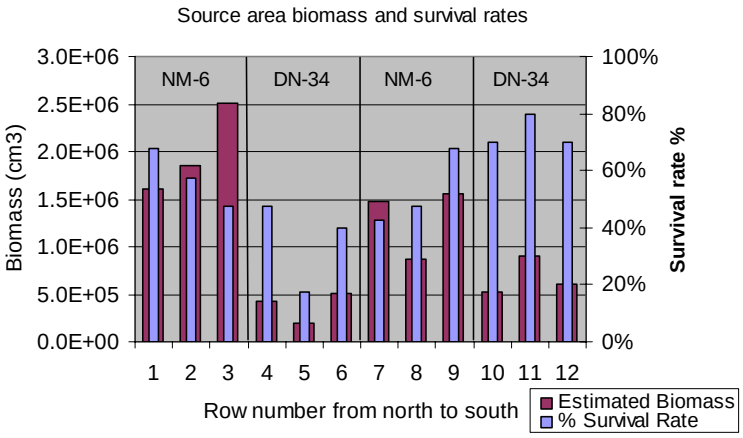

Figure 4. Estimated biomass production and survival rates in source area by row designation.

Groundwater Chemistry Results

Monitoring well locations are shown on Figure 1 and dinoseb concentrations in groundwater are summarized in Table 1. Six-year trends are also displayed in Figures 5 through 7. Dinoseb concentrations varied considerably in some wells during the four sampling rounds. Variability is expected, especially in very shallow wells subject to influence from infiltrating precipitation carrying dinoseb from contaminated soils to the water table. In addition, disturbance of contaminated soils associated with removal of buried containers probably resulted in increased concentrations of dissolved contaminants or “slugs” of dissolved dinoseb being carried past monitoring wells. It is likely that chemical handling and disposal practices along with cleanup efforts resulted in heterogeneous distribution of dinoseb in the subsoil. Dinoseb has an estimated octanol/soil organic carbon partition coefficient of 1250 (Michigan Dept. of Environmental Quality) which puts it in a category of highly sorbed. This estimation is

dependant upon soil characteristics and somewhat dependant upon contaminant concentration. The high K_{oc} may serve to explain some of the great variation in dinoseb concentrations throughout the season. Monitoring well concentrations may vary depending upon large rainfall events that flush dinoseb from soil and into the saturated zone.

Table 1. Groundwater Chemistry Summary

	Monitoring Well	Oct. 04	May 05	Oct. 05	May 06	6-year avg.[1]
CONTROL PLOT	MW-1ABC	<5.0	<5.0	<5.0	<5.0	<5.0
	MW-2ABC	<5.0	<5.0	<5.0	<5.0	<5.0
UPGRADIENT	MW-3	589	126	57	41	400
	MW-10	511	655	1409	2967	1071
	MW-11	76	364	31	99	1314
MID-PLOT	MW-4AB	1498	2717	2004	996	671
	MW-4P 12' bgs	<5.0	18.7	10.3	16.4	8.0
	MW-8	<5.0	<5.0	<5.0	<5.0	29
	MW-9ABC	23.1	6.8	309	205	178
	MW-12AB	<5.0	2.1	9.5	3.5	8.6
DOWNGRADIENT	MW-5ABC	31.3	42.1	15.9	111.0	117
	MW-5P 17' bgs	<5.0	11.5	<5.0	<5.0	<5.0
	MW-6	<5.0	<5.0	56	180	122
	MW-7	<5.0	<5.0	22.5	53.4	20
DOWNGRADIENT (OFF SITE)	DP-1	<5.0	<5.0	no water	<5.0	16.8
	DP-1P 17' bgs	<5.0	<5.0	<5.0	<5.0	372
	DP-1PP 22' bgs	<5.0	<5.0	<5.0	<5.0	<5.0
	DP-1PPP 25' bgs	<5.0	<5.0	<5.0	<5.0	<5.0

All values as parts per billion (ug/L).

Samples taken from wells with "ABC" designation were taken at water table.

1. Averages of values <5.0 µg/L were calculated as 2.5 µg/L - (1/2 of the detection limit)

Contaminant concentration trends for a 6-year period are displayed in Figures 2 through 4. The upgradient wells display spikes suggesting slugs of dinoseb being released from the source area soil, probably associated with large rainfall events. Mid-site wells MW-4 and MW-9 display similar spikes, while MW-8 has consistently been below detection limits since October 2004. Downgradient wells (MW-5, 6, and 7) appear to be trending upwards with the last three samples increasing in dinoseb concentration. This is probably related to a slug of dinoseb migrating from the source area. Significantly, no dinoseb has been detected in downgradient off site wells for the past two years, suggesting that dinoseb has been immobilized within the plantation area.

Groundwater Elevation Data

Hydrogeologic response as groundwater elevation was monitored using AquaRods (Sequoia Scientific, Inc.) placed in observation wells MW-14, MW-15, and MW-16. Data has been collected seasonally since August 2001. Groundwater elevations were normalized for ease of comparison between wells; i.e., beginning AquaRod elevations were subtracted from subsequent

readings making zero the starting point for the recorded period. Readings were also normalized when data loggers were swapped between wells, and after data were downloaded. Normalized groundwater fluctuations for summer seasons of 2004, 2005 and 2006 are shown on Figures 8 through 10 as are daily totals for rainfall events. The water table fluctuated 807 mm, 334 mm and 774 mm during the 2004, 2005 and 2006 data collection periods, respectively. Quick rises in water table elevations corresponded to large rainfall events.

In August 2002 water table elevation data for MW-14 indicated a possible diurnal groundwater elevation fluctuation of up to 8 mm (Figure 11). These fluctuations were not observed in the other monitoring wells in successive years. This is believed to be the result of rapidly fluctuating water table elevations due to extensive regional pumping combined with rainfall events. Since August 2002 the water table has not had more than one recorded day where the water table was not rising or falling quickly. The water table was observed to drop in steps as the water dropped due to pumping, with the steepest steps occurring during the day and flattening at night. However, this might not have been caused by the trees, although the background well (MW-16) did not show the same step function.

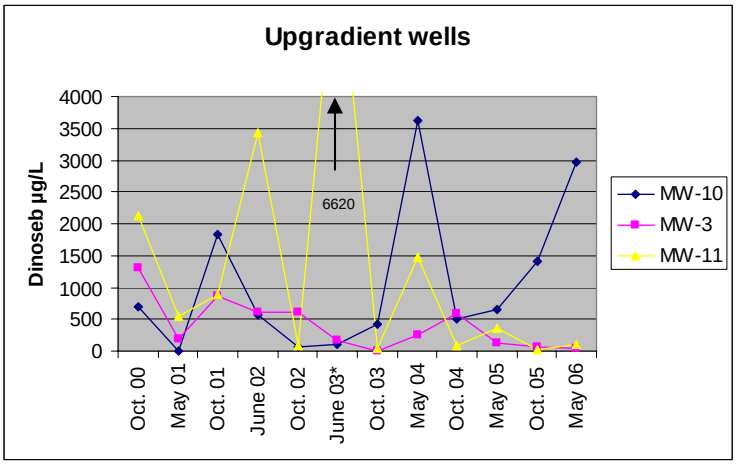

Figure 5. Dinoseb concentrations in upgradient wells for a 6-year period.

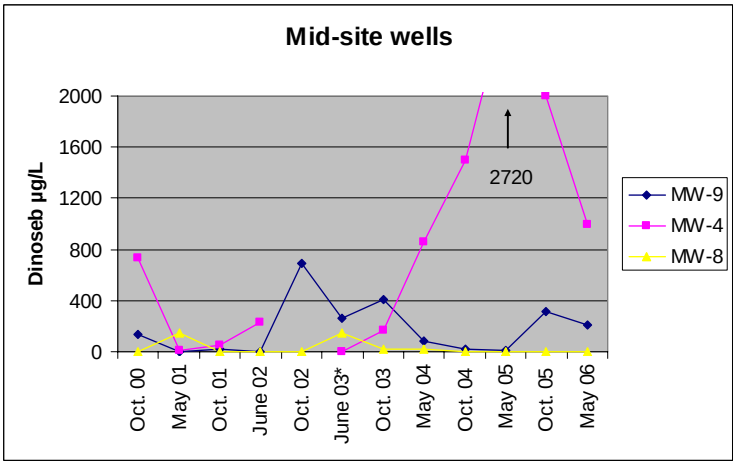

Figure 6. Dinoseb concentrations in mid-site wells for a 6-year period.

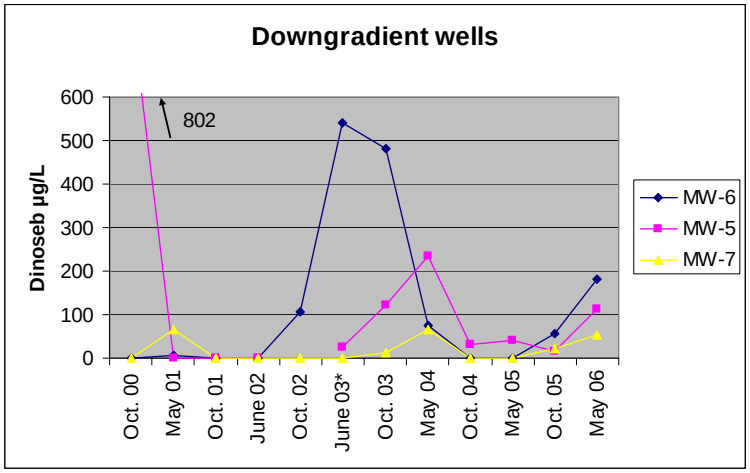

Figure 7. Dinoseb concentrations in downgradient well for a 6-year period.

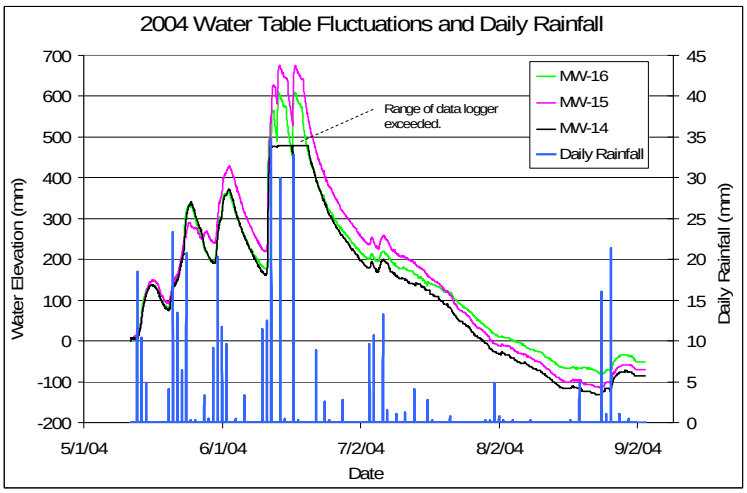

Figure 8. 2004 water table fluctuations and daily rainfall.

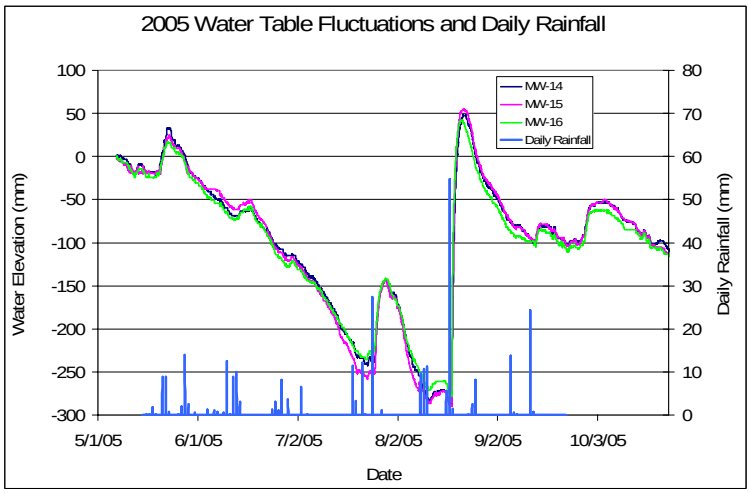

Figure 9. 2005 Water table fluctuations and daily rainfall.

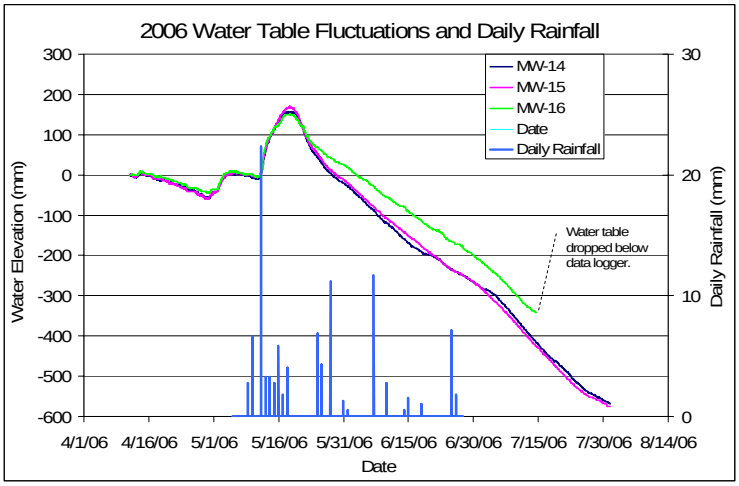

Figure 10. 2006 Water table fluctuations and daily rainfall.

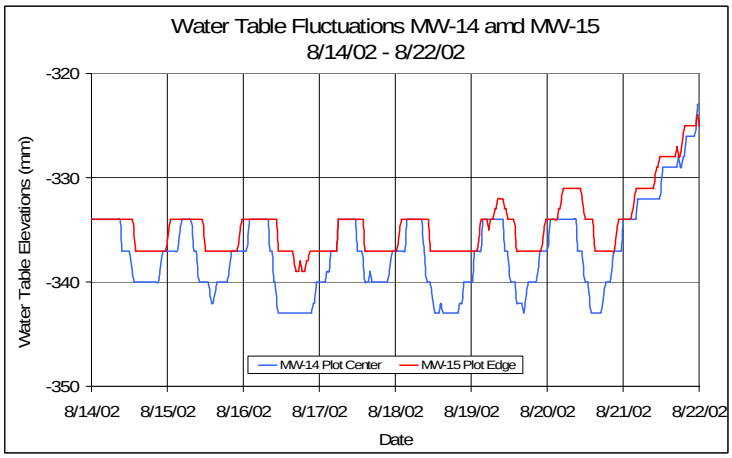

Figure 11. 2002 diurnal water table fluctuations due to influence from trees.

CONCLUSIONS AND RECOMMENDATIONS

There were no significant differences in mortality between the NM-6 and DN-34 hybrid poplars within the source area, however, the NM-6 clone produce 3 times more biomass than the DN-34. There were significant differences between the mortality rates from the source area and the downgradient area. This may be due to toxins in the soil and/or groundwater, or disturbance of the soil from the excavation of buried containers that stripped the topsoil of its water holding capacity and nutrients.

Large variations in dinoseb concentrations were observed in most monitoring wells. The cause for this variability is likely associated with the chemical properties of dinoseb and with seasonal and event-based fluctuations in water elevations and precipitation infiltration rates. Any apparent trends in downgradient monitoring wells must be viewed with caution as other trends have been reversed in other wells on frequent occasion.

Despite high hydraulic conductivity, the groundwater velocity at the site is quite low due to the low groundwater gradient. This low velocity will reduce mass migration rates of contaminants

out of the treatment area and possibly lead to increased degradation of contaminants as the trees mature.

Research has shown (9) that a phytoremediation site planted with eastern cottonwoods (*Populus deltoides*) provided enough dissolved organic carbon to a shallow (<3m) aquifer to lower dissolved oxygen concentrations, consequently providing conditions for in situ reductive dechlorination of trichloroethene. Dinoseb is known to degrade readily in anoxic conditions. An evaluation of oxygen in the saturated and unsaturated zones should be conducted to determine whether the lack of oxygen is leading to degradation of dinoseb. Conceptually, it may be possible that the tree roots "chase" the falling water table in the summer, then die back and decompose when water levels rebound. Does this decomposition deplete oxygen levels enough to initiate conditions favorable to the breakdown of dinoseb?

Rapidly dropping water table elevations due to regional pumping compromised our ability to evaluate diurnal water table fluctuations. An aquifer unexposed to dramatic drawdown might lead to a more conclusive observation of poplar transpiration having a direct affect on daily water table elevations.

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