

Effects of dredging an agricultural drainage ditch on water column herbicide concentration, as predicted by fluvarium techniques

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Abstract: In artificially drained agricultural areas, dredging of drainage ditches is often necessary to ensure adequate field drainage. Stream-simulator (fluvarium) experiments were performed to evaluate the potential of associated bed material changes to impact water column concentrations of atrazine, metolachlor, and glyphosate. In the first experiments, water having high herbicide concentrations flowed across bed sediment collected from a ditch immediately before or after dredging. Afterward, water having initially zero herbicide concentrations flowed across these sediments. Results indicate that the bed sediments remaining after dredging, which had coarser texture and lower organic matter, may contribute to overall higher water herbicide levels in the short term by removing significantly less glyphosate from contaminated water and contributing marginally higher sustained levels of herbicide to uncontaminated water, applicable where sediments exhibit similar dredging characteristic effects. In this case, dredging when herbicide levels are expected to be lowest can help minimize increased transport of some herbicides.

Key words: atrazine—drainage ditch—glyphosate—metolachlor—water quality

Much of the fertile Midwest is artificially drained by a network of subsurface drainage tile (usually located about 1 m [3.3 ft] deep) into drainage ditches and then conveyed to natural waterways. This tile drainage enables producers to farm productive land which would otherwise be too wet. Over time, sediments deposited by field drainage water (through tile or by surface runoff) into ditches become inhibitory to effective field drainage by decreasing channel capacity and eventually eliminating vertical drop from tile outlets. When this occurs, ditches, which are maintained at the county level, are generally dredged to restore drainage efficiency, but the effects of ditch dredging on herbicide transport and water quality are largely unknown.

The herbicides atrazine [2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine] (trade names AAtrex, Bicep II Magnum (with metolachlor), and others), metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-

N-(2-methoxy-1-methylethyl) acetamide] (trade names Dual, Bicep II Magnum (with atrazine), and others), and glyphosate [N-(phosphonomethyl)glycine] (trade names Accord, Roundup, and others) are widely used in the study area, where corn (*Zea mays*) and soybean (*Glycine max*) annual rotation is common.

Herbicide sorption in general occurs by many processes and the relative importance of these is the subject of some debate. These include reversible processes, such as hydrogen bonding, hydrophobic partitioning, and dipolar interaction (Welhouse and Bleam 1993) and irreversible processes such as chemical adsorption and electron transfer (Senesi and Testini 1982). Soil/sediment characteristics governing these processes and their expected impacts on water column atrazine, metolachlor, and glyphosate concentrations are given in table 1.

Atrazine is highly persistent and moderately mobile in the environment, moderately

soluble, and weakly sorbed by soil particles. Atrazine sorption has been found to be influenced by soil pH, organic matter (OM), cation exchange capacity (CEC), iron (Fe) (Singh et al. 1998), exchangeable aluminum (Al) (Johnson and Sims 1998), particle size distribution (Kruger et al. 1996; Zheng and Cooper 1996; Johnson and Sims 1998), and humic matter content (Dousset et al. 1994). Atrazine breakdown is dominated by chemical hydrolysis followed by biodegradation. Adsorption of atrazine occurs to some extent as a reversible process (Gilchrist et al. 1993; Moreau and Mouvet 1997) and in aquatic systems is associated primarily with bed sediments (Apte and Rogers 1993).

Metolachlor is moderately persistent and mobile in the soil environment and is highly persistent in water. It is slightly soluble and moderately sorbed, depending on OM (Weber et al. 2003; Sanyal and Kulshrestha 2004), pH (Wood et al. 1987) and clay content (Weber et al. 2003). Metolachlor degradation may be enhanced in the presence of zerovalent Fe and Al as $Al_2(SO_4)_3$ (Shea et al. 2004) but occurs primarily by aerobic and anaerobic biodegradation processes. Metolachlor sorption occurs to some extent as a reversible process (Pignatello and Huang 1991), and metolachlor has been found to accumulate in bed sediments (Osano et al. 2004).

Glyphosate is moderately persistent in soils, and although highly soluble, is relatively immobile in the environment due to its strong sorption. Glyphosate sorption has been found to be influenced by soil type (Gimsing and Borggaard 2002; Strange-Hansen et al. 2003), OM content (LaFleur 1979; Day et al. 1997), pH (Eberbach 1998; Day et al. 1997; Jonge and Jonge 1999), phosphorus (P) concentration (Jonge and Jonge 1999; Jonge et al. 2001; Prata et al. 2003), temperature (Eberbach 1999) and Fe and Al concentrations (Jonge et al. 2001; Gimsing and Borggaard 2002). Glyphosate sorption is a reversible process (Sprankle et al. 1975), and in aquatic systems is associated primarily with bottom sediments (Feng et al. 1990). Glyphosate is primarily broken down by biodegradation.

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Table 1

Particle size distribution, organic matter content, Mehlich 3-extractable Fe, Al, and P concentrations, and pH of bed material collected from drainage ditches prior to dredging (pre-dredge) and after dredging (dredged), and expected impact on water column herbicide concentrations.

Sediment property	Pre-dredge	Dredged	Expected impact of higher value on water column herbicide concentration		
			Atrazine	Metolachlor	Glyphosate
Sand	57.9%	80.4%	+	+	
Silt	17.1%	3.0%			
Clay	20.1%	14.6%	-	-	-
Organic matter	4.9%	2.0%	-	-	-
Al (mg kg ⁻¹)	313	90	-	-	-
Fe (mg kg ⁻¹)	2180	1190	-	-	-
Phosphorus (mg kg ⁻¹)	151	118			+
pH	6.9	7.2	+	+	+

Elevated levels of herbicides have been observed in Midwest streams (Battaglin et al. 2003). It is therefore important to manage the drainage ditch systems which feed streams in a manner that maximizes herbicide removal from the water column within the ditches and minimizes herbicide release. The primary objective of this research was to evaluate the effects of ditch dredging on flowing water column herbicide concentrations.

Materials and Methods

The St. Joseph River Watershed, which is primarily agricultural (79%) and drains 280,852 ha (693,462 ac) of land in northeast Indiana, northwest Ohio, and south central Michigan, serves as the drinking water source for over 200,000 residents of Fort Wayne, Indiana. The sub-basins upstream from Fort Wayne's Three Rivers Filtration Plant are largely artificially drained corn and soybean cropland. Drainage patterns along with herbicide use in this area lead to elevated herbicide levels in the system of agricultural drainage ditches that supply water to the Three Rivers Filtration Plant. These levels are often above the maximum contaminant level (MCL) allowed in municipal drinking water by the United States Environmental Protection Agency (USEPA) for atrazine (3 µg L⁻¹). The MCL for glyphosate is 700 µg L⁻¹, while none has been established for metolachlor as yet. Despite efforts to reduce herbicide loading to drainage ditches using on-farm best management practices, herbicide levels during the early growing season frequently remain elevated.

The study ditch is tile-fed and drains approximately 1,400 ha (3,460 ac) of largely agricultural land (83%) directly into Cedar Creek. The pre-

dominant soils in this sub-watershed include Blount silt loam (fine, illitic, mesic, Aeric Epiaqualfs), Pewamo silty clay (fine, mixed, active, mesic Typic Argiaquolls), and Glynwood loam (fine, illitic, mesic Aquic Hapludalfs). Prior to the study, the ditch was last dredged in 1996. Due to loss in drainage efficiency, the ditch was again dredged in 2004, resulting in the removal of the upper 30 cm (12 in) of bed material.

Ditch bed material was collected from the 0 to 5 cm (0 to 2 in) depth, immediately before dredging (hereafter referred to as pre-dredge) and immediately after dredging (hereafter referred to as dredged) for fluvium experimental procedures described by Smith and Pappas (2007). Pre-dredge materials were sampled approximately 10 m (33 ft) upstream from dredged materials. Pre-dredge and dredged bed materials were loaded to a depth of 3 to 3.5 cm (1.2 to 1.4 in) into separate rills of the fluvium. Each rill was 8 m (26 ft) long by 0.2 m (0.66 ft) wide by 0.2 m (0.66 ft) deep. Water was continuously re-circulated over the bed material within each rill separately at a rate of 10 L min⁻¹ (2.6 gal min⁻¹). This flow rate maintained a water depth of approximately 2.5 cm (1.0 in). Total water volume in each rill system including head water re-circulating tank storage was 282 L (74.5 gal). Prior to experiments, herbicide-free water was circulated over sediments and sampled hourly for 48 hours to detect effects of initial sediment herbicide concentrations. Atrazine and glyphosate were generally not detected in the water column during this phase, while "initial" metolachlor concentrations averaged 2.7 and 2.1 µg L⁻¹ for pre-dredge and dredged sediments, respectively.

For the first set of experiments, hereafter referred to as "herbicide-spiked" experiments, fluvium water was spiked to initial concentrations of 30 µg L⁻¹ atrazine and 23.7 µg L⁻¹ metolachlor as Bicep II Magnum and separately, 2,000 µg L⁻¹ glyphosate as Roundup. Water samples were collected every 2 hours by automatic sampler. Following 24 hours of sampling, fluvium water was drained by gravity and then replaced with contaminant-free water for "clean-water" experiments. Water samples were then collected hourly for 48 hours, beginning at time = 10 minutes. All samples were filtered (0.45 µm [17.7 microns]) into glass vials and frozen immediately until analysis could be performed. Atrazine and metolachlor were preconcentrated by solid-phase microextraction according to a modified USEPA method 525.2 described by Tugulea et al. (1998) (detection limit = 2 µg L⁻¹), and quantified by gas chromatography with mass spectrometry. Glyphosate was quantified by high performance liquid chromatography with post-column derivitization and fluorescence detection, according to USEPA method 547 (USEPA 1990).

All data represent the average of two fluvium runs as in experiments by Smith et al. (2006). Regression equations were fit to water column herbicide concentration data vs time using JMP 5.1 (SAS Institute Inc., Cary, North Carolina). Herbicide concentrations tended to decrease according to a logarithmic decay during herbicide-spiked experiments, and increase logarithmically as a function of time during clean-water experiments. Prediction confidence limits ($\alpha = 0.05$) were calculated using JMP 5.1 and regression equations were considered significantly different when confidence intervals were exclusive. Assuming a maximum pore space not drained by gravity of up to 50%, up to 26.5 L (7 gal) of water may have carried over from the herbicide-spiked experiments to the clean-water experiments in each rill. Since the total water volume in each rill system was 282 L (74.5 gal), this represents less than 10% of the total water volume. The effect of carryover on observed clean-water concentrations were calculated individually, by assuming that this volume was occupied by water having the final concentration from the previous herbicide-spiked experiments.

Results and Discussion

Atrazine concentrations in the water column did not correlate significantly with time during herbicide-spiked experiments for either the pre-dredge ($r^2 = 0.40$, $P = 0.13$) or dredged ($r^2 = 0.16$, $P = 0.60$) bed material (figure 1), and water-column atrazine concentration did not consistently increase or decrease over time. This was not surprising, considering the high persistence and weak sorption properties of atrazine. Average atrazine concentrations over the duration of the herbicide-spiked experiments were 22.1 and 20.7 $\mu\text{g L}^{-1}$ for pre-dredge and dredged rills, respectively, representing approximately seven times the MCL of 3 $\mu\text{g L}^{-1}$.

During clean-water experiments, initially observed atrazine levels were 2.8 to 3.0 $\mu\text{g L}^{-1}$ (figure 2). Given the final atrazine concentrations of 19.5 and 21.6 $\mu\text{g L}^{-1}$ for pre-dredge and dredged sediments respectively, this could have accounted for initial clean-water experiment concentrations of up to 2 $\mu\text{g L}^{-1}$ due to carryover.

Release of atrazine to the water column was correlated with time (pre-dredge: $r^2 = 0.67$, $P < 0.01$; dredged: $r^2 = 0.77$, $P < 0.001$) and appeared to occur at a greater rate initially from the pre-dredge bed material than the dredged bed material. However, by time = 20 hours, this trend reversed, and generally higher water column atrazine concentrations were observed from dredged sediments. Confidence intervals for pre-dredge and dredged kinetics were largely overlapping (figure 2) but were exclusive from time = 2 to 10 hours. This indicates that atrazine kinetics during this time interval were significantly different between dredging treatments. Since the dredged sediment had lower clay, OM, and Al content, and higher pH, atrazine sorption to dredged sediment would not be expected to have been as strong as sorption to pre-dredge sediment (table 1). Despite the slower release rate of atrazine to the water column, the dredged bed material could result in higher overall atrazine losses due to marginally higher concentrations observed over longer periods of time. Regression equations suggest that dredged water column concentrations would be higher than pre-dredge in the longer term. However, confidence limits do not indicate that this effect was significant during the time window observed (10 minutes to 48 hours).

Figure 1

Water column atrazine concentrations as a function of time during herbicide-spiked experiments, using bed material collected prior to dredging (pre-dredge) and after dredging (dredged).

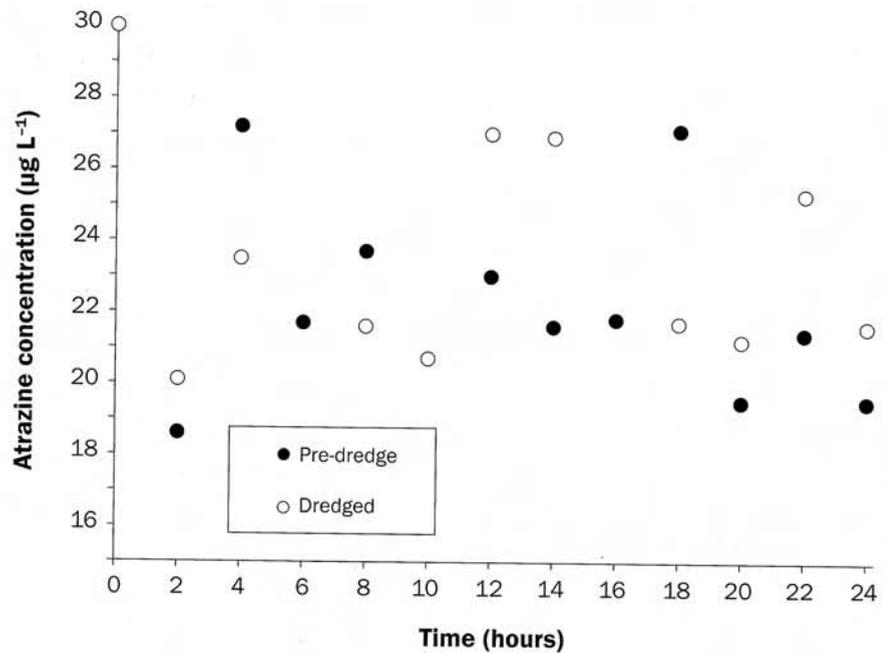
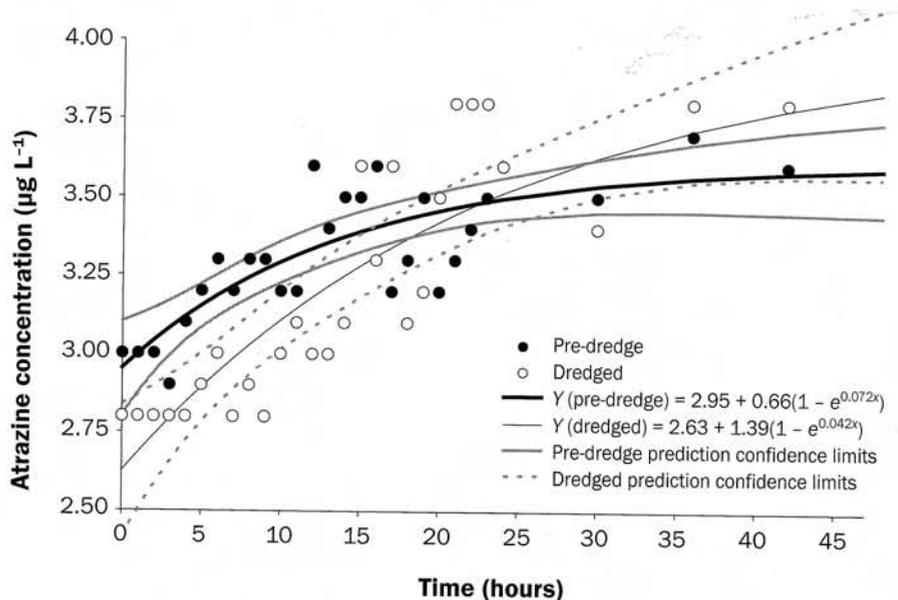


Figure 2

Water column atrazine concentrations as a function of time during clean-water experiments, using bed material collected prior to dredging (pre-dredge) and after dredging (dredged).



Under base-flow conditions, water in the study ditch moves at an average of approximately 0.05 m sec^{-1} (0.16 ft sec^{-1}), as measured by area-velocity meters on 10-minute intervals over the 2005 and 2006 growing seasons. Given the length of the

ditch that was dredged of 13.7 km (8.5 mi), it could take as long as 76 hours for water to reach the confluence of this ditch with Cedar Creek. Measured atrazine concentrations in the study ditch have been observed as high as $122 \mu\text{g L}^{-1}$ associated with runoff events, and levels above $30 \mu\text{g L}^{-1}$ have been observed persisting over a 24-hour duration. Assuming that the clean-water regression equations from fluvium experiments accurately describe atrazine sediment-water dynamics over this period of time at the ditch scale, and water entering the study ditch immediately following such a high-atrazine runoff event was atrazine-free, the concentrations of atrazine in water exiting this ditch section after 76 hours would be $3.6 \mu\text{g L}^{-1}$ if the ditch had not been dredged, or $4.0 \mu\text{g L}^{-1}$ if it had been dredged. This result suggests that impacts of best management practices (BMPs) reducing off-field atrazine losses to zero would not result in atrazine concentrations below the MCL of $3 \mu\text{g L}^{-1}$ at the ditch outlet for some period of time following implementation, regardless of whether the ditch had been dredged. This benefit-dampening effect was previously observed in a study by Shulka and associates where BMP implementation resulted in a 94% and 91% respective reduction in atrazine and metolachlor entering a stream system. Atrazine and metolachlor concentrations at the outlet of the stream system were reduced by only 52% and 78% respectively during the 7 years following herbicide input reduction (Shulka et al. 2001). It is expected that more sediment-bound pollutant would enter the water column as the initial water column concentrations of that pollutant decrease. Sediment-bound pollutants become increasingly mobile to a water column having decreasing concentrations of that pollutant.

During herbicide-spiked experiments, water column concentrations of metolachlor decreased with time when exposed to both pre-dredge and dredged bed material (pre-dredge: $r^2 = 0.69$, $P < 0.01$; dredged: $r^2 = 0.68$, $P < 0.05$) (figure 3). However, at no time were prediction confidence intervals exclusive. Therefore, no significant treatment effect was observed. The regression equations describing how this occurred are valid from 2 to 24 hours and do not describe rapid initial sorption dynamics. Like atrazine, metolachlor is highly persistent in water, but metolachlor is moderately sorbed, so it was expected that concentrations would

Figure 3
Water column metolachlor concentrations as a function of time during herbicide-spiked experiments, using bed material collected prior to dredging (pre-dredge) and after dredging (dredged).

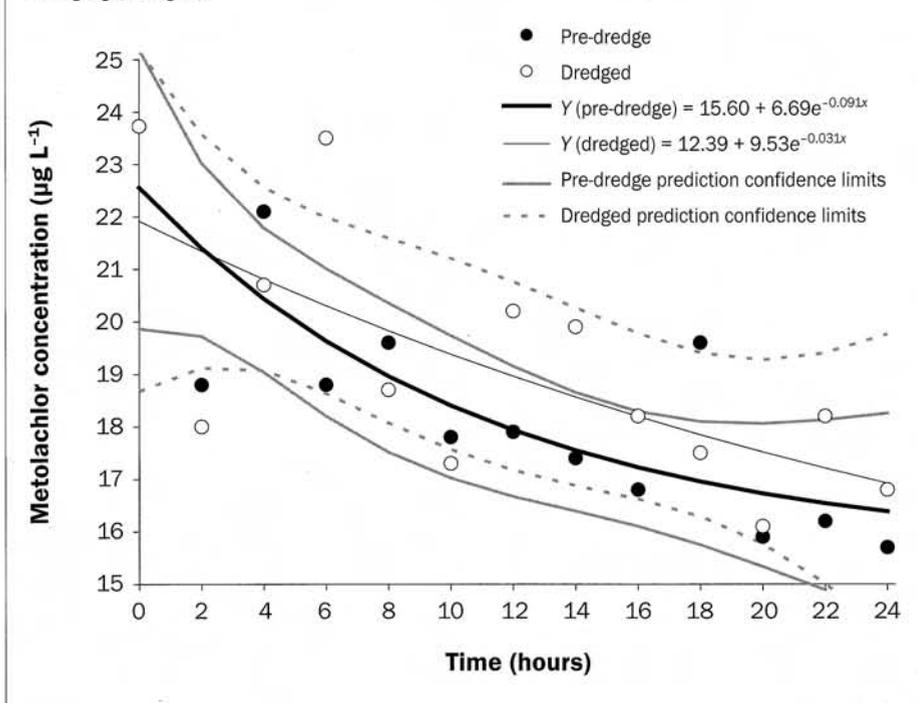
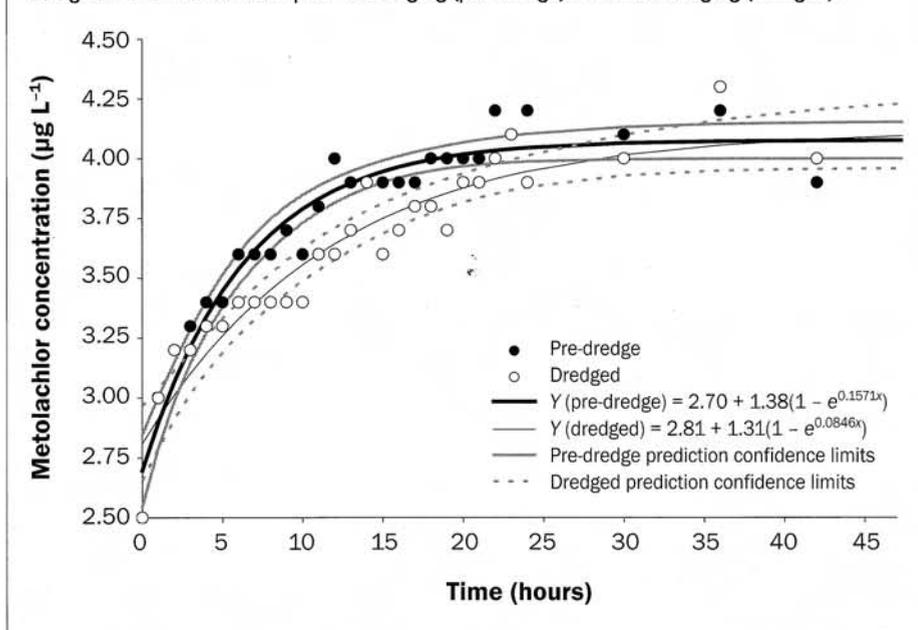


Figure 4
Water column metolachlor concentrations as a function of time during clean-water experiments, using bed material collected prior to dredging (pre-dredge) and after dredging (dredged).



decrease somewhat over time when exposed to sediments. Water column metolachlor concentrations generally decreased slightly more rapidly when exposed to pre-dredge

sediments than dredged sediments. This can be explained by the higher clay and OM contents and lower pH of the pre-dredge sediments, which would positively impact

metolachlor sorption. Additionally, since dredging impacts bed sediment biota (Koel and Stevenson 2002), and metolachlor is broken down primarily by biotic processes, differences in water column metolachlor concentration may have been further impacted by the removal of biomass which occurred during dredging.

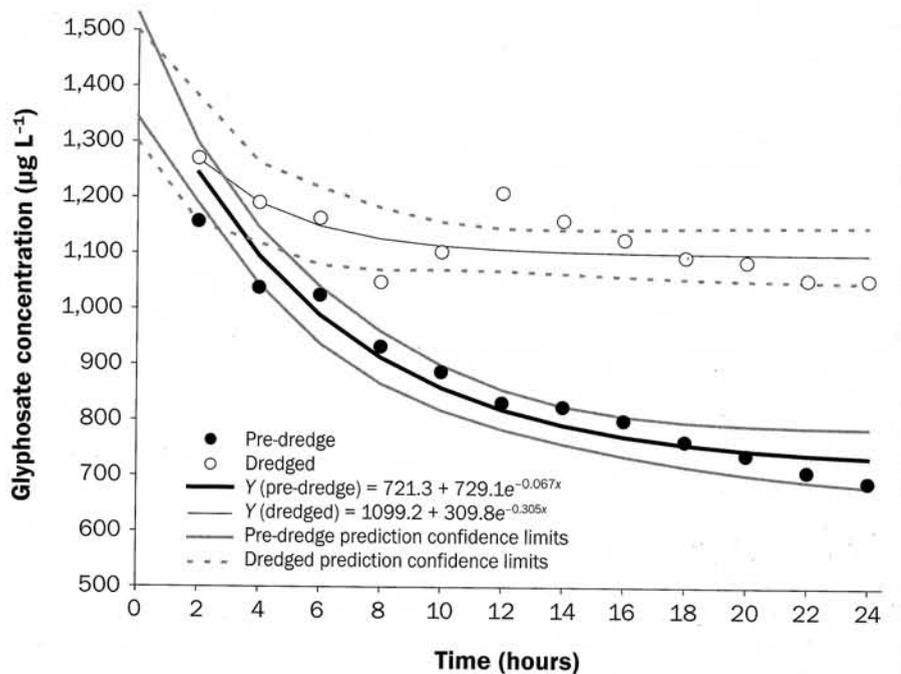
Water column metolachlor concentration patterns were correlated with time during clean-water experiments (pre-dredge: $r^2 = 0.50$, $P < 0.0001$; dredged: $r^2 = 0.38$, $P < 0.0001$) and were similar for pre-dredge and dredged sediments, although water column concentrations tended to be higher for pre-dredge than dredged during the first 30 hours (figure 4). In fact, prediction confidence intervals were exclusive from time = 4 to 21 hours, with pre-dredge sediments yielding higher predicted metolachlor concentrations than dredged. This result may be due in part to higher overall metolachlor levels in pre-dredge sediment resulting from more complete metolachlor sorption by reversible process during the previous herbicide-spiked phase of the experiment. Water column metolachlor concentrations at time = 10 minutes were 2.9 and 3.1 $\mu\text{g L}^{-1}$ for pre-dredge and dredged sediments respectively, indicating a rapid initial release during 0 to 10 minutes, and/or initial contamination due to incomplete removal of pore space water between herbicide-spiked and clean-water experiments. Considering the final metolachlor concentrations from the herbicide-spiked experiments of 15.7 and 16.8 $\mu\text{g L}^{-1}$, for pre-dredge and dredged sediments respectively, there could have been metolachlor carryover resulting in initial clean-water concentrations of up to 1.6 $\mu\text{g L}^{-1}$.

Currently, no MCL has been set by the USEPA for metolachlor, although the lifetime metolachlor non-cancer health advisory level for a 70 kg (154 lb) adult is 70 $\mu\text{g L}^{-1}$ (USEPA 1999). Actual metolachlor concentrations observed in the study ditch were typically well below this level.

Water column glyphosate concentrations were well correlated with time for both pre-dredge ($r^2 = 0.89$, $P < 0.0001$) and dredged ($r^2 = 0.92$, $P < 0.05$) rills during herbicide-spiked experiments. Concentrations dropped dramatically during the first sampling period (0 to 2 hours) (figure 5), from a calculated initial concentration of 2,000 $\mu\text{g L}^{-1}$ to measured 1,270 and 1,157 $\mu\text{g L}^{-1}$ 2-hour

Figure 5

Water column glyphosate concentrations as a function of time during herbicide-spiked experiments, using bed material collected prior to dredging (pre-dredge) and after dredging (dredged).



concentrations for dredged and pre-dredge sediments, respectively. Corresponding concentrations after 24 hours were 1,054 and 690 $\mu\text{g L}^{-1}$, suggesting more rapid glyphosate sorption to pre-dredge sediments than dredged. Prediction confidence intervals were exclusive when time ≥ 5 hours. This significant treatment effect was anticipated due to the strong sorption properties of glyphosate and the characteristic differences between dredged and pre-dredged sediment. Pre-dredge bed material had higher clay, OM, Fe, and Al contents and lower pH which would have influenced glyphosate sorption positively (table 1). The higher P concentration of the pre-dredge sediment was expected to have negatively influenced glyphosate sorption, but this effect was apparently offset by the positive effects of higher clay, OM, Fe, and Al contents. The potential for treatment differences in water column glyphosate concentration trends to have been additionally influenced by biotic differences between pre-dredge and dredged sediments is high, since glyphosate breakdown occurs primarily as biodegradation. Glyphosate levels in the study ditch have not been observed above 50 $\mu\text{g L}^{-1}$. However, edge of field losses in the area have been observed as high as 1,927 $\mu\text{g L}^{-1}$ during early

season runoff events.

During clean-water experiments, glyphosate concentrations were well correlated with time (pre-dredge: $r^2 = 0.94$, $P < 0.0001$; dredged: $r^2 = 0.97$, $P < 0.0001$). Initial glyphosate concentrations were higher for dredged than for pre-dredge sediments, but maximum carryover concentrations were estimated to be as high as 65 $\mu\text{g L}^{-1}$ in pre-dredge rills and 99 $\mu\text{g L}^{-1}$ in dredged rills. Therefore, this entire difference may be attributable to potential differences in initial concentration due to pore water retention and carryover. However, initial glyphosate release during the first 10 minutes may also have been more rapid for dredged sediment than for pre-dredge sediment due to more complete sorption by dredged sediments during the previous herbicide-spiked experiments. This likely resulted in higher initial clean-water sediment glyphosate concentrations. The highest concentration observed was 70 $\mu\text{g L}^{-1}$, approximately 10% of the glyphosate MCL, and apparent equilibrium concentrations were reached within 24 hours. Prediction confidence intervals were always exclusive, but this appeared to be largely due to the intercept parameter representing initial concentration. Since glyphosate sorption is competitive with P (Prata et al.

2003), glyphosate adsorption and desorption would be expected to follow a similar trend as P adsorption and desorption in similar material. In another fluvium study, water column P concentration changes during adsorption and desorption are described as a function of time (Smith and Pappas 2007). Pre-dredge sediments were found to adsorb P more quickly and desorb P more slowly than dredged sediments. Authors attributed dredging effects to changes in particle size distribution, Al and Fe concentrations, and biological activity.

Summary and Conclusions

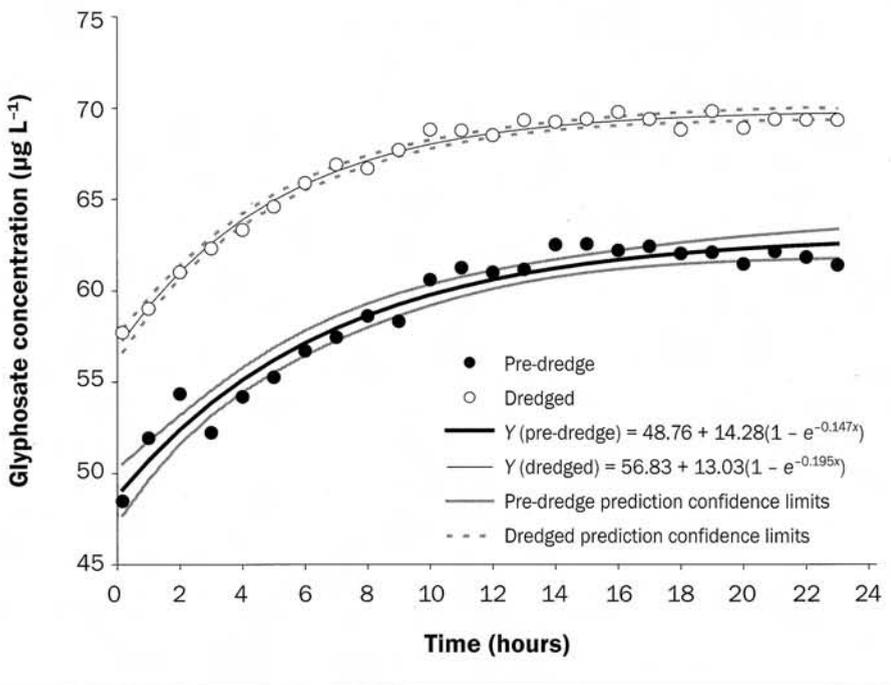
Dredging of drainage ditches in the mid-western United States is necessary to ensure efficient drainage and farmability of fertile land. However, this practice may lead to higher water column concentrations of some locally used herbicides, depending on sediment characteristic changes associated with dredging. In our case, dredging exposed sediment having most notably coarser particle size distribution and lower OM, Al, and Fe contents. Results of this study are applicable to cases where dredging impacts to sediment characteristics are similar.

In fluvium experiments, spiked water column atrazine levels did not drop significantly with time when exposed to pre-dredge or dredged sediments. Metolachlor levels did drop significantly with time. However, the regression equations describing how metolachlor concentrations decreased when exposed to pre-dredge or dredged sediments were generally not different from one another within confidence limits ($\alpha = 0.05$) over the time window observed. Water column glyphosate concentrations decreased more rapidly when exposed to pre-dredge sediments than dredged sediments. This difference was significant when time since initial exposure was greater than five hours.

When "clean" water flowed over sediments previously exposed to herbicide-laden water, regression equations describing atrazine and metolachlor release to the water column suggested that sustained levels of both herbicides would be higher in the longer term. However, this effect was not significant over the time window observed (10 minutes to 48 hours). Water column glyphosate concentrations appeared to reach equilibrium quickly when exposed to herbicide-laden sediment (14 hours). Glyphosate levels in initially "clean" water were found

Figure 6

Water column glyphosate concentrations as a function of time during clean-water experiments, using bed material collected prior to dredging (pre-dredge) and after dredging (dredged).



to be significantly higher from dredged than from pre-dredge sediments from the first observation (time = 10 minutes) to the end of the observation window (24 hours).

Since herbicide concentrations in water entering ditches have been observed above safe drinking water levels and contaminated ditch bed sediments have the potential to impart herbicides to initially uncontaminated water in excess of the safe drinking water limit, it is important to manage drainage ditches with herbicide transport minimization in mind. Ditch managers may minimize the short term negative impacts of ditch maintenance to herbicide water quality by avoiding dredging activities during and immediately before periods when herbicide application and off-field transport are expected to be high: immediately before, during, or immediately after herbicide application. It may be particularly beneficial for ditch managers to work with producers to avoid overlapping dredging activities with herbicide application or high herbicide loss periods.

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