Image caption: On-farm water storage pond. Photo from Mississippi State Extension.

Herbicide Mitigation Potential of Tailwater Recovery Systems in the Cache River Critical Groundwater Area [updated from 2018]

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Abstract: This study initiated an herbicide monitoring record (April 2017 through March 2018) for seven Arkansas tailwater recovery systems. Four herbicides (clomazone, glyphosate, metolachlor, and quinclorac) were readily detectable and peaked seasonally, reflecting interplay of application timing and precipitation. Clomazone and quinclorac, common spring-applied rice herbicides, were elevated in spring (Apr il 1 through June 15) and summer (June 16 through September 15). Metolachlor was elevated in summer only, reflecting mid-season applications to soybean acres. Glyphosate concentrations peaked in summer, but were also elevated in spring and fall (Septempber 16 through December 15), reflecting frequent, broad spectrum glyphosate use. Herbicide concentrations were otherwise low in off-season months and mostly below detection. During the growing season, clomazone, glyphosate, and quinclorac concentrations were higher in ditches than in the linked reservoir. Metolachlor concentrations were similar in magnitude between linked ditches and reservoirs. The observed spatial and temporal patterns in residual herbicide concentrations will inform best management practices for tailwater recovery systems to preserve Arkansas' water resources into the future. Recovered tailwater should be cycled through and sourced from the reservoir before reapplication to minimize the risk of sensitive crop exposure to residual herbicides. Artificial groundwater recharge strategies should source water from reservoirs and only during winter months to minimize the risk to groundwater. Further, the United States Geological Survey and others can use this dataset to improve models of herbicide fate and transport to include the mitigation potential of tailwater recovery systems to reduce herbicide loads from agricultural lands to the Mississippi River Basin.

Key Points:

- Select herbicide concentrations in on-farm reservoir - tailwater recovery systems were frequently detected during the growing season.
- The greatest herbicide concentrations were detected in drainage ditches during the growing season.
- Irrigation from on-farm reservoirs compared to ditches will minimize the risk of off-target cross-crop contamination.
- Strategies to use on-farm reservoir water for managed aquifer recharge should focus on non-growing season.

Introduction

Current agricultural groundwater usage rates in Arkansas are unsustainable, demonstrated by the drawdown of agriculturally important aquifers, such as the Mississippi River Valley Alluvial Aquifer, in recent decades (Konikow, 2013; Schrader, 2015; Reba et al., 2017). Continued groundwater decline is predicted as long as irrigation demand exceeds aquifer recharge (Reed, 2003; Clark et al., 2011; Clark et al., 2013). In addition to problems of water quantity, agricultural field runoff of sediment, nutrients and pesticides contributes to impaired surface water quality (USEPA, 2009). Herbicide usage in the Midsouth is anticipated to intensify in the age of herbicide-resistant weeds (Norsworthy et al., 2013; Riar et al., 2013), increasing the likelihood herbicide residues will be found in surface and ground waters. These water quality and quantity challenges will limit options for safe and appropriate water use in regions of intensive agriculture without effective water conservation strategies.

In areas with groundwater decline, such as the Cache River Critical Groundwater Area (CRCGA), agricultural producers have incorporated on-farm storage - tailwater recovery systems into their irrigation practices by constructing a network of ditches paired with a storage reservoir (Fugitt et al., 2011; Yaeger et al., 2017; Yaeger et al., 2018). Ditches capture field runoff, while reservoirs provide capacity to store tailwater and winter-spring precipitation long-term for an irrigation source during the growing season. The water-saving benefits of on-farm reservoirs have been established, potentially replacing 25-50% of groundwater irrigation (Sullivan and Delp, 2012). But, little is known about how these systems affect water quality in the surrounding landscape or about the persistence and accumulation of herbicides within them. Beyond the primary objective to reduce reliance on groundwater, on-farm storage - tailwater recovery systems offer the potential benefit of conserving water quality in adjacent surface waters by preventing off-site movement of nutrients, sediment, and herbicides through retention and transformation processes. Further, water stored in on-farm reservoirs has been proposed as a suitable water supply during the non-growing season for managed aquifer recharge (MAR) strategies (Reba et al., 2015; Reba et al., 2017). But these systems also pose potential risks of cross-crop impacts if residual herbicides are present at levels that could injure non-target crops when irrigation water is applied. Further, any MAR water supply source must meet water quality and human health safety standards, since enhanced groundwater recharge will enter a municipal water source.

The objective of this study was to initiate a herbicide monitoring data record for tailwater recovery systems located in the CRCGA (Figure 1). Data from this study can be

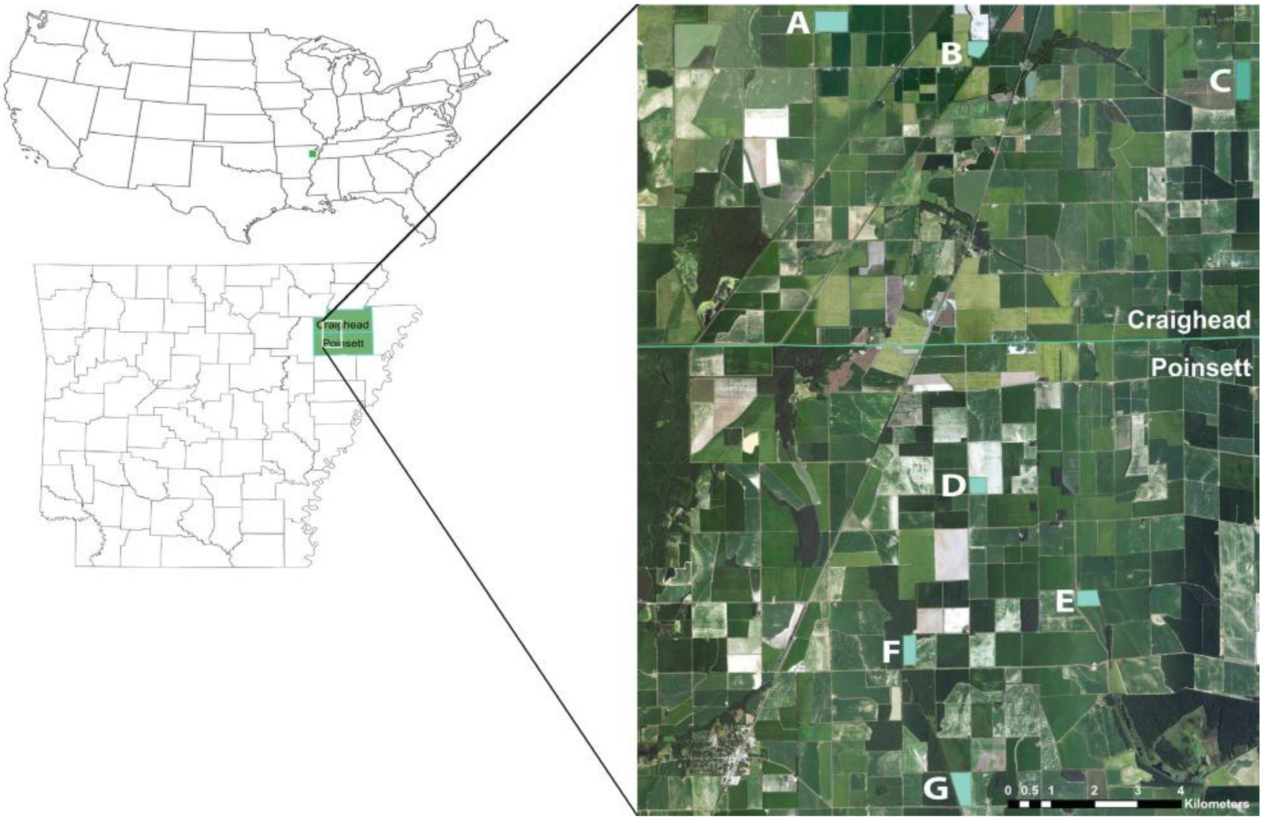

Figure 1. Sample location map of the seven monitored tailwater recovery systems (A-G) west of Crowley's Ridge in Poinsett and Craighead counties, Arkansas.

used to screen recovered tailwater for herbicide concentrations that could lead to cross-crop injuries during the growing season, characterize water quality in tailwater systems in terms of suitability for MAR, and estimate herbicide loads in tailwater recovery systems.

Methods

Seven tailwater systems were selected for herbicide monitoring from the CRCGA in Craighead and Poinsett counties west of Crowley's Ridge (Figure 1). Herbicide application records were collected from producers in early April 2017 and updated throughout the growing season. Based on these records, as well as regional frequency of use and anticipated future use, seven target herbicides were selected: 2,4-D, clomazone (e.g. Command®), dicamba (e.g. Clarity®), glyphosate (e.g. RoundUp®), metolachlor (e.g. Dual®), propanil (e.g. Stam®), and quinclorac (e.g. Facet®) (Table 1). Dicamba and 2,4-D were selected based on anticipated future use with the release of tolerant soybean and cotton cultivars.

Tailwater ditch and reservoir grab samples were collected weekly (April 2017 through March 2018) in high density polyethylene bottles. Samples were stored on ice and shipped overnight for processing by the Residue Lab at the University of Arkansas. Upon receipt, samples were stored at 4°C until filtration through a 0.45 µm nylon membrane within 48 hours. Filtered samples were preserved by freezing until analysis by high performance liquid chromatography with photodiode array detection (HPLC-DAD) following concentration by solid phase extraction (SPE) or by enzyme-linked immunosorbent assay with photometric detection (ELISA; glyphosate only). During SPE, samples were concentrated from 200 mL (aqueous) to 8 mL 50:50 acetonitrile:methanol using Strata-X reverse-phase polymer columns. Columns were conditioned with 10 mL 100% methanol, equilibrated with 0.5% phosphoric acid in ultrapure water, and rinsed with a 20% methanol and 0.5% phosphoric acid solution in ultrapure water prior to elution. Eluates were spiked with 100 mg/L metazachlor to a known concentration to correct for volumetric variability. Eluates were analyzed for concentrations of the target herbicides using HPLC-DAD with a mobile phase gradient of acetonitrile in 0.1% phosphoric acid ranging from 34-64% over 20 minutes. Herbicides were monitored at wavelengths maximizing each compound's absorption intensity (Table 1). Bulk water sample herbicide concentrations were calculated by multiplying the measured concentration in the eluate by the ratio of the eluate and beginning sample volumes after correcting eluate volume for differences in the measured and expected metazachlor concentration. Non-detections or concentrations estimated below reporting limits were censored at the appropriate reporting threshold (Table 1).

Median, mean, and standard deviation of herbicide concentrations were calculated seasonally for all sites combined. Seasons were defined as spring (SPR; March 16 through June 15), summer (SUM; June 16 through September 15), fall (FALL; September 16 through December 15), and winter (WIN; December 16 through March 15). Summary statistics were calculated for ditches and reservoirs across seasons and during the growing season (GS; March 16 through September 15) and off-season (OS; September 16 through March 15). Summary statistics were calculated using analyses adapted for censored datasets (Helsel, 2012). For datasets that were <50% censored, Kaplan Meier survival analysis was used, while robust regression order statistics were used for sites with ≥50-80% censored data. For sites with >80% censored observations, summary statistics could not be calculated. Herbicide concentrations were analyzed for differences in ranks and median concentrations between seasons and between ditch and reservoir subsites using generalized Wilcoxon tests, where increasingly negative or positive score statistics indicate higher and lower median concentration, respectively. Further comparisons were conducted on adja-

Table 1. Chemical name and analysis details for the seven herbicides selected for monitoring in this study. Six herbicides were analyzed using high performance liquid chromatography with diode array detection (HPLC-DAD). Glyphosate was analyzed using enzyme-linked immunosorbent assay (ELISA) with photometric detection. Compounds were measured at wavelengths that maximized absorbance. Reporting limits were set at 10 times the method quantification limit.

Herbicide	Chemical Name	Analysis	Wavelength (nm)	Reporting Limit (µg/L)
2,4-D	2,4-dichlorophenoxyacetic acid	HPLC-DAD	200	0.50
Clomazone	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-1,2-oxazolidin-3-one	HPLC-DAD	195	0.80
Dicamba	3,6-dichloro-2-methoxybenzoic acid	HPLC-DAD	200	0.80
Glyphosate	N-(phosphonomethyl)glycine	ELISA	450	0.50
Metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(1-methoxypropan-2-yl)acetamide	HPLC-DAD	195	2.0
Propanil	N-(3,4-dichlorophenyl) propanamide	HPLC-DAD	210	0.40
Quinclorac	3,7-dichloroquinoline-8-carboxylic acid	HPLC-DAD	226	0.40

cent ditch and reservoir subsites using paired Prentice-Wilcoxon tests. For all analyses, differences were considered significant when $p<0.05$. Summary statistic calculations and generalized Wilcoxon tests were carried out in R 3.1.6 using the NADA and interval packages. Paired Prentice-Wilcoxon tests were conducted in Minitab® 19.

Results and Discussion

Clomazone, glyphosate, metolachlor, and quinclorac were frequently detected in the monitored tailwater ditches and reservoirs (Figure 2A-D). Dicamba, 2,4-D, and propanil were rarely detected or not detected in any of the monitored systems (data not shown). These findings were consistent with producer herbicide application reports. The majority of producers reported applying rice herbicides containing clomazone and/or quinclorac in mid-April 2017, as well as residual herbicides containing metolachlor in mid-June through early July. No producers reported applying 2,4-D or dicamba. One producer reported propanil use, but the compound was not detected in that tailwater system. Propanil is known to rapidly degrade in the environment (Kanawi et al., 2016), and these findings suggest that the sampling intensity of the current scheme may not be sufficient to detect propanil transport in these systems.

Herbicide concentrations peaked during the growing season (Figure 2A-D; Table 2), with different temporal patterns between herbicides likely reflecting an interplay of application timing and precipitation. Clomazone and quinclorac are common spring-applied rice herbicides (Barber et al., 2019), and generalized Wilcoxon tests indicated that concentrations were higher in the monitored tailwater recovery systems in spring and summer (p-value 0.001). Metolachlor concentrations were higher in summer only (p-value 0.001), likely reflecting mid-season applications to soybean acres. Glyphosate concentrations peaked in the summer but were also higher in spring and fall relative to winter (p-value 0.001), likely reflecting the frequent, broad spectrum use of glyphosate. Herbicide concentrations were lowest (p-value 0.001) and usually below detection in off-season months. Clomazone and metolachlor were rarely detected in the tailwater recovery systems outside of the growing season, such that summary statistic calculations were not possible. Glyphosate and quinclorac detections were frequent in fall and winter, but concentrations were low in magnitude compared to peak summer months.

Differences in herbicide concentrations between ditches and reservoirs were also observed (Table 3) and were most apparent when data were partitioned into growing season and off-season datasets and when ditches and reservoirs were paired within sites. During the growing season, the paired Prentice-Wilcoxon tests indicated that concentrations of clomazone, glyphosate, and quinclorac were higher in the ditches than in the adjacent reservoirs (p-value <0.001). The trend of higher concentration in ditches than reservoirs was clearest for glyphosate, with results from all seasons and both paired and unpaired subsites supporting this interpretation. In contrast, no differences were found between metolachlor concentrations in ditch and reservoir subsites during the growing season for either analysis (p-value>0.05), with the concentration maxima in a similar range for ditches and reservoirs (Table 2).

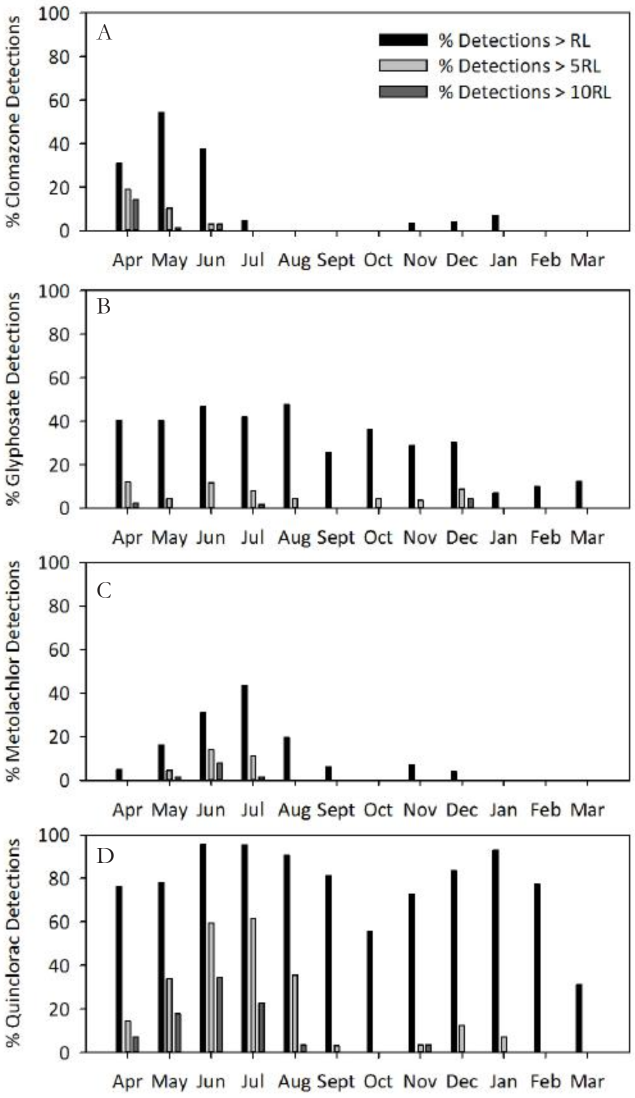

Figure 2. Frequency of herbicide detections: detections greater than the reporting limit (RL), detections > 5 times the reporting limit (5RL), and detections > 10 times the reporting limit (10RL). These values are expressed as a percentage of the total number of samples for the month, during the period April 2017 through March 2018 for A) clomazone, B) glyphosate, C) metolachlor, and D) quinclorac.

For both metolachlor and quinclorac, generalized Wilcoxon test results indicated that reservoir concentrations exceeded ditch concentrations during the off-season (p-value 0.002). For quinclorac, paired Prentice-Wilcoxon test results substantiated this finding for linked reservoirs and ditches (p-value<0.001). Higher reservoir concentrations could reflect more frequent flushing in ditches during the wetter

Table 2. Summary statistics of herbicide concentrations by season for the four herbicides that were frequently detected in the tailwater recovery systems. For datasets with >80% censored observations, mean and standard deviation (StDev) could not be estimated, and median was known only to be below the reporting limit. Results of generalized Wilcoxon tests comparing concentration ranks and medians between seasons are reported for spring (SPR; March 16 through June 15), summer (SUM; June 16 through Septempter 15), fall (FALL; September 16 through December 15), and winter (WIN; December 16 through March 15). Increasingly negative score statistics indicate higher median herbicide concentration; while increasingly positive score statistics indicate lower median herbicide concentration. Seasonal differences were considered significant when p<0.05, with lower case letters indicating seasons or season groupings that were statistically different.

	n				Median (µg/L)				Wilcoxon Score Statistic				
Compound	**SPR**	**SUM**	**FALL**	**WIN**	**SPR**	**SUM**	**FALL**	**WIN**	**SPR**	**SUM**	**FALL**	**WIN**	**Wilcoxon p**
Clomazone	142	141	106	71	0.57	<0.80	<0.80	<0.80	-43.91 a	1.08 b	26.62 c	16.21 c	0.001
Glyphosate	141	129	103	71	0.45	0.57	0.20	<0.50	-6.57 ab	-16.99 a	6.483 b	17.08 c	0.001
Metolachlor	142	141	106	71	<2.0	1.06	<2.0	<2.0	14.34 b	-42.47 a	16.73 b	11.4 b	0.001
Quinclorac	142	141	106	71	0.90	2.0	0.6	0.50	-1.09 b	-49.15 a	27.89 c	22.36 c	0.001

	Mean (µg/L)				StDev (µg/L)				Maximum (µg/L)			
Compound	**SPR**	**SUM**	**FALL**	**WIN**	**SPR**	**SUM**	**FALL**	**WIN**	**SPR**	**SUM**	**FALL**	**WIN**
Clomazone	2.2	-	-	-	6.5	-	-	-	67	2.0	3.0	2.0
Glyphosate	0.86	0.96	1.4	<0.50	1.1	1.0	9.3	-	5.2	6.2	95	3.4
Metolachlor	-	3.2	-	-	-	5.6	-	-	20	32	2.0	<2.0
Quinclorac	3.4	2.7	0.84	0.66	8.5	4.5	1.9	0.39	62	37	20	3.0

winter months, but the herbicide concentrations and detected differences between reservoirs and ditches during this period were small in magnitude relative to the growing season. For metolachlor, this finding appears to have been driven by a few low-level detections in reservoirs during fall months and was not substantiated when concentrations were compared only between linked ditches and reservoirs.

Residual concentrations of three of the seven monitored herbicides were higher in ditches than in reservoirs during the months surrounding herbicide application. This finding is congruent with the concept that herbicide residues are diluted along the flow path by mixing with increasingly large water volumes with lower residual concentrations, as well as degradation over time. While herbicide concentrations in tailwater systems have not been extensively monitored, Mattice et al. (2010) found a similar pattern for clomazone and quinclorac residues within four river networks in the region, including the Cache River. In that study, concentrations decreased moving downstream, as basin flow increased. However, a previous 13-month study comparing herbicide and nutrient concentrations in the ditches and reservoirs of a tailwater recovery system in the region found no water quality differences (Moore et al., 2015).

Conclusions

Herbicides applied to fields adjacent to tailwater recovery systems were frequently detected in the monitored ditches and reservoirs during the 2017 growing season, with higher concentrations in ditches than in reservoirs for clomazone, glyphosate, and quinclorac. Study findings support the following recommendations to minimize risk of cross-crop contamination when recycling tailwater: 1) use reservoir water for surface irrigation and 2) cycle tailwater through the reservoir for treatment of residual herbicides before reuse. The lowest herbicide concentrations occurred in the winter or fall-winter for all herbicides. During the off-season, metolachlor and quinclorac concentrations were higher in reservoirs than in ditches, but concentrations were low and subsite differences were minor compared to the growing season. These findings support targeting winter months (mid-December to mid-March) to use on-farm reservoirs as source water for MAR strategies in order to protect groundwater quality. The herbicide residue monitoring record initiated in this study and the observed patterns between seasons and subsites will inform best management practices for tailwater recovery systems to preserve Arkansas' water resources into the future. Further, the United States Geological Survey and others can use this dataset to improve models of herbicide fate and transport to include the mitigation potential of tailwater recovery systems to reduce herbicide loads from agricultural lands to the Mississippi River Basin.

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Table 3. Summary statistics of herbicide concentrations by subsites for the four herbicides that were frequently detected in the tailwater recovery systems. Summary statistics were calculated both across seasons and for the growing season (GS) and off- season (OS). For datasets with >80% censored observations, mean and standard deviation (StDev) could not be estimated, and median was known only to be below the reporting limit. Results of generalized Wilcoxon tests comparing concentration ranks and medians between ditches and reservoirs (Rsvr) are reported, with increasingly negative or positive score statistics indicating higher or lower median herbicide concentrations, respectively. Results of paired Prentice-Wilcoxon test comparing herbicide concentrations between linked ditches and reservoirs are reported, with a positive median difference indicating higher concentrations in ditches and a negative median difference indicating higher concentrations in reservoirs. Differences between ditches and reservoirs were considered significant when p<0.05 for both tests.

		n		Median (µg/L)		Wilcoxon Score Statistic		
Herbicide	**Dataset**	**Ditch**	**Rsvr**	**Ditch**	**Rsvr**	**Ditch**	**Rsvr**	**Wilcoxon p**
Clomazone	All	251	209	0.13	<0.80	-8.43	8.43	0.088
Clomazone	GS	156	127	0.29	<0.80	-8.36	8.36	0.056
Clomazone	OS	95	82	<0.80	<0.80	-1.33	1.33	0.27
Glyphosate	All	244	200	0.55	0.18	-51.04	51.04	0.002
Glyphosate	GS	150	120	0.71	0.28	-29.9	29.9	0.002
Glyphosate	OS	94	80	0.28	<0.50	-18.78	18.78	0.002
Metolachlor	All	251	209	<2.0	<2.0	8.92	-8.92	0.082
Metolachlor	GS	156	127	0.48	0.78	-0.57	0.57	0.9
Metolachlor	OS	95	82	<2.0	<2.0	10.66	-10.66	0.002
Quinclorac	All	251	209	0.80	0.90	1.34	-1.34	0.828
Quinclorac	GS	156	127	2.0	0.90	-20.78	20.78	0.002
Quinclorac	OS	95	82	0.40	0.70	21.89	-21.89	0.002

	Paired Prentice-Wilcoxon test		Median (µg/L)		StDev (µg/L)		Maximum (µg/L)	
Herbicide	**Median Difference**	**p**	**Ditch**	**Rsvr**	**Ditch**	**Rsvr**	**Ditch**	**Rsvr**
Clomazone	-0.078	<0.001	1.2	-	5.0	-	67	6.0
Clomazone	0.078	<0.001	1.9	-	6.2	-	67	6
Clomazone	0.08	0.083	-	-	-	-	3.0	<0.80
Glyphosate	0.50	<0.001	1.4	0.36	6.1	0.52	95	4.1
Glyphosate	0.50	<0.001	1.3	0.47	1.2	0.56	6.2	4.1
Glyphosate	0.50	<0.001	1.6	-	9.8	-	95	3.0
Metolachlor	0.20	0.83	-	-	-	-	32	22
Metolachlor	0.20	0.39	2.4	1.8	5.3	3.1	32	22
Metolachlor	0.072	0.056	-	-	-	-	2.0	2.0
Quinclorac	-0.019	0.67	3.2	1.0	7.3	0.74	62	6.0
Quinclorac	0.44	<0.001	4.6	1.2	8.8	0.89	62	6.0
Quinclorac	-0.34	<0.001	0.77	0.77	2.0	0.3	20	2.0

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