Groundwater and Surface Water Monitoring for Pesticides and Nitrate, East Shore, Flathead Lake, Montana



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Cover photo: Flathead Lake cherry orchard; photo credit Dan Poff, MDA

Introduction

In 1989, the Montana Agricultural Chemical Groundwater Protection Act was passed (MCA Title 80, Chapter 15, Sections 80-15-101 through 80-15-414). Section 80-15-103 states that it is the policy of the state to: protect groundwater and the environment from impairment or degradation due to the use of agricultural chemicals including all pesticides and nitrogen fertilizers, allow for the proper and correct use of agricultural chemicals, provide for the management of agricultural chemicals to prevent, minimize, and mitigate their presence in groundwater, and provide for education and training of agricultural chemical applicators and the general public on groundwater protection, agricultural chemical use, and the use of alternative agricultural chemicals. Under this Act, it is the directive of the Ground-Water Protection Program (GWPP) of the Technical Services Bureau of the Montana Department of Agriculture (MDA) to monitor the occurrence and concentration of agricultural chemicals in the waters of the State of Montana.

In the Flathead Lake basin in northwestern Montana, the GWPP of the MDA monitors groundwater quality at several sites. In response to detections of the insecticide imidacloprid at monitoring sites on the east shore of Flathead Lake in 2007 and 2008, an expanded sampling event was conducted in the region in 2009. Domestic wells completed in shallow, unconfined aquifers and bedrock aquifers in addition to several springs were sampled along the east shore of Flathead Lake south of Wood's Bay and east of Polson.

The objective of the project was to investigate the potential occurrence and distribution of agricultural chemicals in groundwater in the main orchard areas along the east shore. Adjacent to Flathead Lake, commercial apple and cherry orchards encompass ~1,100 acres with main concentrations occurring in the MDA project area (Makepeace and Mladenich, 1996). Sampling events were conducted in February and September 2009 to identify in-season pesticide applications. This report documents MDA observations in reference to previous investigations concerning the hydrogeology and water quality of the aquifers along the east shore of Flathead Lake.

East Shore Hydrogeology

Montana Bureau of Mines and Geology (MBMG)

The MBMG released a report on groundwater resources in the Flathead Lake area in 2004 (LaFave et al.). Included in this report was a discussion on the Flathead Lake perimeter subarea including brief descriptions of the available aquifers and water quality data from 32 wells. The Flathead Lake perimeter subarea was described as the east and west edges of Flathead Lake in addition to Finley Point and Polson Bay on the southern shore. Authors noted that most of the groundwater development was within a few miles of the lake.

LaFave et al. documented a total of 2,021 wells in the subarea with nearly 80% (n=1552) completed in a bedrock aquifer (2004). Approximately 17% of wells in the subarea are completed in deep and intermediate aquifers. Only 4% (n=88) of all wells were determined to have been completed in a shallow aquifer. Median well depth on the east side of the lake was 200 feet total depth (TD).

Water quality data included 15 samples from wells completed in bedrock and 17 samples from wells completed in intermediate and deep alluvial aquifers. Groundwater samples were collected from 1974-1996 with most samples collected in 1984 and 1996. Results suggested that groundwater in the Flathead Lake perimeter subarea is good quality and meets US EPA drinking water standards for natural constituents (LaFave et al., 2004). The median nitrate-N (NO₃⁻N) concentration in the bedrock aquifers (*n*=21) was 0.3 mg L⁻¹. Nitrate-N concentrations in deep alluvial and intermediate aquifers (*n*=19) had a maximum concentration of 1.3 mg L⁻¹ and a median of 0.2 mg L⁻¹.

Geologic conditions in the area are described by LaFave et al., 2004:

Various thicknesses of unconsolidated surficial deposits rest on bedrock along the east and west shores of Flathead Lake. Deposits of post-glacial alluvium (median thickness 17 feet from well logs), discontinuous accumulations of till (median thickness 50 feet), glacial-lake deposits (median thickness 55 feet), and deep alluvium generally thicken toward the shoreline of Flathead Lake and toward the centers of tributary stream valleys near the lake. The thickest accumulations of deep alluvium are in pre-glacial drainages developed in bedrock and in areas where outwash accumulated in front of advancing glaciers.

Subsurface geology in the subarea comprises several different types and periods of deposition thus creating a range of drainage conditions and patterns that rapidly evolve spatially across the project area.

Confederated Salish-Kootenai Tribes (CKST)

The CKST performed a more detailed study of the geology of the Flathead Lake perimeter as part of a Total Maximum Daily Load (TMDL) investigation (Makepeace and Mladenich, 1996). As part of the TMDL model calibration, geologic units were mapped and quantified and their respective properties examined. Orchards tend to overlie 3 of the 9 mapped units along the east and south shores of the lake. On Finley Point, two units are intermixed: proglacial sand and silt sediments and marginal and proglacial glaciofluvial sediments. The latter unit is also the dominant unit found north of Yellow Bay. Along the east shore, subglacial tills and extensive sequences of proglacial outwash and ice marginal glaciofluvial deposits are also found (Makepeace and Mladenich, 1996).

Glaciofluvial sediments are prominent north of Yellow Bay and are generally coarse bedded, silt through cobble-sized material. Proglacial deposits tend to be well sorted sands and gravels lacking fine sand and clays. These sediments are highly permeable with low water holding capacity. The proglacial sands and silts found on Finley Point are well sorted with moderate to high permeability and moderate water holding capacity. Marginal tills tend to have high bulk density largely comprised of silt and clay deposits with interspersed clasts (Makepeace and Mladenich, 1996). These sediments have high water holding capacities and low primary permeability. Marginal tills are the dominant sediment type between Blue Bay and Yellow Bay.

The authors discovered that identification of "discrete, continuous aquifer systems" proved difficult "because of lateral discontinuity of sediments" in addition to the rapid gain in elevation along the east shore (Makepeace and Mladenich, 1996). Groundwater flow paths to Flathead Lake along the east shore are likely two different systems. A deeper more regional flow path discharges offshore and is reflected by the proclivity of domestic wells in excess of 200 feet along the east shore. A shallower, more localized flow path may be intercepted by the lake prior to reaching domestic wells and is evidenced by the large number of groundwater springs found between the numerous creek drainages in the Mission Mountain range (Makepeace and Mladenich, 1996).

In the study area, precipitation exceeds evapotranspiration rates providing significant recharge to shallow aquifers from precipitation. The 40-year precipitation mean at Bigfork (COOP ID# 240755) for 1969-2009 is ~22 in yr⁻¹. The authors also suggest that there are extensive areas where shallow groundwater is moving downslope along the east shore. The hydraulic characteristics of the geology and soils and available water in excess of evapotranspiration rates imply that a well-flushed system exists in most of the orchard region with a few exceptions.

Hydrographs

There are two long-term hydrographs available for the southern portion of the Flathead Valley. The USGS-CKST Dry Creek Well (MBMG ID 6024) has a record of measurement from 1/9/85-1/9/08. It is located due south of Mission Reservoir and alongside Dry Creek. The USGS-Makepeace monitoring well (MBMG ID 703168) has a record of measurement from 9/13/90-12/15/08. It is located 2.5 miles due east of US93/MT200 and is in close proximity to the Jocko River. Mean daily values from these long-term datasets are displayed in Figure 1.

In the Flathead Valley region, minimum aquifer storage occurs in late March/early April while peak aquifer storage occurs in mid-July/early August. The USGS-Makepeace and USGS-CSKT wells are located in close proximity to surface waters and likely receive significant recharge from stream flow.



Mapping Resources

Utilizing the index-overlay method, ArcGIS was used to produce maps of wells and springs in the project area. The project area was defined by cadastral data for parcels with continuous cropping practices. As orchard production constitutes the main agricultural commodity produced in this area, continuous cropped acres was used as an indirect measurement to quantify orchard extent and distribution. The project area covered 13.91 mi² (~8900 ac) and extended along the east shore of Flathead Lake from 4 miles south of Wood's Bay to approximately 4 miles east of Polson, MT (Figure 2). According to the MBMG GWIC database, there are 506 wells in the project area with a range of 0–803 ft TD and a mean of 185.0 ft TD. Of these, wells \leq 50 ft TD constitute only 8.7% (*n*=44). GWIC was also used to research existing water-quality and hydrograph data for wells in the project area.



In addition, MDA utilized Montana Department of Natural Resources and Conservation (DNRC) data. The DNRC produced a digital coverage of water rights points of diversion (WRDiv). All groundwater source types identified as groundwater, springs, or unnamed tributaries along with additional filters¹, were identified as potential sampling sites. Cadastral coverages were used to identify landowners to verify sites and obtain permission to sample.

MDA sample collection

On February 2, 2009, the MDA collected groundwater samples from 9 wells and 2 springs (n=11). On September 1, 2009, samples were collected from 9 wells, 4 springs and 2 surface waters (n=15). This sampling event included 6 new sampling points in addition to 9 of the sites that had been sampled in February. As part of regular monitoring activities by the GWPP, samples were collected from LAK-1, FCP-1 and BIOSPRING on 5/11/09 and 7/28/09. LAK-1 is part of the Permanent Monitoring Well (PMW) network of the MDA. GWPP monitoring efforts are augmented by collection from BIOSPRING and FCP-1. Results from these samples are included in this report. A total of 32 samples were collected by the GWPP in the course of this project.

All wells were sampled after purging at least three well casing volumes or until field parameters (temperature, pH, specific conductivity, and dissolved oxygen) had stabilized if the water level or well depth was unknown. MDA utilized standard operating procedures (SOPs) for groundwater and surface water collection, discharge measurements, and transportation². Recorded water quality parameters for all samples may be found in Appendix C.

This sampling event focused on wells completed in alluvium or glacial drift and/or located within or in close proximity to orchard operations. In sampled wells, the mean depth of well screens³ below the ground surface was 102 feet and mean total depth was 113 feet (Table 1). Sampling locations were chosen to optimize geographic distribution and well demographics in the project area (Figure 2). Groundwater and surface water site characteristics may be found in Table 1 and 2 respectively.

Both surface water and groundwater samples were collected in 900-mL amber glass jars, put on ice, and transported to the MDA Analytical Laboratory at Montana State University in Bozeman per MDA SOPs. The samples were analyzed using the Universal Method, an analytical method developed by the MDA Analytical Bureau for the detection of pesticides in water. The Universal Method analyzes for 95 pesticides and degradates. The MDA lab also performed all nitrate-N/nitrite-N analyses. A list of analytes and their respective limits of quantification for the Universal Method is included in Appendix B.

¹ Means of diversion: dam, developed spring, dike, ditch, flowing, headgate, instream, livestock direct from source, pipeline, pit, pump, or spring box

² Static water level measurement (GWPP-01), well purging (GWPP-02), water quality parameter measurement (GWPP-03), discharge measurements (GWPP-05), surface water sample collection (GWPP-06), sample transportation (GWPP-08), and sample custody and security (GWPP-09)

³ For this calculation, well logs that lacked this information were assumed to have open bottoms.

Table 1. Groundwater site information											
Site ID	Source	Water use	Total Depth (ft bgs)	Screened Interval (ft bgs)	Water Level (ft bgs)						
BIOSPRING	SP	D	-	-	-						
FLC-1	W	D	118	Open bottom	56						
FLC-2	W	D	100	UNK	74.9						
FLC-3	W	D	134	Open bottom	98						
FLC-4	W	D	180	Open bottom	90						
FLC-5	W	D	90	UNK	35						
FLC-6	W	D	200	190-200	108						
FLC-7	W	D	103 96.5-103		79						
FLC-8	W	U	60	UNK	UNK						
FLC-9	SP	D	-	-	-						
FLC-10	SP	U	-	-	-						
FLC-12	SP	U	-	-	-						
FLC-13	W	D/I	117	Open bottom	48						
FLC-15	W	D	185	184-185	67						
FCP-1	W	М	40	Open bottom	7						
LAK-1	W	М	30	20-30	17.5						
bgs = below groun stockwater; SP = s	nd surface; I spring; SW =) = domestic = surface wa	c; I = irrigati iter; UNK=u	on; M = monitori inknown; W = we	ing; S =						

Table 2. Surface water site information											
Site ID	Location description	Date	Discharge (cfs)								
FLC-11	Lolo Creek at MT 35	9/1/2009	< 1								
FLC-14	Unnamed intermittent stream at point 150 ft SE of FLC-1	9/1/2009	< 1								
cfs = cubic	e feet per second										

Analytical results

The results of surface and groundwater analysis from the 2009 sampling events found few detections of pesticides or NO_3 N (Table 2). In total, 12 different pesticides and degradates were detected in 17 of the 32 samples collected. The 4 spring locations had a weighted mean of 1.25 detections per sample while all wells had a weighted mean of 0.88 detections per sample. The weighted mean for wells completed in aquifers comprised of alluvium, glacial till, or glacial drift was 0.94 pesticide detections per sample. All pesticide detections in bedrock aquifers were from FLC-5 out of 4 wells that met this

description. No pesticides were detected near or at established human health standards (HHS) for drinking water.

The only detection in the 2 surface water samples was for the herbicide 2,4-D at FLC-15. This sample was collected from an intermittent stream in the southern end of the project area approximately 150 feet southeast of FLC-1. Of further interest, detections of 2,4-D and MCPA were only observed in the September sampling event. Located on Finley Point, wells FLC-2 and FLC-4 had detections of both herbicides. BIOSPRING and FLC-10, both springs, had detections of MCPA in the September sampling event.

Wells FLC-1, -7, -13 and FCP-1 had no pesticide detections in 2009 although FCP-1 had a verified detection of imidacloprid in 2007-2008. The spring at FLC-12 and the surface water sample collected at FLC-11 also yielded no pesticide detections.

PMW LAK-1 also has a history of detections of atrazine and degradates deethyl atrazine and deisopropyl atrazine as well as prometon and simazine. In 2009, all of these with the exception of deisopropyl atrazine were detected in this monitoring well.

Table 3. Summary of Pesticide and Nitrate-N Detections, East Shore of Flathead Lake, 2009															
							Ana	lyte (and	l Common	Trade Nan	nes)				
Site ID	Date	Source	2,4-D (μg/L)	Aminopyralid (Milestone) (µg/L)	Atrazine (Atrazine, Aatrex) (µg/L)	Bromacil (Krovar) (µg/L)	Deethyl atrazine (µg/L)	Deisopropyl atrazine (µg/L)	Imidacloprid (Provado) (µg/L)	MCPA (µg/L)	Metolachlor ESA (µg/L)	Nitate-N (mg/L)	Simazine (Pramitol) (µg/L)	Prometon (Pramitol) (µg/L)	Propiconazole (Bumper, Stratego) (μg/L)
	2/2	SP	ND	ND	ND	ND	ND	ND	0.029	ND	ND	ND	ND	ND	ND
BIOSPRING	5/11	SP	ND	ND	ND	ND	ND	ND	0.069	ND	ND	ND	ND	ND	ND
DIOSI MIVO	7/28	SP	ND	ND	ND	Q	ND	ND	0.036	ND	ND	1	ND	ND	ND
	9/1	SP	ND	ND	ND	ND	ND	ND	0.042	Q	ND	1.2	ND	ND	ND
FLC-1	2/2	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FLC-I	9/1	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FLC 2	2/2	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TLC-2	9/1	GW	0.0099	ND	ND	ND	ND	ND	ND	0.0027	ND	ND	ND	ND	ND
FLC 3	2/2	GW	ND	ND	Q	ND	ND	ND	ND	ND	Q	ND	ND	ND	ND
1120-5	9/1	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FLC-4	2/2	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	9/1	GW	0.023	ND	ND	ND	ND	ND	ND	Q	ND	ND	ND	ND	ND
FLC-5	2/2	GW	ND	ND	Q	ND	Q	Q	ND	ND	ND	ND	ND	ND	ND
	9/1	GW	ND	ND	Q	ND	Q	Q	ND	ND	ND	ND	ND	ND	ND
FLC-6	2/2	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FLC-7	2/2	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.5	ND	ND	ND
	9/1	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.3	ND	ND	ND
FLC-8	2/2	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	10	ND	0.011	ND
	9/1	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	9	ND	Q	ND
Human Heal	th Stand	lard	70		3*	90	3*	3*	400	4	100	10	4	100	
μg/L = micrograms SP = spring; GW = degradates are addit	per liter groundw tive	$(1 \ \mu g/L = 1)$ vater; Q = a	nalyte detect	ted below	analytic:	al method	l limit of	mg/L = 1 quantitat	i part per m ion (see A	ppendix B fo	= not dete or limits of	of quantit	v = surfac tation); *a	ce water; atrazine and	1

	Table 3. (cont.) Summary of Pesticide and Nitrate-N Detections, East Shore of Flathead Lake, 2009														
				Analyte (and Common Trade Names)											
Site ID	Date	Source	2,4-D (µg/L)	Aminopyralid (Milestone) (µg/L)	Atrazine (Atrazine, Aatrex) (µg/L)	Bromacil (Krovar) (µg/L)	Deethyl atrazine (µg/L)	Deisopropyl atrazine (µg/L)	Imidacloprid (Provado) (µg/L)	MCPA (µg/L)	Metolachlor ESA (μg/L)	Nitate-N (mg/L)	Simazine (Pramitol) (µg/L)	Prometon (Pramitol) (µg/L)	Propiconazole (Bumper, Stratego) (µg/L)
ELC O	2/2	SP	ND	0.068	ND	ND	ND	ND	0.0049	ND	ND	ND	ND	ND	0
FLC-9	9/1	SP	ND	ND	ND	ND	ND	ND	0.0066	ND	ND	ND	ND	ND	0.027
FLC-10	9/1	SP	ND	ND	ND	ND	ND	ND	ND	Q	ND	ND	ND	ND	ND
FLC-11	9/1	SW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FLC-12	9/1	SP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FLC-13	9/1	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FLC-14	9/1	SW	0.0047	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FLC-15	9/1	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.3	ND	ND	ND
	2/2	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FCP-1	5/11	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	7/28	GW	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.3	ND	ND	ND
IAK 1	5/11	GW	ND	ND	Q	ND	0.0029	ND	ND	ND	ND	5.4	0.0057	0.13	ND
	7/28	GW	ND	ND	ND	ND	0.0028	ND	ND	ND	ND	3.3	0.0043	0.078	ND
Human H	Iealth S	tandard	70		3*	90	3*	3*	400	4	100	10	4	100	
$\mu g/L = mics$ SP = spring degradates	rograms ;; GW = are addit	per liter (1 groundwate tive	$\mu g/L = 1$ parent par	rt per billio te detected	n); mg/L l below ar	= milligra nalytical r	ams per liter nethod limi	r (1 mg/L t of quant	= 1 part per itation (see	million); Appendi	ND = not R B for li	ot detecte mits of qu	d; SW = \overline{sur} uantitation);	face water; *atrazine a	nd

Nitrate-N was detected in several wells and MDA monitoring sites. Nitrate-N concentrations in FLC-7, FCP-1, FLC-15, and BIOSPRING were within the range of natural background levels in groundwater (2-3 mg L⁻¹). The HHS for NO₃¬N (\geq 10 mg/L) was met at FLC-8. This well has a total depth of 60 feet and is no longer used for domestic supply⁴. Elevated NO₃¬N concentrations were observed at LAK-1 located north of Yellow Bay. This well⁵ has a history of elevated NO₃¬N detections since its completion in September 2004 (Figure 3). There was not a significant correlation between NO₃¬N and static water level (SWL) for the limited dataset. Nitrate-N detections at LAK-1 do not corroborate with other shallow groundwater samples taken from FCP-1 and the other spring sources. A comparison with MBMG data from wells in the project area also shows relatively low NO₃¬N concentrations in shallow and deep aquifers (Appendix A⁶).



Uses of Pesticides Detected in Water Samples

Detections of atrazine and its degradates were observed in wells FLC-3, FLC-5, and LAK-1. Imidacloprid was quantified in samples collected from spring sources at FLC-9 and BIOSPRING. Single detections of aminopyralid, bromacil, and metolachlor ESA (a

⁴ FLC-8 was abandoned due to elevated NO₃⁻N concentrations and low yield.

⁵ PMW LAK-1 is found in Appendix A under MBMG ID 213971.

⁶ Contains 4 records (MBMG ID: 77520, 133023, 137610, 157640) used in the water quality analysis for the Flathead Lake perimeter subarea in LaFave et al., 2004; MBMG sampled FLC-1 (77511) and FLC-13 (77561) previously; Appendix A also includes records for a well on the property of the Flathead Biological Station (MBMG ID 196430).

degradate of metolachlor) were also observed. Simazine was only detected in LAK-1 and propiconazole was only found in FLC-9.

Atrazine was widely used in agriculture before it became a restricted-use herbicide in 1993. In Montana, it is currently registered for use in corn and soybeans and in wheat (fallow) and wheat (stubble) applications. Atrazine and its degradates have proven to be very persistent in the environment and are commonly detected in surface water and groundwater in Montana and across the United States.

Soil sterilants are herbicides used in rights-of-way, industrial sites, parking lots and other places where long-term weed control is desired. Herbicides in this category include bromacil and prometon. Many herbicides detected in the project area may also be used in rangeland, pasture and alfalfa such as aminopyralid and MCPA. Simazine also has some orchard applications and MCPA is also used in small grains and both have noncropland uses as well. 2,4-D is a general-use herbicide that has a broad spectrum of applications to agricultural crops as well as noncropland uses.

The only insecticide detected in the project area, imidacloprid is used to treat structures, seeds, soil, and crops including cherries. It is most commonly applied as a soil and foliage treatment, and as a seed dressing.

Propiconazole is a fungicide that is often used on grasses grown for seed, corn, sorghum, and oats. It also is used in turf and ornamentals and includes foliar applications to cherries. It was the only fungicide detected in the study.

Discussion

The most significant finding from the study was that no pesticide detections were observed in excess of established HHS where such standards exist. According to the CSKT TMDL report, the majority of orchard acreage around Flathead Lake overlies marginal and proglacial glaciofluvial sediments (Makepeace and Mladenich, 1996). Therefore, the land use with the greatest pesticide and fertilizer applications along the east and south shores of Flathead Lake tends to overlie soils with high infiltration rates and low water holding capacity. This suggests that groundwater in these areas is susceptible to contamination from agricultural chemicals. The hydrogeologic and meteorological characteristics of the study area imply a well-flushed groundwater system along much of the east shore particularly in the glaciofluvial sediments north of Yellow Bay and the proglacial sands and silts on Finley Point.

Nitrate-N has several potential sources including fertilizers, manure and septic effluent, and natural sources. The sources of the nitrates detected during this project were not determined. The HHS was met at FLC-8 and elevated concentrations were observed at LAK-1. However, in all other samples, NO_3 N was not detected or within natural background concentrations in groundwater (2-3 mg L⁻¹). This observation is corroborated by MBMG data from the project area (Appendix A). The weighted average of the MBMG data from 23 wells (mean TD=198.5 ft) was 1.18 mg L⁻¹ NO₃ N. From the MDA study, the weighted mean from 12 wells (mean TD=113.0 ft) was 1.50 mg L⁻¹

 $NO_3 N^7$. For springs (*n*=4), the weighted mean was 0.14 mg L⁻¹ NO₃ N. The lack of NO₃ N detections are possibly due to denitrification in low oxygen conditions or a matter of dilution with depth. However, Makepeace and Mladenich stated that the lack of organic carbon in glacially derived sediments limits denitrification in the aquifer system on the east shore (1996). Nitrate-N may be a concern in some shallow wells in the project area although the lack of NO₃ Concentrations in excess of background levels in FCP-1 and the spring sources do not provide conclusive backing.

Imidacloprid detections

In 2009, imidacloprid was detected in 2 spring sources (BIOSPRING, FLC-9). BIOSPRING is one of three MDA monitoring sites on the east shore of Flathead Lake and one of two MDA sites with previous imidacloprid detections. BIOSPRING is a public water supply for the Flathead Biological Station. Imidacloprid is a very persistent, highly soluble insecticide with a half-life of 129 d. in the water/sediment interface (PPDB, 2009, 2010). It has a high risk of leaching to groundwater as it sorbs poorly to soil particles. Imidacloprid was introduced to replace the insecticide azinphos methyl which is being phased out in the region. These insecticides are used mainly to control the western cherry fruit fly which is a quarantined pest.

The recharge area for BIOSPRING includes several cherry orchards. FLC-9 is an untreated, domestic supply located approximately 2 miles north of BIOSPRING. The property contains a cherry orchard in addition to a pesticide storage facility. There is little orchard acreage up-gradient of this property. Imidacloprid was not detected at any other sampling sites in the project area. It had previously been detected in a shallow observation well (FCP-1; TD = 40 ft.) located 250 ft up-gradient of BIOSPRING.

Only 4 wells (FLC-5, -6, -7, and -15) in the study were completed in bedrock. According to well log reports, all other wells were completed in Pleistocene alluvium, glacial till or glacial drift. This suggests that imidacloprid is delivered to surface waters from spring sources via preferential flow paths in shallow groundwater. However, imidacloprid was not detected in 2 other springs (FLC-10, -12). FLC-10 does receive recharge from an orchard operation. A groundwater sample was collected in August 2008 from BIOSPRING and sent to the Environmental Isotope Laboratory at the University of Waterloo in Ontario, Canada for tritium analysis in order to provide an estimate of the groundwater age. The groundwater sample from the spring contained 8.4 T.U. (1.1 SD) suggesting that the groundwater was likely last in contact with the atmosphere in the early 1960s or post-1980 suggesting relatively young groundwater and potentially short residence times in the shallow groundwater flow system.

The lack of imidacloprid detections in groundwater wells may also be attributed to the depth of sampling below the ground surface. The average total depth of the wells in this study was 113 feet. As imidacloprid was only introduced to the region in the last several years, it is possible that not enough time has elapsed for downward migration to reach wellheads. Dilution and dispersion effects may also prevent the occurrence of positive

⁷ Assumes that non-detects (ND) = 0.

detections in deeper wells. A good example of this is the paired groundwater samples collected at FLC-8 (TD=60 ft) and FLC-15 (TD=185 ft). The two wells were drilled next to each other. Nitrate-N (9 mg L⁻¹) and prometon (Q) were detected in FLC-8 on 9/1/09. On the same date, NO₃⁻⁻N was detected at 2.3 mg L⁻¹ and prometon was not detected in adjacent FLC-15; the probable result of greater dilution in the deeper well.

It is also possible that other transport pathways are responsible for imidacloprid detections in the two spring sources. In previous investigations, the GWPP has detected imidacloprid in 5 different wells on the Greenfields Bench in north-central Montana and in a domestic well in the Gallatin Valley.

2,4-D and MCPA detections

The herbicides 2,4-D and MCPA are non-persistent chemicals with low half-lives in the water-sediment interface (29 d. and 17 d. respectively) (PPDB, 2009, 2010). These chemicals were not detected in the February sampling event but were observed in September 2009. MCPA was observed in wells FLC-2 and FLC-4 and in the springs FLC-10 and BIOSPRING. 2,4-D was detected in the same two wells and in FLC-14, the intermittent stream near well FLC-1 in September 2009. Given the non-persistent nature of these chemicals, this suggests that detections were from within-season applications in the project area. Examining these detections as indirect groundwater tracers, this also verifies that shallow groundwater flow is fairly rapid in parts of the project area and provides evidence that agricultural chemicals are not prevalent in the shallow groundwater flow system. It is interesting that imidacloprid was not detected in FLC-10 or on Finley Point in areas where orchard operations are concentrated. The reasons for this are unclear if imidacloprid is being applied in those areas.

According to Makepeace and Gillard (2001), Finley Point is a semi- to fully confined aquifer comprised of well-sorted sand and gravel and the eastern half has moderately high vulnerability to pesticide leaching to groundwater. The authors estimated that it is 100+ feet to the top of the principle aquifer. The 4 wells sampled on the eastern half of the landform have a mean total depth of 126 ft. As these wells yielded few detections, this suggests that agricultural chemicals are not significantly impacting groundwater resources on Finley Point. Of further note, the area around FLC-1, which had no detections, was considered an area of low aquifer vulnerability to pesticides. As Makepeace and Gillard (2001) did not investigate aquifer characteristics and vulnerability north of Finley Point, it is not possible to definitively make this assessment for other parts of the MDA project area.

Other detections

Atrazine has been a restricted-use herbicide since 1993. It should be noted that atrazine and its metabolites are cumulative⁸, but only one well had multiple detections of the parent and metabolites (FLC-5) and all detections were below the reporting limits. Of

⁸ Detections of atrazine, deethyl atrazine, deethyl deisopropyl atrazine, and deisopropyl atrazine are additive.

note, FLC-5 has a total depth of 90 feet and is completed in bedrock. The detection of enduring pesticides in a bedrock aquifer of intermediate depth is interesting. Atrazine was also detected in FLC-3; a domestic well 134 feet deep completed in glacial drift. It is likely that these detections are the result of legacy uses, but their detection at such depths is noteworthy. In addition to corn and soybeans, atrazine is also labeled for post-harvest applications for wheat (stubble) and as a soil treatment in wheat (fallow) in Montana. It also has a few noncropland applications.

Along the east shore, the primary aquifer is fractured bedrock. Contamination of the bedrock aquifer is possible where fractures reach the surface or extend into overlying, unconfined, shallow aquifers. This likely explains the presence of pesticides in FLC-5. Of the 12 wells in the study, 4 were completed in bedrock according to well logs. The remaining wells (n=8) were completed in alluvium, glacial till, or glacial drift. Bedrock wells accounted for 6 of the 21 pesticide detections (28.6%) with all detections in FLC-5. LaFave et al. (2004) theorized that confining units along the east shore were likely not continuous and that there was hydraulic connectivity between the shallow and intermediate aquifers and the deeper bedrock aquifers.

Conclusions

Sampling of surface and groundwater along the east shore of Flathead Lake found few detections of pesticides and all detections were well below HHS for drinking water. Overall, the results from this limited sampling event suggest that groundwater in unconfined aquifers along the east and south shores of Flathead Lake is clean and generally free of agricultural pesticides and NO₃⁻N. The same conclusions for the Flathead Lake perimeter subarea were reached for natural constituents in a report from MBMG (LaFave et al., 2004).

The east shore of Flathead Lake contains complex hydrogeology due to the proximity of the Mission Mountain range and stratigraphy influenced by past retreats and advances of the Cordilleran ice sheet. As described by LaFave et al. (2004), the median thickness of shallow aquifers is 40 ft but values can exceed 200 ft for individual wells. Intermediate aquifers are found at depths greater than 75 ft below the ground surface and are generally confined to semi-confined by overlying low permeability till. Along the Mission Mountain range, streams traversing from bedrock to basin fill deposits become losing streams and constitute an important source of aquifer recharge to shallow and intermediate aquifers. Makepeace and Mladenich (1996) also suggest that there are extensive areas where shallow groundwater is moving downslope along the east shore emerging as springs and seeps between the main drainages. These shallow flows paths recharge the shallow aquifers and discharge as springs and seeps along the mountain fringe. Deeper flow paths in the basin fill recharge the intermediate and bedrock aquifers and discharge into Flathead Lake directly.

The hydraulic characteristics of the geology and soils and available water in excess of evapotranspiration rates imply that a well-flushed system exists in most of the orchard region with a few exceptions. This results in the rapid movement and dilution of agricultural chemicals in the principal aquifers. However, there are still unanswered questions regarding some of the pesticide detections in the project area. The MDA will not expand the study further as all detections were several orders of magnitude below established standards for drinking water. The GWPP will continue to monitor groundwater quality at selected sites along the east shore. Water quality is generally excellent and orchard operations and other agriculture were not found to be significantly impacting groundwater resources in reference to HHS in this study.

Literature Cited

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Appendix A

MBMG Water Quality Data

Collection date	Data Source	MBMG ID (M	Source	Well total	Nitrate-N	Dissolved solids	Specific conductance (uS cm ⁻¹)	pH	Temperature (deg. C)
uute		number)		depth	$(mg L^{-1})$	$(mg L^{-1})$	(us em)		(uegi e)
3/22/2004	MBMG GWIC	76819	well	118	0.05	-	329	-	-
11/26/2007	MBMG GWIC	76819	well	118	0.06	-	318	-	-
6/8/2001	MBMG GWIC	77511	well	440	4.09	-	637	-	-
4/30/2004	MBMG GWIC	77511	well	440	3.56	-	694	-	-
6/19/2002	MBMG GWIC	77512	well	180	1.99	395.93	709	6.87	10.2
9/30/2002	MBMG GWIC	77512	well	180	1.7	365.58	593.3	7.2	10.1
4/2/2003	MBMG GWIC	77512	well	180	2.75	428.34	784	7.37	9.8
6/20/2002	MBMG GWIC	77515	well	126	< 0.5	164.18	273	7.76	10.2
10/24/1996	MBMG GWIC	77520	well	324	< 0.25	325.07	524	7.24	10.4
8/11/1996	MBMG GWIC	77525	well	235	0.8	-	-	6.7	10.7
12/18/2003	MBMG GWIC	77552	well	80	0.1	-	416	-	-
12/13/1983	MBMG GWIC	77561	well	117	0.08	-	-	7.7	-
10/29/2004	MBMG GWIC	77566	well	122	< 0.01	-	282	-	-
7/18/1990	MBMG GWIC	77571	well	220	0.02	-	270	-	-
1/9/2006	MBMG GWIC	77621	well	70	0.7	-	612	-	-
8/22/1996	MBMG GWIC	78465	well	120	1.2	225.21	371	7.9	9.7
7/14/1996	MBMG GWIC	79185	well	60	<2.5	-	-	7.5	10.1
6/14/2002	MBMG GWIC	79185	well	60	1.49	240.31	404	7.39	9.9
10/2/2002	MBMG GWIC	79185	well	60	1.6	239.49	381.3	7.58	9.7
4/3/2003	MBMG GWIC	79185	well	60	1.52	245.16	432.3	8.1	9.4
8/22/1996	MBMG GWIC	133023	well	565	< 0.25	274.76	462	7.8	10.5
1/21/2003	MBMG GWIC	133041	well	195	0.1	-	999	-	-
8/22/1996	MBMG GWIC	137610	well	360	< 0.25	259.33	446	7.7	11
10/17/1996	MBMG GWIC	157640	well	100	< 0.25	168.2	284	7.9	10.4
2/1/2002	MBMG GWIC	188149	well	321	0.04	-	380	-	-
8/3/2002	MBMG GWIC	193908	well	420	7.16	-	544	-	-
6/14/2002	MBMG GWIC	196430	well	14.6	< 0.5	160.47	228	7.18	8.8
9/25/2002	MBMG GWIC	196430	well	14.6	< 0.5	160.84	255	7.44	10.6
4/1/2003	MBMG GWIC	196430	well	14.6	< 0.5	151.4	267.8	7.66	5.1
3/7/2006	MBMG GWIC	207059	well	200	< 0.01	-	303	-	-
8/16/2005	MBMG GWIC	209511	well	145	0.18	-	301	-	-
11/30/2005	MBMG GWIC	209511	well	145	0.14	-	291	-	-
10/27/2004	MBMG GWIC	213971	well	32.4	6.93	395.73	520	7.3	9.6

Appendix B

Universal Method Analyte List and Limits of Quantification (LOQ)

2009 MDA Universal Method Analytes and the Limits of Quantification (LOQ)											
Analyte Name	LOQ	Units	Analyte Name	LOQ	Units						
2,4-D	0.0045	ug/L (ppb)	Hexazinone	0.0059	ug/L (ppb)						
2,4-DB	0.091	ug/L (ppb)	Hydroxy atrazine	0.0064	ug/L (ppb)						
2,4-DP	0.011	ug/L (ppb)	Imazalil	0.01	ug/L (ppb)						
3-OH Carbofuran	0.01	ug/L (ppb)	Imazamethabenz methyl acid met.	0.0052	ug/L (ppb)						
Acetochlor	0.14	ug/L (ppb)	Imazamethabenz methyl ester	0.001	ug/L (ppb)						
Acetochlor ESA	0.01	ug/L (ppb)	Imazamox	0.012	ug/L (ppb)						
Acetochlor OA	0.0042	ug/L (ppb)	Imazapic	0.011	ug/L (ppb)						
Alachlor	0.11	ug/L (ppb)	Imazapyr	0.011	ug/L (ppb)						
Alachlor ESA	0.011	ug/L (ppb)	Imazethapyr	0.01	ug/L (ppb)						
Alachlor OA	0.0034	ug/L (ppb)	Imidacloprid	0.0018	ug/L (ppb)						
Aldicarb	0.0028	ug/L (ppb)	Linuron	0.011	ug/L (ppb)						
Aldicarb sulfone	0.0011	ug/L (ppb)	Malathion	0.028	ug/L (ppb)						
Aldicarb sulfoxide	0.056	ug/L (ppb)	МСРА	0.0023	ug/L (ppb)						
Aminopyralid	0.053	ug/L (ppb)	MCPP	0.0022	ug/L (ppb)						
Atrazine	0.0022	ug/L (ppb)	Metalaxyl	0.012	ug/L (ppb)						
Azinphos methyl	0.037	ug/L (ppb)	Methomyl	0.0016	ug/L (ppb)						
Azinphos methyl oxon	0.031	ug/L (ppb)	Metolachlor	0.012	ug/L (ppb)						
Azoxystrobin	0.0011	ug/L (ppb)	Metolachlor ESA	0.0025	ug/L (ppb)						
Bentazon	0.0011	ug/L (ppb)	Metolachlor OA	0.021	ug/L (ppb)						
Bromacil	0.0074	ug/L (ppb)	Metsulfuron methyl	0.026	ug/L (ppb)						
Carbaryl	0.04	ug/L (ppb)	Nicosulfuron	0.011	ug/L (ppb)						
Carbofuran	0.0052	ug/L (ppb)	Nitrate as Nitrogen	1.0	mg/L (ppb)						
Chlorpyrifos	0.031	ug/L (ppb)	Nitrite as Nitrogen	0.1	ug/L (ppb)						
Chlorsulfuron	0.0056	ug/L (ppb)	NOA 407854	0.0052	ug/L (ppb)						
Clodinafop-propargyl-acid metabolite	0.013	ug/L (ppb)	NOA 447204	0.01	mg/L (ppm)						
Clopyralid	0.022	ug/L (ppb)	Picloram	0.14	mg/L (ppm)						
Cyproconazole	0.0051	ug/L (ppb)	Prometon	0.0051	ug/L (ppb)						
Deethyl atrazine	0.0017	ug/L (ppb)	Propachlor	0.0028	ug/L (ppb)						
Deisopropyl atrazine	0.01	ug/L (ppb)	Propachlor OA	0.0094	ug/L (ppb)						
Diazinon	0.01	ug/L (ppb)	Propiconazole	0.01	ug/L (ppb)						
Dicamba	0.051	ug/L (ppb)	Prosulfuron	0.005	ug/L (ppb)						
Difenoconazole	0.02	ug/L (ppb)	Simazine	0.0026	ug/L (ppb)						
Dimethenamid	0.01	ug/L (ppb)	Sulfometuron methyl	0.01	ug/L (ppb)						
Dimethenamid OA	0.0038	ug/L (ppb)	Sulfosulfuron	0.0054	ug/L (ppb)						
Dimethoate	0.0011	ug/L (ppb)	Tebuconazole	0.01	ug/L (ppb)						
Disulfoton	0.13	ug/L (ppb)	Tebuthiuron	0.0011	ug/L (ppb)						
Disulfoton sulfone	0.014	ug/L (ppb)	Terbacil	0.0051	ug/L (ppb)						
Disulfoton sulfoxide	0.064	ug/L (ppb)	Terbufos	0.17	ug/L (ppb)						
Diuron	0.01	ug/L (ppb)	Tetraconazole	0.0062	ug/L (ppb)						
Epoxyconazole	0.028	ug/L (ppb)	Thifensulfuron	0.026	ug/L (ppb)						
Ethion	0.39	ug/L (ppb)	Tralkoxydim	0.0051	ug/L (ppb)						
Ethofumesate	0.025	ug/L (ppb)	Tralkoxydim acid	0.005	ug/L (ppb)						
Ethoprop	0.012	ug/L (ppb)	Triadimefon	0.0057	ug/L (ppb)						
Fenamiphos	0.0011	ug/L (ppb)	Triadimenol	0.026	ug/L (ppb)						
Fenbuconazole	0.0053	ug/L (ppb)	Triallate	0.039	ug/L (ppb)						
Flufenacet OA	0.0053	ug/L (ppb)	Triasulfuron	0.026	ug/L (ppb)						
Flumetsulam	0.063	ug/L(ppb)	Triclopyr	0.011	ug/L (ppb)						
Glutaric Acid	0.0074	ug/L (ppb)	Triticonazole	0.032	ug/L (ppb)						
Halosulfuron methyl	0.01	ug/L (ppb)			5 41-7						

Appendix C

MDA Sample Water Quality Parameters

MDA Water Quality Parameters, Flathead Lake, 2009											
Site ID	Collection Date	Temperature (°C)	Field pH	Field specific conductance (uS cm-1)	Field dissolved oxygen (mg L ⁻¹)	Field dissolved oxygen (%)					
	2/2/2009	7.57	7.54	299	13.87	113.8					
BIOSPRING	5/11/2009	6.87	7.91	259	13.94	114					
	7/28/2009	7.07	8.29	288	12.85	106.2					
	9/1/2009	7.23	7.55	407	12.52	103.9					
	2/2/2009	9.62	7.73	355	2.64	23.2					
FLC-1	9/1/2009	9.6	7.78	303	2.43	21.3					
ELC 2	2/2/2009	9.9	7.59	317	1.83	16					
FLC-2	9/1/2009	10.27	7.66	273	1.56	14.2					
FLCO	2/2/2009	10.67	7.82	287	2.83	25.6					
FLC-3	9/1/2009	10.75	7.84	244	2.56	23					
	2/2/2009	9.98	7.79	293	1.04	9.1					
FLC-4	9/1/2009	10.44	7.8	249	0.86	7.5					
ELC 5	2/2/2009	8.14	7.49	493	11.61	98.3					
FLC-5	9/1/2009	8.87	7.55	407	12.27	105.7					
FLC-6	2/2/2009	9.85	7.52	540	12.21	108					
FLC 7	2/2/2009	10.96	7.36	537	5.57	50.4					
FLC-7	9/1/2009	11.11	7.41	461	8.27	75.2					
FLC 9	2/2/2009	10.23	7.57	511	6.06	54.4					
FLC-8	9/1/2009	10.95	7.4	518	10.2	92.6					
FLCO	2/2/2009	6.75	7.65	330	13.42	110					
FLC-9	9/1/2009	16.44	7.67	295	9.89	101.1					
FLC-10	9/1/2009	11.8	8	156	11.53	106.6					
FLC-11	9/1/2009	12.05	8.12	152	11.04	102.6					
FLC-12	9/1/2009	11.46	7.72	270	6.06	55.7					
FLC-13	9/1/2009	13.06	7.62	269	0.29	2.8					
FLC-14	9/1/2009	13.99	7.71	387	7.05	68.6					
FLC-15	9/1/2009	10.7	7.44	398	7.75	69.8					
	2/2/2009	7.78	7.37	295	9.31	77.8					
FCP-1	5/11/2009	7.37	7.79	234	12.94	107.5					
	7/28/2009	7.25	8.01	316	12.18	101.1					
LATZ 1	5/11/2009	9.83	7.73	538	12.56	109.8					
LAK-1	7/28/2009	9.43	8.02	644	11.4	100.3					