

Helena Valley Ground Water: Pharmaceuticals, Personal Care Products, Endocrine Disruptors (PPCPs) and Microbial Indicators of Fecal Contamination

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Abstract

The city of Helena, Montana and its surrounding valley (fig.1) are experiencing marked population growth with attendant proliferation of onsite wastewater disposal (septic tanks and drainfields) systems. Thirty eight public and private domestic water supplies deriving ground water from the Quaternary/Tertiary valley fill aquifer and various bedrock formations were sampled in the summer and fall of 2005 for pharmaceutically active compounds, personal care products, and endocrine disrupting compounds (PPCP as used here).

The two most frequently detected PPCPs are sulfamethoxazole (SMX) and the herbicide atrazine, with detection frequencies of 80% and 40%, respectively. Atrazine demonstrates a strong correlation with chloride and total dissolved solids (TDS). Because chloride and TDS are commonly used inorganic indicators of water-quality degradation from domestic wastewater discharge, the correlation suggests that atrazine could be occurring in domestic wastewater. This hypothesis should be verified in subsequent investigations

The wells were also sampled for microbial indicators of fecal contamination and for inorganic constituents. There is a poor correlation between the microbial indicators of fecal contamination and PPCP occurrence, with zero detections of either *E.coli* or the somatic or male specific coliphage. Total coliform was detected at only 8 sites.

Introduction

Twenty-two PPCPs have been detected in ground water used for drinking water for private and public water supplies in the Helena valley, Montana. PPCPs are a group of compounds that include antibiotics, hormones, and drugs. Results of several recent studies (Godfrey, 2004, Hinkle, 2005, Heberer, 2004) show that PPCPs are present in relatively low concentrations [nanogram per liter (ng/L) to microgram per liter (µg/L ranges)] in municipal and domestic wastewater as well as in some surface and ground water. The presence of these compounds in ground water and surface water has drawn public attention not only because of potential health risks from exposure to one or a mixture of these chemicals, but also because the primary mode of entry into our environment is not from manufacturing discharge but from widespread and continual use in human and veterinary and clinical practice (Lancet, 2002) and discharge associated with domestic wastewater. Low levels of various PPCPs in ground water provide clear evidence that domestic wastewater is a source of contamination. In spite of a growing body of evidence describing their distribution in the environment, little is known about their mobility and persistence in ground water or surface water, nor are their effects on human health and aquatic ecosystems well understood.

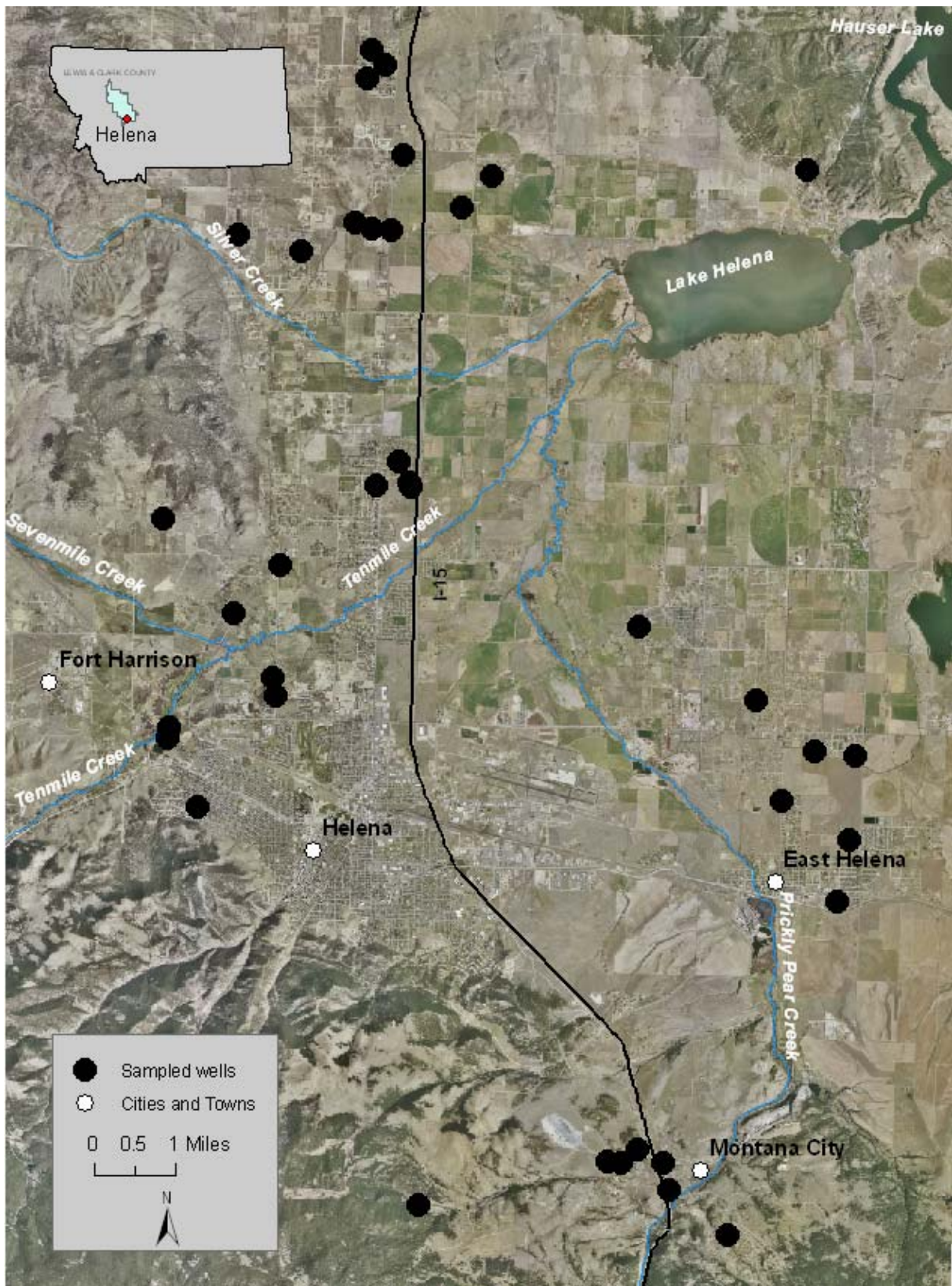


Figure 1. General location of the Helena valley, Montana

The proposed Ground Water Rule of the National Primary Drinking Water Regulations (40 CFR Parts 141 and 142, May 10, 2000) recognizes the need for a targeted risk-based regulatory strategy that identifies those systems with source-water contamination and systems deriving ground water from hydrogeologically “sensitive” aquifers. Among other stipulations of the proposed Ground Water Rule, public water supplies may be required to monitor ground-water sources for multiple indicators of fecal contamination; under the proposed rule both a bacterium (*E.coli* or enterococci) and a virus (male specific and somatic coliphage) could be used as indicators. Previous investigators have found coliphage, PPCPs, and other organic wastewater compounds in ground water and in septic tanks (onsite wastewater). In each study the types of analytes differ somewhat. In a shallow unconfined sandy aquifer near La Pine Oregon, the U.S. Geological Survey (Hinkle, 2005) found 45 organic wastewater compounds in onsite wastewater. In ground-water samples only 9 of the 45 wastewater compounds were found, along with sulfamethoxazole (SMX), acetaminophen, and caffeine. They found that the reactivity of this particular suite of organic wastewater compounds may limit their usefulness as tracers of onsite wastewater discharged into aquifers. In the same study coliphage was frequently detected in onsite wastewater but was only occasionally detected (8 occurrences) at low concentrations in wells, with a consistent absence in replicate or repeat samples. The authors speculate that coliphage was probably attenuated to less than 1 plaque forming unit (PFU)/100 mL before reaching the sampled wells.

Heberer (2004) noted that more than 60 pharmaceutical residues have been detected in surface water but only a very limited number of the compounds have been found in ground water and suggests that not only is there a small number of ground-water studies, but the compounds are likely removed or attenuated during transport into ground water. USGS investigators (2005) found that nitrate and chloride concentrations in onsite wastewater exhibited small variability among systems but that concentrations of individual organic wastewater compounds varied dramatically among different onsite wastewater treatment systems - not uncommonly by several orders of magnitude - suggesting that loading rates of wastewater compounds might be highly variable.

After the analysis of 42 septic tanks and influent to and effluent from the public wastewater treatment facility (WWTF) for Missoula, Montana, Godfrey and Woessner (2004) found 18 pharmaceutically active compounds in septic tanks, 12 in the WWTF influent and 9 in the WWTF effluent. The most frequently detected non-prescription drugs were acetaminophen, caffeine, and nicotine; frequently found prescription drugs were codeine, trimethoprim, and carbamazepine. In a similar evaluation of organic wastewater compounds in septic tanks at about 20 sites in New Jersey, Szabo (2004) found 4-nonylphenol, phenol, caffeine, cotinine, menthol, 3-beta-coprostanol, cholesterol, and β -sitosterol.

Background

The Helena valley in west-central Montana comprises about 330 square miles (207,400 acres) and is underlain by about 6,000 feet of valley fill composed of Tertiary sediments unconformably overlain by about 100 feet of Quaternary alluvium. Because of the

hydraulic interconnection of water-yielding zones, the valley fill deposits function as one complex aquifer system (Briar, 1992). Surface water enters the valley from Prickly Pear, Tenmile, Sevenmile, and Silver Creeks and from the Missouri River after it has been diverted into irrigation canals. Ground water and surface water discharges principally to Lake Helena and ultimately to the Missouri River. The Helena valley is bounded by folded and fractured sedimentary, metamorphic, and igneous bedrock of Precambrian to Cretaceous age (fig. 2). Figure 2 also shows ground-water level contours that depict flow from the south, west, and north margins of the valley toward Lake Helena.

Ground-water quality in the valley fill deposits is characterized as a calcium bicarbonate type with a median pH of 7.5. As shown on Table 1, arsenic, uranium and nitrate are elevated in ground-water samples at a few locations in the Helena Valley. The maximum values are 17.1 $\mu\text{g/L}$ for arsenic, [Maximum Contaminant Level (MCL) = 10 $\mu\text{g/L}$], 29.1 $\mu\text{g/L}$ for uranium (MCL=30 $\mu\text{g/L}$) and 12.4 mg/L for nitrate (MCL = 10 mg/L). Irrigation with arsenic-laden Missouri River water is a possible explanation for the elevated arsenic concentrations. Uraniferous rocks in surrounding bedrock are the probable source of elevated uranium. Elevated nitrate could be indicative of water-quality degradation from domestic wastewater; agricultural sources are possible but less numerous than those derived from domestic wastewater.

Historically a mining and agricultural area, the city of Helena and its surrounding valley is now experiencing dramatic increases in the density of individual onsite wastewater disposal facilities and residential wells. As shown on figure 3, the number of wells installed per year from 1973 through 1994 has averaged about 190. But in the period from 1995-2005 the average number of wells installed has escalated to 284 per year. It can be assumed that most of these wells are being installed to serve residences that are not served by city water or sewer services.

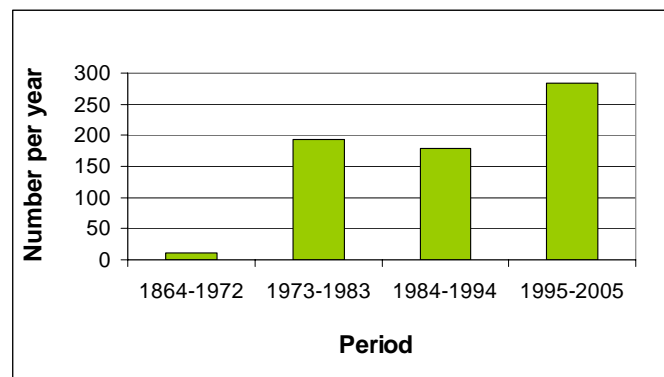
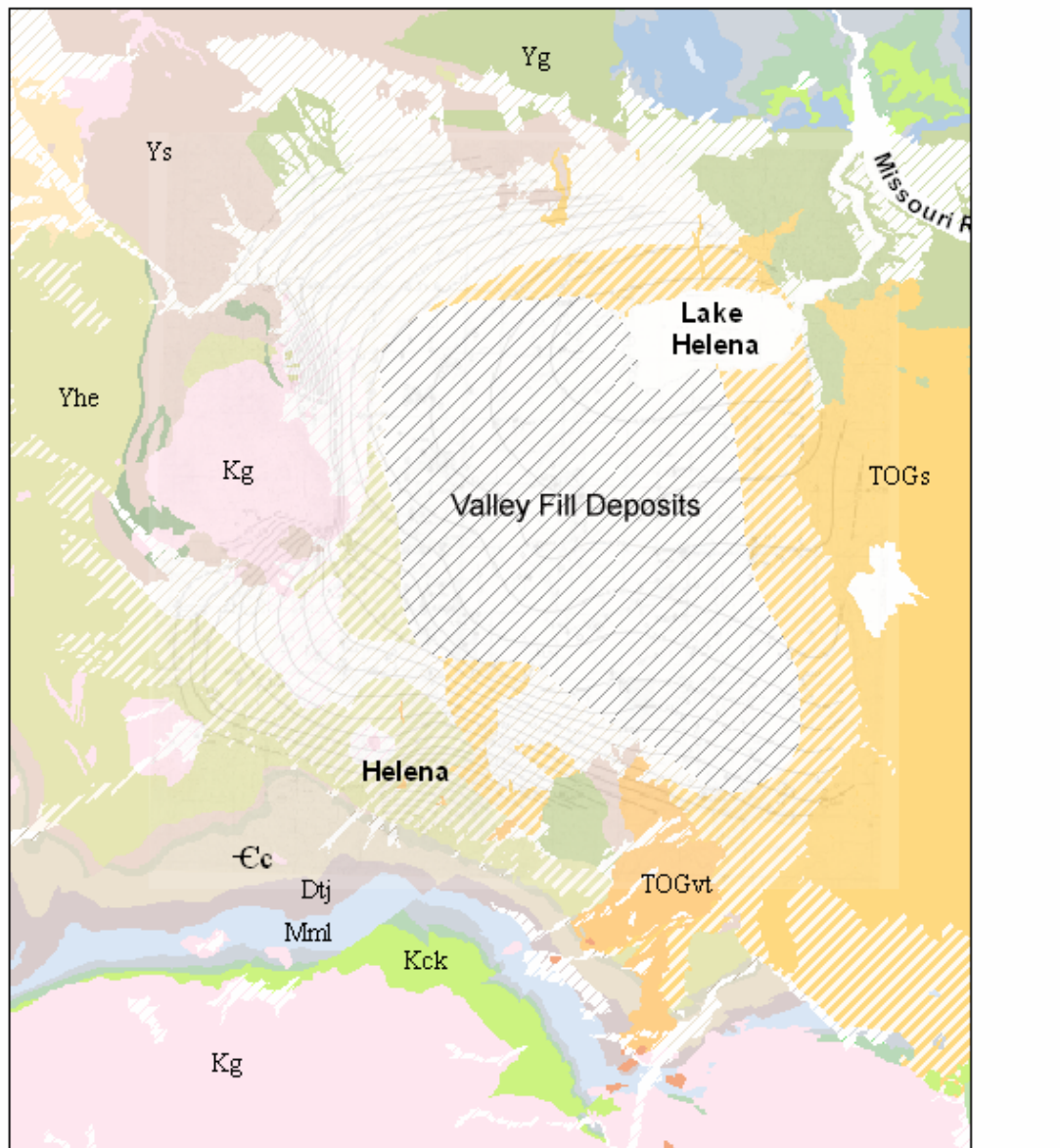


Figure 3. Annual number of new well installations in the Helena valley from 1864 – 2005.



Ground-Water Level Contours

Figure 2. Bedrock geology and water-level contours for the Helena valley, Montana. Modified from Thamke and Reynolds (2002) and Briar and Madison (1992).

A microbial occurrence survey of the Helena valley was conducted in April 2004 by Steve Kilbreath and Joe Meek of the Montana Department of Environmental Quality (DEQ) and Kathy Moore of the Lewis and Clark County Water Quality Protection District (LCWQPD). Results of that survey showed positive male specific coliphage occurrence in 10 of 19 sampled wells in the Helena valley with no detections of either of *E.coli* or enterococci. Subsequent re-sampling in August 2004 produced negative results for all coliphage, *E.coli*, and enterococci (Steve Kilbreath, Kathy Moore, and Joe Meek, unpub. data, 2004).

Methods

Thirty-eight wells representing both bedrock- (n=12) and valley fill-(n=26) aquifers, were sampled for total coliform, *E.coli*, enterococci, male specific- and somatic coliphage in April, June and November 2005. During the same period, 35 wells were sampled for 28 PPCPs and inorganic constituents. Eighteen wells serve small public water supplies with the remainder serving private residences. Well depths range from 39 to 425 feet (Table 1).

Wells were flushed prior to sampling until the field parameters of pH, specific conductance and temperature were stable as per the Montana Bureau of Mines and Geology (MBMG) Standard Operating Procedure for Collection of Ground-Water Samples for Inorganic Analyses (2004).

Samples for the analysis of male specific and somatic coliphage were collected and analyzed in accordance with proposed EPA Method 1601: Male Specific (F+) and Somatic Coliphage in Water by Two-Step Enrichment Procedure (USEPA, 2000). Total coliform, *E.coli*, and enterococci samples were collected and analyzed using Autoanalysis Colilert (MDPHHS, 2004) and Enterolert systems (MDPHHS, 2004), respectively.

Samples for the analysis of PPCPs were collected as grab samples in 1-L amber bottles. After arrival at the lab, Columbia Analytical Services in Kelso, WA prepared the samples using EPA Method 3535 and analyzed the samples using LC/MS/MS (Columbia Analytical Services, 2005).

Samples to be analyzed for inorganic constituents were field-filtered and preserved prior to shipment to the MBMG Analytical Laboratory. The sampling procedures follow the MBMG Standard Operating Procedures for Collection of Ground-Water Samples for Inorganic Analyses (2004). The inorganic analytical methods follow those as published in the MBMG Analytical Division Fee Schedule (1999).

Each well site is assigned a unique identification number that can be cross-referenced to the Montana Ground-Water Information Center (GWIC ID). All pertinent well construction, site inventory and water-quality data may be found on the website, <http://mbmggwic.mtech.edu>.

Table 1. Results of dissolved inorganic analyses for 35 well sites in the Helena Valley with maximum, minimum and median values.

Gwic Id	Sample Date	Total Well Depth (ft)	Water Temp	Field pH	Field S.C.	Lab pH	Lab Specific Conductance (umhos/cm2)	Total Dissolved Solids (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	Fe (mg/l)	Mn (mg/l)	SiO2 (mg/l)	HCO3 (mg/l)	CO3 (mg/l)	SO4 (mg/l)	Cl (mg/l)	NO3 (mg/l)	F (mg/l)	OPO4 (mg/l)
62523	5/24/05	50	10.3	7.3	376	7.85	510	315.2	70.7	20.6	10.9	2.3	0.0	<0.001	20.8	298.0	0.0	38.2	4.8	0.0	0.1	<0.05
64826	5/23/05	42	10.2	7.9	285	8.19	532	333.8	54.8	25.3	25.6	0.8	0.0	<0.001	26.4	264.0	0.0	53.4	15.1	1.9	0.4	<0.05
5756	5/23/05	66	10.1	7.8	625	7.92	840	790.2	83.7	34.9	56.9	3.5	0.0	0.0	274.0	386.0	0.0	111.0	29.5	5.4	0.4	0.7
62570	5/23/05	70	12.6	7.3	1667	7.57	2580	1810.8	221.0	119.0	235.0	6.9	0.0	<0.001	35.1	616.0	0.0	538.0	342.0	9.9	<1.0	<1.0
64806	5/23/05	41		7.8	611	7.42	846	528.7	47.4	21.6	115.0	1.1	0.0	<0.001	38.4	421.0	0.0	71.8	17.1	8.6	0.3	<0.05
194850	5/24/05	180	1	7.3	523	7.78	702	446.3	93.4	30.8	16.2	3.3	0.0	<0.001	19.6	353.0	0.0	90.8	17.6	0.7	<0.05	<0.05
62369	5/31/05	110	10.2	7.7	341	7.58	838	546.5	53.1	23.5	119.0	1.2	0.0	0.0	40.8	418.5	0.0	75.4	17.6	9.5	0.2	<0.05
62575	5/31/05	93	10.1	7.6	229	7.59	863	543.3	51.9	22.8	118.0	1.2	0.0	0.0	39.9	419.9	0.0	75.4	17.6	9.4	0.2	<0.05
65388	6/5/05	87	10.1	7.5	578	7.76	587	364.0	63.8	26.0	28.9	1.7	0.0	<0.001	19.3	201.1	0.0	76.1	45.2	3.9	0.0	0.0
170202	6/5/05	300	10.3	7.6	378	7.52	508	312.5	58.2	14.5	27.9	5.6	0.0	0.0	13.7	228.1	0.0	62.7	17.1	0.0	0.4	<0.05
187850	5/30/05	100	10.2	7.7	452	7.75	607	364.5	61.8	25.2	27.2	1.7	0.0	<0.001	19.0	199.3	0.0	83.9	43.5	3.8	0.2	<0.10
206394	5/30/05	200	10.1	7.8	943	7.68	1288	731.5	128.0	60.3	35.6	2.3	<0.005	0.0	16.2	160.1	0.0	159.0	240.0	11.2	<0.63	0.0
165085	7/15/05	201	10.8	7.3	252	7.77	273	199.0	29.7	6.5	14.1	3.3	0.0	0.0	45.7	130.8	0.0	29.2	4.9	0.9	0.3	<0.05
220274	7/14/05		12.4	7.3	617	7.64	607	397.4	80.3	24.3	19.3	3.5	<0.005	<0.001	27.0	255.9	0.0	87.4	27.1	2.0	0.4	<0.05
220272	7/15/05		12.7	7.6	689	7.94	729	425.7	67.2	34.8	26.7	1.8	0.0	<0.001	17.7	188.2	0.0	83.6	96.4	4.7	0.0	0.0
58685	7/15/05	310	17.4	7.5	504	7.78	462	268.8	44.5	22.6	13.9	2.9	<0.005	<0.001	19.8	215.0	0.0	51.5	7.1	0.0	0.5	0.1
58712	7/14/05	148	12.2	7.2	902	7.41	838	511.4	96.8	44.3	29.8	4.8	<0.005	<0.001	21.8	309.9	0.0	115.0	35.8	10.4	0.0	0.0
165017	7/19/05	94	12.3	7.4	444	7.85	462	288.9	51.9	12.4	34.6	2.1	0.0	<0.001	9.1	237.2	0.0	44.7	15.7	1.5	0.1	<0.05
65071	7/19/05	39	10.9	7.1	470	7.54	467	280.7	54.8	14.3	20.7	3.2	<0.005	<0.001	20.8	197.4	0.0	49.4	16.6	3.5	0.2	<0.05
61051	7/20/05	123				7.31	451	288.8	59.1	14.7	17.3	3.2	0.0	<0.001	23.1	195.4	0.0	59.6	13.4	2.0	0.2	<0.05
61055	7/19/05	145	11.2	7.0	351	7.34	395	261.9	51.6	13.2	14.8	3.1	0.0	<0.001	23.5	183.7	0.0	54.4	9.4	1.2	0.2	<0.05
62802	7/19/05	130	15.5	7.4	561	7.78	543	325.7	55.3	29.5	17.0	2.5	0.0	<0.001	14.7	230.6	0.0	66.4	22.4	4.2	0.1	<0.05
62779	7/19/05	50	11.3	7.3	461	7.67	438	271.4	47.8	16.1	21.0	3.9	0.2	0.1	22.0	205.2	0.0	42.7	15.8	0.0	0.6	0.1
58737	7/19/05	207	11.1	7.0	549	7.41	524	320.8	75.1	17.1	10.6	5.5	0.1	0.0	24.0	198.6	0.0	61.0	17.2	12.4	<0.05	<0.05
134497	7/19/05	145	16.3	7.3	661	7.61	649	398.1	67.6	30.6	24.7	5.5	0.1	0.0	24.0	255.9	0.0	116.0	1.1	1.0	1.1	0.4
220386	7/22/05		11.7	7.4	411	7.78	564	377.2	60.7	17.0	37.1	3.4	0.0	<0.001	31.0	147.9	0.0	126.0	26.1	2.5	0.6	<0.05
153703	7/22/05	257				8.27	377	243.5	43.2	11.4	20.6	3.0	<0.005	<0.001	23.5	145.4	0.0	57.1	11.4	1.3	0.4	<0.05
182549	7/22/05	100	13.9	7.3	299	7.85	379	241.1	46.2	10.0	20.7	3.2	<0.005	<0.001	19.9	177.9	0.0	39.5	12.9	0.8	0.3	<0.05
60800	7/22/05	100	13.2	7.4	444	7.91	445	287.0	52.9	12.7	28.3	3.3	<0.005	<0.001	19.9	204.7	0.0	50.8	15.6	2.3	0.3	<0.05
134635	7/29/05	120	13.9	7.6	402	8.08	486	271.1	41.5	17.2	24.8	1.2	0.0	<0.001	22.7	214.5	0.0	40.8	17.0	0.0	0.2	<0.05
130936	7/29/05	140	15	7.7	379	8.04	418	251.3	44.8	14.8	22.0	2.1	<0.005	<0.001	18.1	202.3	0.0	36.5	13.3	0.0	0.1	<0.05
64880	7/29/05	86	11.7	7.4	574	7.95	658	390.5	67.1	18.8	51.6	2.4	0.0	<0.001	19.9	274.2	0.0	67.4	19.9	8.4	<0.05	<0.05
177845	8/1/05	198	10.6	7.2	524	7.53	543	334.8	66.9	26.0	11.6	11.4	0.0	0.1	19.9	253.2	0.0	54.8	17.2	1.9	0.3	<0.05
61619	8/1/05	70	11.4	6.9	338	7.74	341	216.2	40.6	8.8	17.3	3.0	0.0	<0.001	22.3	128.1	0.0	50.8	9.2	0.8	0.2	<0.05
177799	8/2/05	425	19.1	7.3	746	8.01	795	577.5	86.4	22.0	69.5	4.2	0.3	0.0	35.7	206.5	0.0	210.0	44.8	0.5	2.4	<0.05
	Maximum			7.9	1667	8.3	2580.0	1810.8	221.0	119.0	235.0	11.4	0.3	0.1	274.0	616.0	0.0	538.0	342.0	12.4	2.4	0.7
	Minimum			6.9	229	7.3	273.0	199.0	29.7	6.5	10.6	0.8	0.0	0.0	9.1	128.1	0.0	29.2	1.1	0.0	0.0	0.0
	Median			7.4	470	7.8	543.0	333.8	58.2	21.6	24.8	3.1	0.0	0.0	22.0	214.5	0.0	62.7	17.1	2.0	0.3	0.0

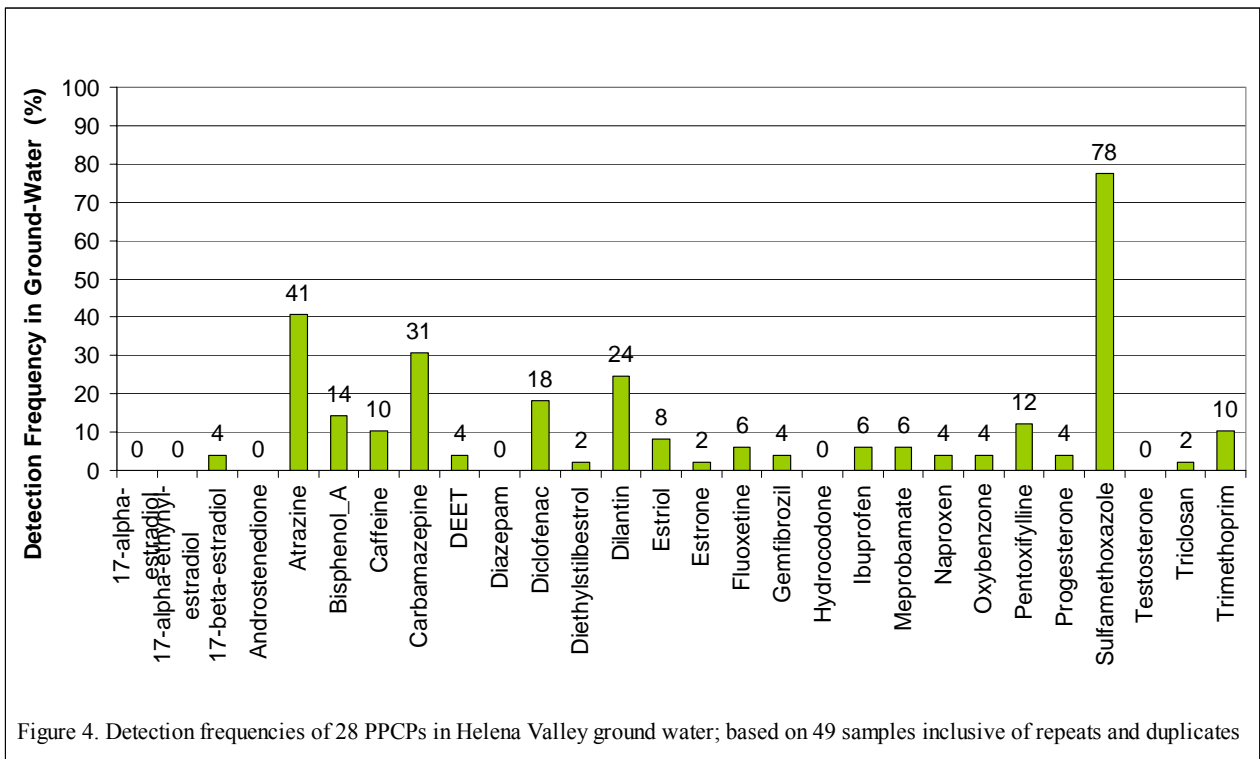
Table 1. Results of dissolved inorganic analyses for 35 well sites in the Helena Valley with maximum, minimum and median values, continued.

Gwic Id	Sample Date	As (ug/l)	B (ug/l)	Ba (ug/l)	Be (ug/l)	Br (ug/l)	Cd (ug/l)	Co (ug/l)	Cr (ug/l)	Cu (ug/l)	Li (ug/l)	Mo (ug/l)	Ni (ug/l)	Pb (ug/l)	Sb (ug/l)	Se (ug/l)	Sr (ug/l)	Ti (ug/l)	Tl (ug/l)	U (ug/l)	V (ug/l)	Zn (ug/l)	Zr (ug/l)
62523	5/24/05	0.0 <30		25.8 <2		<50	<1	<2	<2	4.2	6.4	10.7 <2	<2	<2	<1	385.0 <1	<5		6.3 <5		2.3 <2		
64826	5/23/05	1.8	69.9	47.7 <2		<50	<1	<2	<2	<2		35.7 <10	<2	<2	<2	1.0	441.0 <1	<5		5.9 <5		4.4 <2	
5756	5/23/05	2.7	88.9	68.0 <2		<100	<1	<2	<2	2.6	19.0 <10		<2	<2	<2	3.0	654.0 <1	<5		29.1	6.1	14.2 <5	
62570	5/23/05	0.0 <150		33.6 <2		<100	<1	<2	<10	<5		25.6 <10		3.3 <10	<10	7.8	940.0 <1	<25		17.7 <10		522.0 <2	
64806	5/23/05	2.0 <30		184.0 <2		<50	<1	<2	<2	<2		12.8 <10	<2	<2	<2	1.5	347.0 <1	<5		4.7 <5		8.5 <2	
194850	5/24/05	2.0 <30		184.0 <2		<50	<1	<2	<2	<2		12.8 <10	<2	<2	<2	1.5	347.0 <1	<5		4.7 <5		8.5 <2	
62369	5/31/05	3.2	188.0	35.6 <2		<50	<1	<2		2.2	44.7	30.3 <10	<2	<2	<2	1.7	502.0	1.1 <5		10.6	6.7	28.6 <2	
62575	5/31/05	3.2	188.0	36.4 <2		<50	<1	<2		2.2	25.0	29.7 <10	<2	<2	<2	1.8	492.0 <1	<5		10.7	6.8	15.4 <2	
65388	6/5/05	1.5 <30		61.3 <2		<500	<1	<2	<2		2.5	17.4 <10	<2	<2	<2	4.3	519.0 <1	<5		3.9 <5		14.5 <2	
170202	6/5/05	1.7	31.8	33.0 <2		109.0 <1		<2	<2		3.9	48.4 <10	<2		3.6 <2	4.3	638.0 <1	<5		5.5 <5		58.0 <2	
187850	5/30/05	1.6 <30		59.9 <2		203.0 <1		<2		3.2 <2		16.5 <10	<2	<2	<2	4.6	509.0 <1	<5		3.8 <5		7.9 <2	
206394	5/30/05	3.0 <30		99.0 <2		642.0 <1		<2	<2		3.4	20.9 <10	<2	<2	<2	13.3	1107.0	1.7 <5		4.3 <5		23.1 <2	
165085	7/15/05	1.0 <30		62.6 <2		<50	<1	<2	<2	<2		17.0 <10	<2	<2	<2	1.3	285.0 <1	<5		2.5 <5		10.5 <2	
220274	7/14/05	7.4	37.6	24.5 <2		77.0 <1		<2	<2		2.3	16.2 <10	<2	<2	<2	3.5	389.0 <1	<5		7.5 <5		12.1 <2	
220272	7/15/05	2.4 <30		72.5 <2			<1	<2	<2	<2		16.0 <10	<2	<2	<2	7.5	676.0 <1	<5		4.2 <5		28.3 <2	
58685	7/15/05	5.3	31.3	21.4 <2		<50	<1	<2	<2		4.0	9.6 <10	<2	<2	<2	1.6	247.0 <1	<5		4.5 <5		92.7 <2	
58712	7/14/05	4.0	77.7	86.0 <2		<500	<1	<2	<2		13.8	15.3	13.1 <2		6.3 <2	6.1	339.0 <1	<5		11.0 <5		10.5 <2	
165017	7/19/05	1.9	90.4	45.4 <2		<50	<1	<2	<2		22.5	10.6 <10	<2		4.5 <2	<1	242.0 <1	<25		0.0 <25		9.7 <2	
65071	7/19/05	2.7 <30		69.5 <2		<50	<1	<2	<2		2.1	22.6 <10	<2	<2	<2	<1	298.0 <1	<5		3.3 <5	<2		<2
61051	7/20/05	2.0 <30		61.6 <2		<50	<1	<2	<2		29.7	29.0 <10		3.4 <2	<2	<1	329.0 <1	<5		4.0 <5		19.3 <2	
61055	7/19/05	2.1 <30		54.1 <2		<50	<1	<2	<2	<2		29.1 <10	<2	<2	<2	<1	295.0 <1	<5		3.4 <5		2.6 <2	
62802	7/19/05	1.6 <30		29.1 <2		<50	<1	<2		2.1	8.5	10.2 <10	<2	<2	<2	2.0	226.0 <1	<20		2.2 <5		2.4 <2	
62779	7/19/05	17.1	59.2	33.8 <2		<50	<1	<2	<2		<2	47.1 <10	<2	<2	<2	<1	314.0 <1	<5		6.5 <5		7.4 <2	
58737	7/19/05	1.3 <30		4.0 <2		<50	<1	<2	<2		8.8	12.4 <10	<2		2.2 <2	<1	329.0 <1	<5		13.5	7.4	2.0 <2	
134497	7/19/05	0.0	32.0	21.6 <2		<100	<1	<2	<2	<2		12.4 <10	<2		2.2 <2	3.1	333.0 <1	<5		8.4 <5		2.9 <2	
220386	7/22/05	1.8	32.3	25.3 <2		178.0 <1		<2	<2	<2		20.0 <10	<2	<2	<2	7.1	503.0 <1	<5		7.3 <5	<2		<2
153703	7/22/05	1.8 <30		52.8 <2		83.0 <1		<2	<2		6.9	15.3 <10	<2	<2	<2	3.0	391.0 <1	<5		7.5 <5		2.9 <2	
182549	7/22/05	1.1	69.8	43.5 <2		<50	<1	<2	<2	<2		16.6	10.6 <2	<2	<2	1.1	425.0 <1	<5		10.3 <5		14.5 <2	
60800	7/22/05	1.8	62.7	51.0 <2		<50	<1	<2	<2	<2		18.2	18.4 <2	<2	<2	<1	494.0 <1	<5		20.1 <5	<2		<2
134635	7/29/05	2.1	90.4	59.6 <2		<50	<1	<2	<2	<2		18.9 <10	<2	<2	<2	1.4	272.0 <1	<5		2.6 <5		8.4 <2	
130936	7/29/05	1.8	77.4	71.5 <2		<50	<1	<2	<2		3.0	8.0 <10	<2	<2	<2	<1	212.0 <1	<5		1.8 <5	<2		<2
64880	7/29/05	2.7	59.2	48.9 <2		<50	<1	<2	<2		18.4	10.3 <10	<2	<2	<2	2.4	201.0 <1	<5		2.6 <5		16.5 <2	
177845	8/1/05	1.9 <30		14.5 <2		<50	<1	<2	<2	<2		18.6 <10	<2	<2	<2	2.4	201.0 <1	<5		2.6 <5		16.5 <2	
61619	8/1/05	1.7 <30		49.5 <2		<50	<1	<2	<2		22.0	16.5 <10	<2	<2	<2	4.2	327.0 <1	<5		4.6 <5		89.2 <2	
177799	8/2/05	11.4	315.0	15.9 <2		<50	<1	<2	<2	<2		85.8 <10	<2	<2	<2	2.8	708.0 <1	<5		2.2 <5		19.3 <2	
	Maximum	17.1	315.0	184.0 <2		642.0 <1		<2		3.2	44.7	85.8	18.4	3.4	6.3 <2	13.3	1107.0	1.7 <5		29.1	7.4	522.0 <2	
	Minimum	0.0	31.3	4.0 <2		77.0 <1		<2		2.1	2.1	6.4	10.6	3.3	2.2 <2	1.0	201.0	1.1 <5		0.0	6.1	2.0 <2	
	Median	1.9	69.9	48.9 <2		143.5 <1		<2		2.2	6.9	17.0	11.9	3.4	3.6 <2	2.9	347.0	1.4 <5		4.7	6.7	12.1 <2	

Results and Discussion

As shown on figures 4 and 5 and in Table 2, out of 28 PPCP analytes sampled from 38 sites, only 6 were not detected in ground water. Detection frequencies, concentrations, and locations of the PPCPs in ground-water samples are shown in figures 4, 5, and 6, respectively. The most frequently detected PPCPs are sulfamethoxazole (SMX), atrazine, carbamazepine, dilantin, and diclofenac with detection frequencies of 78-, 41-, 31-, 24-, and 18 percent, respectively. Concentrations of SMX range from no detection (ND) to 490 $\eta\text{g/L}$. Maximum concentrations of atrazine, carbamazepine, dilantin, and diclofenac are 130 $\eta\text{g/L}$, 420 $\eta\text{g/L}$, 22 $\eta\text{g/L}$, and 46 $\eta\text{g/L}$ respectively. Table 2 also shows that the occurrence and level of PPCP seems to have little or no correlation to the producing aquifer for each sampled well.

The locations of sites with samples containing SMX, atrazine and types of wastewater discharges in the Helena valley mapped on figure 7 indicate that although point-sources of wastewater discharges (municipal, storm water, industrial and a concentrated animal feeding operation) occur within the valley, onsite wastewater discharge appears to dominate water-quality samples. As used on figure 7, the definitions of high and moderate density are greater



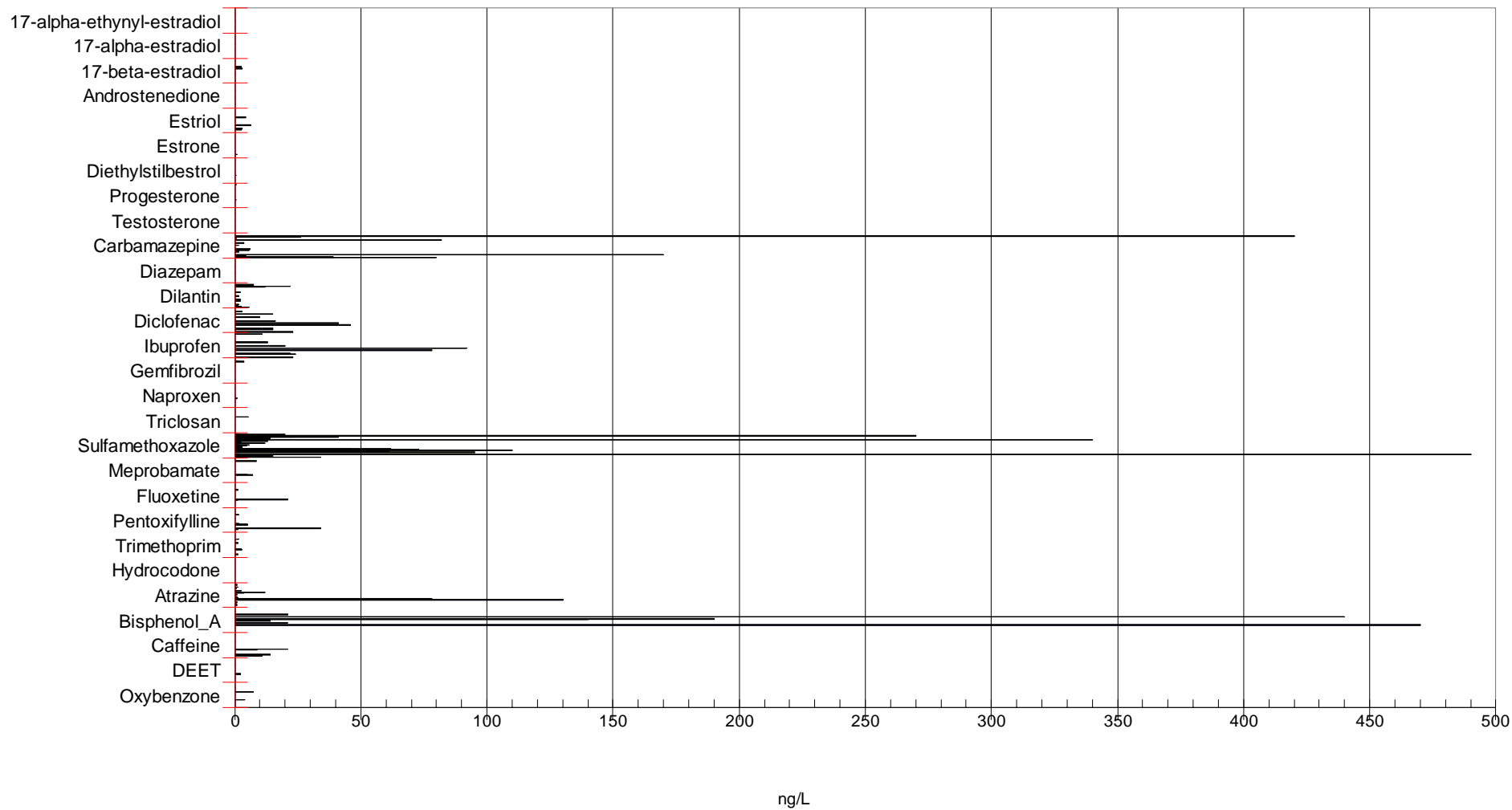
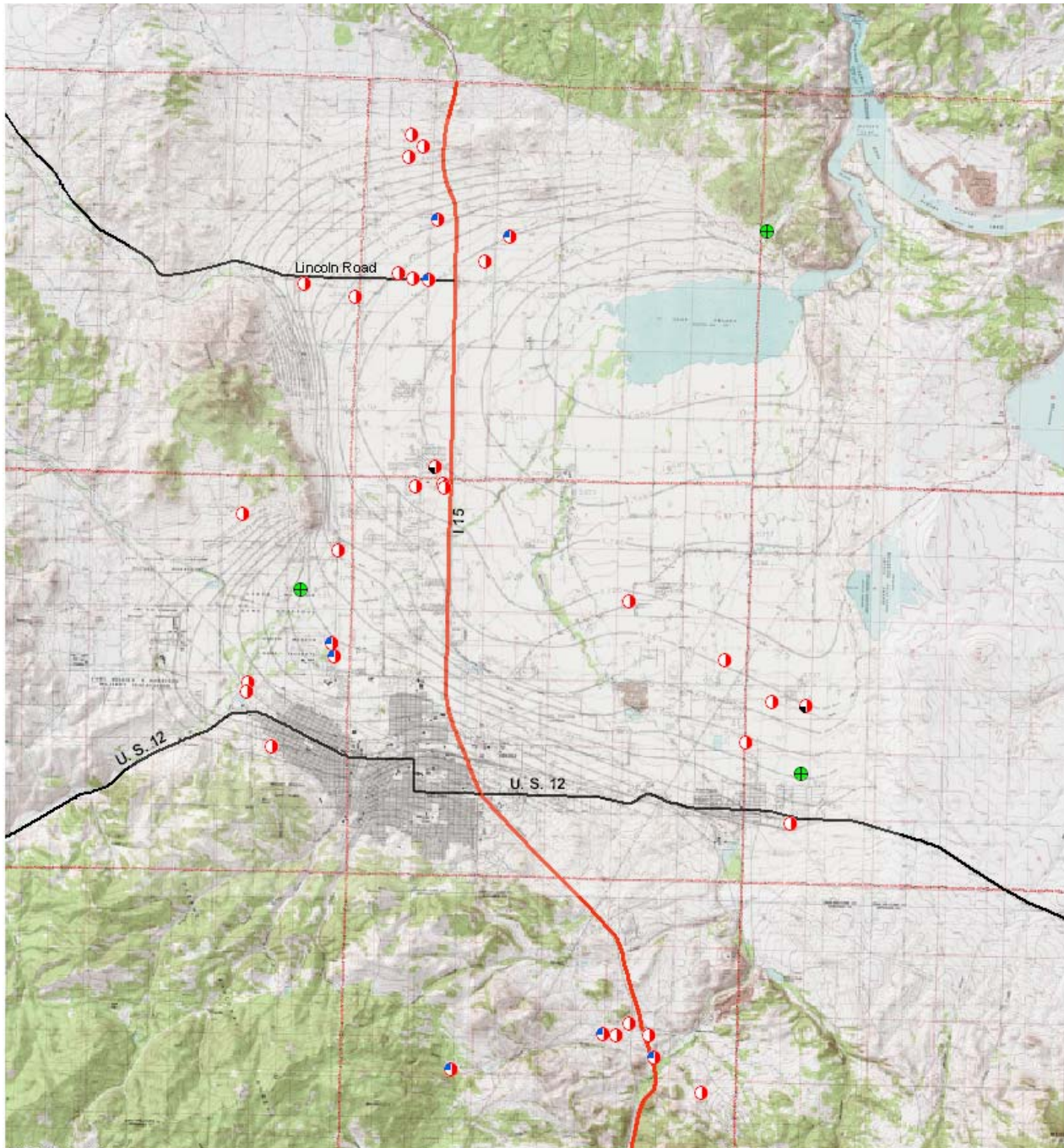


Figure 5. PPCP concentrations.



Explanation:

38 Sites Sampled
 18 PWSs included



Microbial indicators sampled and analyzed for each site:
 Total Coliform (8 sites positive for at least one sampling event)
 Escherichia coli (zero positive samples)
 Enterococci (2 sites positive for at least one sampling event)
 Coliphage - Male Specific and Somatic (zero positive samples)

Endocrine Disrupting and Pharmaceutically Active
 Compounds (EDCs and PACs): Positive detects at 35 of 38 sites



Figure 6. Locations and results of PPCPs and microbial indicators.

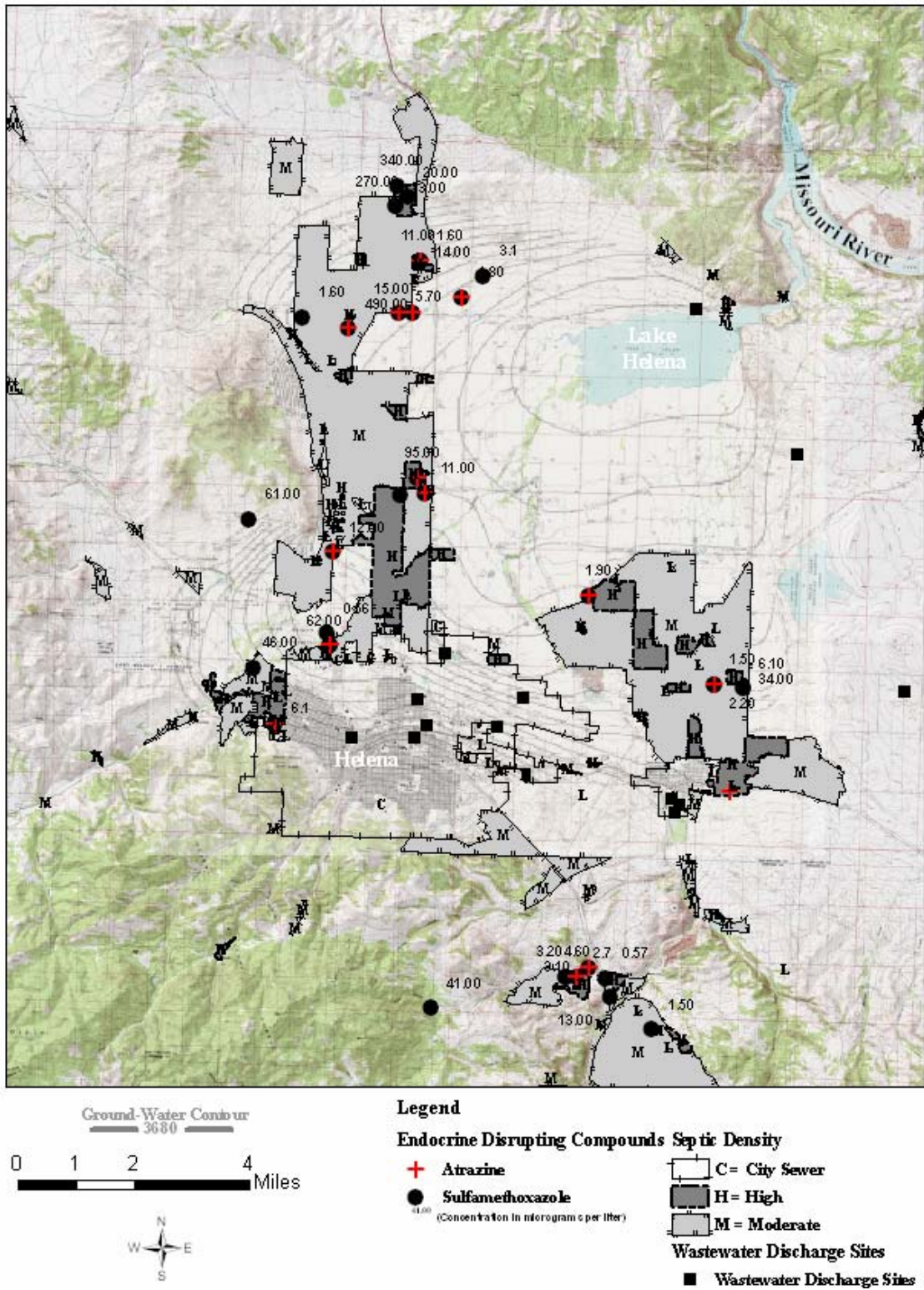


Figure 7. Wastewater discharges, SMX, and atrazine in the Helena valley.

than 300 septic systems (750 persons) per square mile and between 50 (125 persons) and 300 septic systems per square miles, respectively. Figure 8 and Table 3 correlate and compare the occurrence of chloride, nitrate, and total dissolved solids (TDS) with SMX and atrazine, the two most frequently detected PPCPs. Chloride, nitrate, and TDS are commonly used inorganic surrogate “indicators” of contamination from domestic wastewater systems. SMX showed no correlation (coefficient < 50%) to chloride, nitrate, or TDS. But atrazine demonstrated 80% correlation with chloride and almost 90% correlation with TDS, suggesting that atrazine may be occurring in domestic wastewater. Atrazine is a triazine herbicide used for the control of broadleaf and grassy weeds so its presence in domestic wastewater is not expected. SMX is undoubtedly also occurring in domestic wastewater, but it may not be conservative in its flow through septic tanks, perhaps being oxidized by chlorine or other compounds that may be found in wastewater (Dodd, 2004). Complete results of the inorganic analyses can be found at the website, <http://mbmgwic.mtech.edu>.

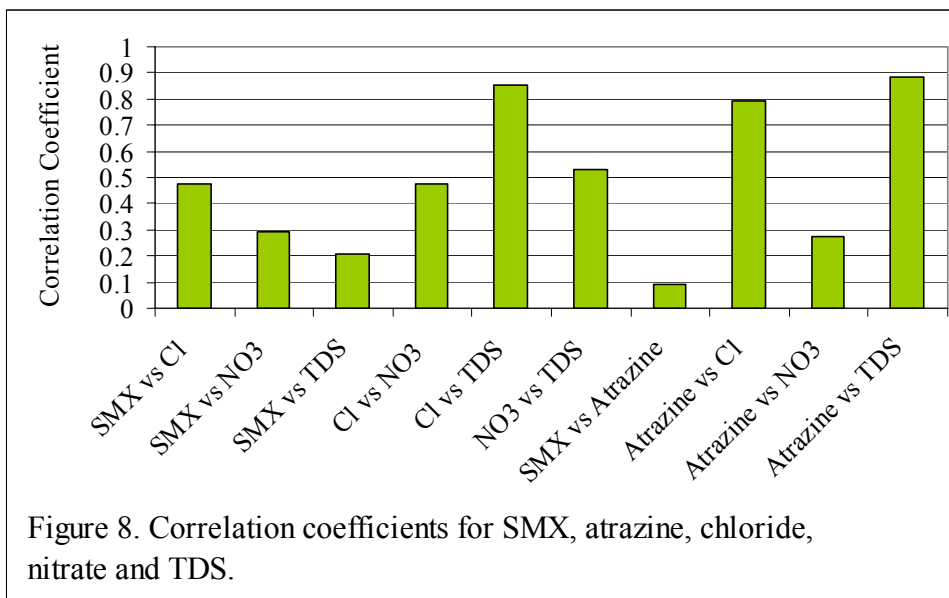


Table 4 presents the results of microbiological analyses of samples collected simultaneously with PPCP samples. As shown on Table 4 and on figure 6, there were no positive detections of male specific coliphage, somatic coliphage, or *E.coli* at any of the 38 sites. Yet PPCPs were detected at 32 of the 35 sites. Enterococci were present at 2 different sites at 3 different times of the year (April, July, and November). Ten positive total coliform samples were detected at 8 different sites. Although the 19 sites used by Kilbreath and others in 2004 were included in the sampling network for this project, his findings were not substantiated in this work. Sample site location within the valley (figure 6) does not appear to affect the presence or absence of PPCPs or microbial indicators of fecal contamination.

Table 3. Sulfamethoxazole (SMX), atrazine, total dissolved solids (TDS), chloride and nitrate in ground-water samples.

GWIC ID	SMX (ng/L)	Atrazine (ng/L)	TDS (mg/l)	Cl (mg/l)	NO3 (mg/l)
5756	12.00	3.50	790.2	29.5	5.4
58685	0.57	0.00	268.8	7.1	0.0
58712	3.10	1.20	511.4	35.8	10.4
58737	41.00	0.00	320.8	17.2	12.4
60800	34.00	0.00	287.0	15.6	2.3
60987	0.00	0.54	377.2	26.1	2.5
61051	11.00	1.30	288.8	13.4	2.0
61619	1.90	0.79	216.2	9.2	0.8
62369	61.00	0.00	546.5	17.6	9.5
62523	0.00	0.00	315.2	4.8	0.0
62570	110.00	130.00	1810.8	342.0	9.9
62575	0.56	0.00	543.3	17.6	9.4
62802	6.1	2.6	325.7	22.4	4.2
64806	3.1	0.00	528.7	17.1	8.6
64826	1.80	0.91	333.8	15.1	1.9
64880	5.70	0.96	390.5	19.9	8.4
65071	95.00	0.82	280.7	16.6	3.5
65388	490.00	0.59	364.0	45.2	3.9
134497	13.00	0.00	398.1	1.1	1.0
134635	14.00	0.66	271.1	17.0	0.0
137172	2.00	0.00	251.3	13.3	0.0
153703	0.00	0.00	243.5	11.4	1.3
165017	15.00	0.54	288.9	15.7	1.5
165085	0.00	0.00	199.0	4.9	0.9
170202	0.00	0.00	312.5	17.1	0.0
177799	2.7	12.00	577.5	44.8	0.5
177845	1.50	0.00	334.8	17.2	1.9
182549	2.20	0.68	241.1	12.9	0.8
187850	20.00	0.00	364.5	43.5	3.8
194850	1.60	0.00	446.3	17.6	0.7
206394	340.00	0.00	731.5	240.0	11.2
220272	270.00	0.00	425.7	96.4	4.7
220274	4.60	0.00	397.4	27.1	2.0

Table 4. Total coliform, *E.coli*, enterococcus and coliphage in ground-water samples.

GWIC ID	DPHHS Lab ID#	Sample Collection Date	Total Coliform, cfu**/100 ml	E. Coli, cfu/100 ml	Enterococci, cfu/100 ml	Coliphage, Male Specific	Coliphage, Somatic	GWIC ID	DPHHS Lab ID#	Sample Collection Date	Total Coliform, cfu**/100 ml	E. Coli, cfu/100 ml	Enterococci, cfu/100 ml	Coliphage, Male Specific	Coliphage, Somatic
60800	W0504-1598	04/27/05	<1	<1	1	Neg	Neg	177799	W0506-2231	06/07/05	<1	<1	<1	Neg	Neg
	W0511-4702	11/02/05	<1	<1	<1	Neg	Neg		W0511-4673	11/02/05	<1	<1	<1	Neg	Neg
177845	W0511-4670	11/02/05	<1	<1	<1	Neg	Neg	182549	W0504-1574	04/27/05	<1	<1	<1	Neg	Neg
165017	W0507-2958	07/19/05	4	<1	<1	Neg	Neg		W0511-4695	11/02/05	<1	<1	<1	Neg	Neg
	W0511-4686	11/02/05	<1	<1	<1	Neg	Neg	134497	W0507-2963	07/19/05	16	<1	<1	Neg	Neg
64826	W0504-1577	04/27/05	<1	<1	<1	Neg	Neg		W0511-4672	11/02/05	165	<1	<1	Neg	Neg
	W0511-4678	11/02/05	<1	<1	<1	Neg	Neg	62802	W0507-2960	07/19/05	<1	<1	<1	Neg	Neg
65388	W0505-1674	05/04/05	<1	<1	<1	Neg	Neg		W0511-4850	11/09/05	<1	<1	<1	Neg	Neg
	W0511-4687	11/02/05	<1	<1	<1	Neg	Neg	58685	W0506-2232	06/07/05	<1	<1	<1	Neg	Neg
60987	W0504-1597	04/27/05	<1	<1	<1	Neg	Neg		W0511-4674	11/02/05	<1	<1	<1	Neg	Neg
	W0511-4705	11/02/05	<1	<1	<1	Neg	Neg	206394	W0505-1673	05/04/05	<1	<1	<1	Neg	Neg
	W0504-1582	04/27/05	<1	<1	<1	Neg	Neg		W-511-4685	11/02/05	<1	<1	<1	Neg	Neg
153703	W0505-1677	05/04/05	<1	<1	<1	Neg	Neg	64806	W0504-1576	04/27/05	<1	<1	<1	Neg	Neg
	W0511-4694	11/02/05	<1	<1	<1	Neg	Neg		W0511-4677	11/02/05	4	<1	<1	Neg	Neg
65071	W0507-2959	07/19/05	<1	<1	2	Neg	Neg	134632	W0506-2235	06/07/05	1	<1	<1	Neg	Neg
	W0511-4682	11/02/05	<1	<1	<1	Neg	Neg		W0511-4680	11/02/05	<1	<1	<1	Neg	Neg
186800	W0511-4851	11/09/05	<1	<1	<1	Neg	Neg		W0511-4681	11/02/05	<1	<1	<1	Neg	Neg
194850	W0504-1580	04/27/05	<1	<1	<1	Neg	Neg	61051	W0507-2955	07/19/05	<1	<1	<1	Neg	Neg
	W0511-4684	11/02/05	<1	<1	<1	Neg	Neg		W0511-4704	11/02/05	<1	<1	<1	Neg	Neg
62369	W0505-1675	05/04/05	<1	<1	<1	Neg	Neg	61055	W0507-2956	07/19/05	<1	<1	<1	Neg	Neg
	W0511-4700	11/02/05	<1	<1	<1	Neg	Neg	58737	W0507-2962	07/19/05	4	<1	<1	Neg	Neg
62575	W0505-1676	05/04/05	9	<1	<1	Neg	Neg		W0511-4671	11/02/05	<1	<1	<1	Neg	Neg
	W0511-4698	11/02/05	12	<1	<1	Neg	Neg	220272	W0506-2230	06/08/05	<1	<1	<1	Neg	Neg
62570	W0504-1601	04/27/05	1	<1	<1	Neg	Neg		W0511-4683	11/02/05	<1	<1	<1	Neg	Neg
	W0511-4696	11/02/05	<1	<1	<1*	Neg	Neg	62779	W0507-2961	07/19/05	<1	<1	<1	Neg	Neg
	W0511-4697	11/02/05	<1	<1	1*	Neg	Neg	62523	W0504-1603	04/27/05	<1	<1	<1	Neg	Neg
62597	W0511-4849	11/09/05	<1	<1	<1	Neg	Neg		W0511-4701	11/02/05	<1	<1	<1	Neg	Neg
58712	W0506-2233	06/07/05	<1	<1	<1	Neg	Neg	61619	W0504-1600	04/27/05	<1	<1	<1	Neg	Neg
	W0511-4675	11/02/05	<1	<1	<1	Neg	Neg		W0511-4703	11/02/05	<1	<1	<1	Neg	Neg
	W0511-4676	11/02/05	<1	<1	<1	Neg	Neg	187850	W0504-1578	04/27/05	<1	<1	<1	Neg	Neg
170202	W0504-1575	04/27/05	<1	<1	<1	Neg	Neg		W0511-4689	11/02/05	<1	<1	<1	Neg	Neg
	W0511-4679	11/01/05	<1	<1	<1	Neg	Neg								
	W0511-4691	11/01/05	<1	<1	<1	Neg	Neg								
220274	W0506-2234	06/07/05	<1	<1	<1	Neg	Neg								
	W0511-4669	11/02/05	2	<1	<1	Neg	Neg								
64880	W0504-1579	04/27/05	<1	<1	<1	Neg	Neg								
	W0511-4688	11/02/05	<1	<1	<1	Neg	Neg								
165085	W0507-2957	07/19/05	<1	<1	<1	Neg	Neg								
	W-511-4692	11/02/05	<1	<1	<1	Neg	Neg								
	W0511-4693	11/02/05	<1	<1	<1	Neg	Neg								
137172	W0504-1581	04/27/05	<1	<1	<1	Neg	Neg								
	W0511-4690	11/02/05	<1	<1	<1	Neg	Neg								
160324	W0504-1599	04/27/05	<1	<1	<1	Neg	Neg								
5756	W0504-1602	04/27/05	<1	<1	<1	Neg	Neg								
	W0511-4699	11/02/05	<1	<1	<1	Neg	Neg								

* Growth in Enterococcus media

** cfu = colony forming units

The lack of positive coliphage detections in the presence of PPCPs point to its unsuitability as an indicator of fecal contamination in ground water. Whether coliphage is being attenuated in the subsurface as suggested by USGS (2005) or whether the poor reproducibility of results is attributable to laboratory or sampling error, the argument can be made that coliphage results are difficult to reproduce in the field, casting its utility as an indicator organism into question. Based on Table 4, it appears that of the five microorganisms, total coliform is the most reliable indicator of fecal contamination. Both *E.coli* and enterococci are associated with fresh sewage. A drawback to using these two indicators in regional ground-water settings is that they may die out more quickly or be less mobile in the subsurface than some waterborne pathogens, thereby rendering them even less suitable as indicator organisms than coliphage.

Conclusions

The Helena Valley in west-central Montana is experiencing rapid growth into previously un-sewered areas that rely on septic tanks and drainfields for onsite wastewater treatment and disposal. Detections of PPCPs in drinking water derived from wells is consistent with the findings of other investigators who are evaluating the occurrence of these compounds in ground-water and septic systems.

SMX and atrazine, the two most frequently detected compounds, were found at frequencies of 80% and 40% of samples, respectively. A comparison of SMX and atrazine with chloride, TDS and nitrate shows that atrazine demonstrates a strong correlation with chloride and TDS, two typical inorganic indicators of ground-water degradation from domestic wastewater. Further sampling and analysis of septic tank effluent should be conducted to verify whether atrazine is occurring in domestic wastewater.

While there are limited detections of total coliform and enterococci, PPCPs are consistently detected in the absence of both male specific and somatic coliphage as well as *E.coli*. These results present implications for the suitability of coliphage and *E.coli* as indicators of fecal contamination in ground water. Total coliform, though detected at only 8 sites, was superior to coliphage as an indicator organism in this ground-water setting.

The human and aquatic effects from chronic exposure and ingestion of PPCPs at $\mu\text{g/L}$ or sub- $\eta\text{g/L}$ concentrations are mostly unknown as are potential synergistic or additive effects of exposure and ingestion of PPCP mixtures such as those found in the Helena valley. Since the ground water ultimately discharges to the Missouri River, it is hoped that effects on human health and aquatic ecosystems become better understood.

Future investigations should include fate and transport studies that evaluate the role of various aquifer properties and water-quality parameters in controlling PPCP sorption and degradation and coliphage survival and attenuation in the subsurface. PPCP fate in advanced onsite wastewater treatment systems should also be further evaluated.

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