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Relation Between Organic-Wastewater Compounds, Groundwater Geochemistry, and Well Characteristics for Selected Wells in Lansing, Michigan

Scientific Investigations Report 2013–5139

U.S. Department of the Interior
U.S. Geological Survey

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SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2013

Suggested citation:
Haack, S.K., and Luukkonen, C.L., 2013, Relation between organic-wastewater compounds, groundwater geochemistry, and well characteristics for selected wells in Lansing, Michigan: U.S. Geological Survey Scientific Investigations Report 2013–5139, 36 p., http://pubs.usgs.gov/sir/2013/5139/.

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Conversion Factors, Abbreviated Water-Quality Units, and Abbreviations

Inch/Pound to SI

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Volume	
million gallons (Mgal)	3,785	cubic meter (m^3)

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

AHTN	acetyl hexamethyl tetrahydronaphthalene
BWL	Lansing Board of Water and Light
CLLE	continuous liquid-liquid extraction
DEET	*N,N*-Diethyl-*meta*-toluamide
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatography/mass spectrometry
HHCB	hexahydrohexa-methylcyclopentabenzopyran
LRL	laboratory reporting level
LT-MDL	long-term method detection limit
MDL	method detection limit
NFM	National Field Manual
NWQL	National Water Quality Laboratory
OWC	organic-wastewater compound
R^2	coefficient of determination
USGS	U.S. Geological Survey
VOC	volatile organic compound

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Abstract

In 2010, groundwater from 20 Lansing Board of Water and Light (BWL) production wells was tested for 69 organic-wastewater compounds (OWCs). The OWCs detected in one-half of the sampled wells are widely used in industrial and environmental applications and commonly occur in many wastes and stormwater. To identify factors that contribute to the occurrence of these constituents in BWL wells, the U.S. Geological Survey (USGS) interpreted the results of these analyses and related detections of OWCs to local characteristics and groundwater geochemistry.

Analysis of groundwater-chemistry data collected by the BWL during routine monitoring from 1969 to 2011 indicates that the geochemistry of the BWL wells has changed over time, with the major difference being an increase in sodium and chloride. The concentrations of sodium and chloride were positively correlated to frequency of OWC detections. The BWL wells studied are all completed in the Saginaw aquifer, which consists of water-bearing sandstones of Pennsylvanian age. The Saginaw aquifer is underlain by the Parma-Bayport aquifer, and overlain by the Glacial aquifer. Two possible sources of sodium and chloride were evaluated: basin brines by way of the Parma-Bayport aquifer, and surficial sources by way of the Glacial aquifer. To determine if water from the underlying aquifer had influenced well-water geochemistry over time, the total dissolved solids concentration and changes in major ion concentrations were examined with respect to well depth, age, and pumping rate. To address a possible surficial source of sodium and chloride, 25 well, aquifer, or hydrologic characteristics, and 2 groundwater geochemistry variables that might influence whether, or the rate at which, water from the land surface could reach each well were compared to OWC detections and well chemistry.

The statistical tests performed during this study, using available variables, indicated that reduced time of travel of water from the land surface to the well opening was significantly correlated with detections of OWCs. No specific well or aquifer characteristic was correlated with OWC detections; however, wells with detections tended to have less modeled confining material thickness (as simulated in the regional groundwater flow model), which is an estimate of the amount of clay or shale between the Glacial and Saginaw aquifers. Additional analyses and collection of other data would be required to more conclusively identify the source and to determine the potential vulnerability of other wells because each BWL well may have a somewhat unique set of characteristics that governs its response to pumping. Therefore, it is possible that a relevant explanatory variable was not included in this analysis. The current patterns of geochemistry, and the relation between these patterns and volume of pumpage for the BWL wells, indicates other wells may be susceptible to OWCs in the future.

Introduction

Manufactured and natural organic compounds such as pharmaceuticals, antibiotics, surfactants, flame retardants, plasticizers, steroids, and other trace organics that are used and disposed of by modern society are widely recognized as environmental contaminants (Daughton and Ternes, 1999; Halling-Sørensen, and others, 1998; Boxall and others, 2003). Human and animal wastewater effluents are among the most important source pathways for many of these compounds into the aquatic environment (Ternes, 1998; Boxall and others, 2003; Paxéus, 2004; Glassmeyer and others, 2005; Lindqvist and others, 2005; Miao and others, 2005; Conn and others, 2006; Kinney and others, 2006; Reiner and others, 2007). These chemicals are often referred to as organic-wastewater compounds (OWCs) or micropollutants. Pharmaceuticals and a wide range of other OWCs have been detected in groundwater that serves as a drinking water source (Focazio and others, 2008). Pharmaceuticals also have been detected in finished drinking water (Reddersen and others, 2002; Zühlke and others, 2004; Jones and others, 2005; Benotti and others, 2009; Huerta-Fontela and others, 2011).

Selected OWCs have been extensively studied in groundwater that underlies cities (Osenbrück and others, 2007; Musolff and others, 2010), and there has been recent interest in the effects of the urban hydrologic cycle on groundwater quality in urban areas and on OWC detection (Eiswirth and Hötzl, 1997; Lerner, 2002; Schirmer and others, 2013). In the urban setting, groundwater is susceptible to recharge from not only precipitation directly, such as in parks and yards, but also from leakage from drains and pipes intended to carry drinking water, stormwater, industrial wastes, or sewage. In many urban areas, more water enters from leaking infrastructure than as recharge by precipitation (Lerner, 2002). Stormwater may recharge groundwater through a wide array of urban artificial recharge systems intended to convey stormwater away from impervious surfaces, such as grass filters, drainage swales, retention ponds and basins, and in some cases, subsurface infrastructure (Pitt and others, 1999). Stormwater may be contaminated with nutrients, pesticides, metals, pathogens from animal feces, and dissolved minerals (Pitt and others, 1999). Stormwater also may be contaminated with other organic compounds such as those that come from gasoline and oil, automobile exhaust, and industrial activity, as well as selected OWCs (Pitt and others, 1999; Vogel and others, 2009). Leaking underground infrastructure that carries sewage or industrial wastes has been reported to have a large influence on the detection of selected OWCs in urban groundwater (Eiswirth and Hötzl, 1997; Osenbrück and others, 2007; Musolff and others, 2010). In fact, some OWCs and pharmaceuticals have been used, along with nutrients, isotopes, industrial chemicals, and bacteria, as tracers of urban infrastructure failure (Barrett and others, 1999; Fenz and others, 2005; Strauch and others, 2008; Musolff and others, 2010).

Other studies by the USGS National Water-Quality Assessment Program have focused on understanding water-quality conditions and how natural and human activities affect these conditions. For example, recent studies have focused on identifying factors that affect vulnerability and the pathways and processes through which contaminants reach public-supply wells (Eberts and others, 2013). Wells with a larger percentage of young water are more vulnerable because contaminants may be rapidly transported to the well, and there is less time for chemical concentrations to be attenuated. Aquifers with highly permeable recharge areas or zones of high preferential flow are more vulnerable to surface contamination. Water recharging the aquifer that moves through urban areas or manmade recharge areas has the potential to pick up contaminants as it moves into the aquifer system. In addition, younger waters might be more vulnerable to contamination from human activities in urban or agricultural areas than older waters, which may have recharged the groundwater system before many of the contaminants associated with these activities were widely used. Natural geochemical conditions in the aquifer control contaminant behavior, such as mobility, transformation, or delayed transport. For example, in oxic conditions, some contaminants are not degraded and may be transported longer distances while other contaminants may be less mobile. Pumping stresses, particularly seasonal changes in pumping schedules, may affect groundwater quality and the age of the water withdrawn by the well. Higher pumping rates may induce recharge from different areas than when pumping is less or intermittent and will increase the area contributing water to a well. Additional important factors that may affect the vulnerability of wells to contamination are short circuits to the natural hydrologic cycle, which occur when water moves through sinkholes, dissolution features, or unplugged abandoned wells.

Analysis of Michigan surface-water samples (1998–2005) uncovered that the OWCs detected most frequently in Michigan were similar to those reported frequently in other studies nationwide (Haack, 2009). In 2010, chemical analyses of samples collected from 20 Lansing Board of Water and Light (BWL) production wells indicated the presence of 16 OWCs that are widely used in industrial and environmental applications and that commonly occur in many wastes and stormwater. Evaluation of the identified chemicals, with regard to well characteristics and groundwater-recharge areas, may be helpful in identifying factors that contribute to the occurrence of these chemicals in BWL wells. In 2012, the U.S. Geological Survey (USGS) entered into a cooperative agreement with the Tri-County Regional Planning Commission to interpret the results of these analyses and relate detections to well, aquifer, hydrologic, and land-use characteristics—specifically urban impervious areas.

Purpose and Scope

This report describes the investigation of well, aquifer, hydrologic, local characteristics, and general groundwater-chemistry variables (collected during routine monitoring by the BWL) and their relation to water-sample analyses for OWCs collected as part of this study from 20 Lansing area wells (table 1). Variables investigated include (1) well characteristics such as age and depth; (2) aquifer characteristics such as type, hydraulic conductivity, and composition; (3) hydrologic variables such as frequency of use and typical volumes of use; (4) general well-water quality such as major ion composition; and (5) local characteristics such as urban impervious areas and the 5, 10, and 20 year time-of-travel areas for wellhead protection. In this study, time-of-travel areas were defined as areas through which water moves from the wellhead-protection area to the pumping well in the specified amount of time. Relations among chemical detections and measured well variables are analyzed using statistical and geochemical methods. Statistical methods include Spearman Rank correlation, the nonparametric Wilcoxon-Mann-Whitney test, and discriminant analysis. Major ion composition is described using Piper plots and boxplots to characterize the geochemical changes in water quality revealed by historical data.

Table 1. Comparison of selected characteristics for sampled wells.

[NA, not available; -- not applicable]

Characteristic	LN-1	LN-2	LN-4	LN-5	LN-6
Age, in years	86	68	59	45	45
Number of organic wastewater compound detections	0	0	1	13	0
Well depth, in feet	500	388	400	436	410
Casing depth, in feet	NA	NA	NA	46	43.3
Percent aquifer material in the glacial deposits	43	6	65	0	88
Percent aquifer material in the Saginaw aquifer	76	84	78	78	66
Percent marginal aquifer material in the glacial deposits	43	0	0	0	0
Percent marginal aquifer material in the Saginaw aquifer	7	13	2	3	22
Percent confining material in the glacial deposits	0	60	0	100	0
Percent confining material in the Saginaw aquifer	6	4	20	19	13
Percent partially confining material in the glacial deposits	0	31	0	0	0
Percent partially confining material in the Saginaw aquifer	11	0	0	0	0
Glacial deposit thickness, in feet	30	35	43	45	40
Modeled confining material thickness, in feet	73.5	13.1	24.4	8.4	7.1
Modeled sandstone thickness, in feet	260.5	314.5	267.0	260.1	262.1
Estimated percent of Saginaw intercepted by well	100	94	100	100	100
Estimated completion below the Parma-Bayport interface, in feet	−89.1	21.3	−38.7	−90.5	−72.5
Minimum travel time from water table to upper sandstone layer, in years	14.5	3.9	2.4	1.2	1.2
Median travel time from water table to upper sandstone layer, in years	23.5	8.8	6.7	2.6	2.6
Minimum travel time from water table to middle sandstone layer, in years	32.6	14.9	6.7	4.0	4.2
Median travel time from water table to middle sandstone layer, in years	72.7	38.0	21.7	10.6	9.8
Estimated percent impervious area in 5-year time-of-travel area	--	10	56	35	1
Estimated percent impervious area in 10-year time-of-travel area	--	5	49	29	1
Estimated percent impervious area in 20-year time-of-travel area	9	18	72	41	1
Estimated total pumping simulating 1920–2005 conditions in the groundwater model, in million gallons	10,484.9	9,112.2	6,289.5	5,296	2,848
Estimated total pumping simulating 2000–5 conditions in the groundwater model, in million gallons	817.7	1,417.3	652.0	1,291.3	100.5

Table 1. Comparison of selected characteristics for sampled wells.—Continued

[NA, not available; -- not applicable]

Characteristic	LN-8	LN-9	LN-11	LN-12	LN-14
Age, in years	43	32	43	40	38
Number of organic wastewater compound detections	1	0	3	0	4
Well depth, in feet	345	395	360	390	377
Casing depth, in feet	NA	65	53	112.5	77
Percent aquifer material in the glacial deposits	0	21	100	23	47
Percent aquifer material in the Saginaw aquifer	80	89	89	96	86
Percent marginal aquifer material in the glacial deposits	52	15	0	0	0
Percent marginal aquifer material in the Saginaw aquifer	2	2	0	0	3
Percent confining material in the glacial deposits	0	5	0	5	7
Percent confining material in the Saginaw aquifer	8	2	11	4	10
Percent partially confining material in the glacial deposits	48	60	0	73	43
Percent partially confining material in the Saginaw aquifer	11	7	0	0	0
Glacial deposit thickness, in feet	62	62	40	110	70
Modeled confining material thickness, in feet	2.5	.6	16.0	4.5	1.1
Modeled sandstone thickness, in feet	235.1	248.5	253.9	242.6	262.1
Estimated percent of Saginaw intercepted by well	100	100	100	100	100
Estimated completion below the Parma-Bayport interface, in feet	.9	−61.2	−20.7	−39.4	−29.8
Minimum travel time from water table to upper sandstone layer, in years	4.8	8.2	4.8	5.4	2.5
Median travel time from water table to upper sandstone layer, in years	25.4	17.4	9.6	7.7	4.9
Minimum travel time from water table to middle sandstone layer, in years	37.7	27.0	12.3	8.9	6.6
Median travel time from water table to middle sandstone layer, in years	64.4	70.7	27.0	17.4	13.2
Estimated percent impervious area in 5-year time-of-travel area	49	--	0	--	26
Estimated percent impervious area in 10-year time-of-travel area	43	61	1	13	26
Estimated percent impervious area in 20-year time-of-travel area	32	52	1	10	21
Estimated total pumping simulating 1920–2005 conditions in the groundwater model, in million gallons	1,447.9	5,109.4	2,961.3	2,849.9	3,067.4
Estimated total pumping simulating 2000–5 conditions in the groundwater model, in million gallons	447.9	1,142.9	336.9	491.1	737

Table 1. Comparison of selected characteristics for sampled wells.—Continued

[NA, not available; -- not applicable]

Characteristic	LN-15	LN-16	LN-17	LN-18	LN-19
Age, in years	38	36	43	42	17
Number of organic wastewater compound detections	2	2	0	1	3
Well depth, in feet	416	335	352	398	310
Casing depth, in feet	70.3	77.3	73.3	76.7	103
Percent aquifer material in the glacial deposits	36	15	58	70	78
Percent aquifer material in the Saginaw aquifer	100	82	68	90	77
Percent marginal aquifer material in the glacial deposits	0	0	0	16	0
Percent marginal aquifer material in the Saginaw aquifer	0	1	0	1	2
Percent confining material in the glacial deposits	45	0	0	7	0
Percent confining material in the Saginaw aquifer	0	14	28	9	16
Percent partially confining material in the glacial deposits	18	79	34	0	21
Percent partially confining material in the Saginaw aquifer	0	3	3	0	5
Glacial deposit thickness, in feet	66	47	65	74	95
Modeled confining material thickness, in feet	1.0	11.9	7.7	2.0	4.6
Modeled sandstone thickness, in feet	245.7	243.7	208.6	222.4	226.1
Estimated percent of Saginaw intercepted by well	100	97	100	100	90
Estimated completion below the Parma-Bayport interface, in feet	−103.8	8.2	−16.2	−63.8	22.0
Minimum travel time from water table to upper sandstone layer, in years	1.8	4.2	5.0	4.3	1.3
Median travel time from water table to upper sandstone layer, in years	3.3	10.0	10.8	14.9	3.8
Minimum travel time from water table to middle sandstone layer, in years	5.6	17.5	21.0	30.2	7.2
Median travel time from water table to middle sandstone layer, in years	10.9	54.8	25.9	61.4	28.6
Estimated percent impervious area in 5-year time-of-travel area	8	40	1	35	0
Estimated percent impervious area in 10-year time-of-travel area	8	39	14	34	7
Estimated percent impervious area in 20-year time-of-travel area	7	31	13	20	7
Estimated total pumping simulating 1920–2005 conditions in the groundwater model, in million gallons	3,868.8	2,668.3	864.0	3,171.9	1,076.6
Estimated total pumping simulating 2000–5 conditions in the groundwater model, in million gallons	1,273.2	754.8	108.3	857.3	1,076.6

Table 1. Comparison of selected characteristics for sampled wells.—Continued

[NA, not available; -- not applicable]

Characteristic	LN-20	LN-22	LN-23	LN-24	LN-28
Age, in years	46	54	59	86	56
Number of organic wastewater compound detections	0	0	1	0	0
Well depth, in feet	405	430	410	430	445
Casing depth, in feet	54	NA	NA	NA	NA
Percent aquifer material in the glacial deposits	82	68	86	100	76
Percent aquifer material in the Saginaw aquifer	69	56	63	54	66
Percent marginal aquifer material in the glacial deposits	0	0	0	0	0
Percent marginal aquifer material in the Saginaw aquifer	11	4	10	33	10
Percent confining material in the glacial deposits	15	0	0	0	2
Percent confining material in the Saginaw aquifer	20	31	23	13	24
Percent partially confining material in the glacial deposits	0	32	0	0	22
Percent partially confining material in the Saginaw aquifer	0	9	2	0	1
Glacial deposit thickness, in feet	34	62	35	65	45
Modeled confining material thickness, in feet	11.9	93.9	22.0	48.4	75.0
Modeled sandstone thickness, in feet	282.1	261.3	271.5	218.8	270.7
Estimated percent of Saginaw intercepted by well	100	96	100	100	98
Estimated completion below the Parma-Bayport interface, in feet	1.2	16.2	−44.3	−78.2	9.1
Minimum travel time from water table to upper sandstone layer, in years	3.3	32.6	2.3	26.1	20.0
Median travel time from water table to upper sandstone layer, in years	21.9	59.0	5.1	39.1	34.0
Minimum travel time from water table to middle sandstone layer, in years	19.6	64.6	6.6	45.4	43.1
Median travel time from water table to middle sandstone layer, in years	123.7	92.2	25.5	89.5	72.5
Estimated percent impervious area in 5-year time-of-travel area	0	--	50	--	--
Estimated percent impervious area in 10-year time-of-travel area	8	--	64	--	--
Estimated percent impervious area in 20-year time-of-travel area	16	--	72	--	77
Estimated total pumping simulating 1920–2005 conditions in the groundwater model, in million gallons	5,880.0	5,555.5	4,909.2	6,959.8	4,674.2
Estimated total pumping simulating 2000–5 conditions in the groundwater model, in million gallons	1,435.3	412.5	297	297.5	674.4

Previous Studies

Previous studies have contributed to the knowledge of the groundwater resources in the Tri-County region (fig. 1) and were used in the analysis of the groundwater chemistry and the determination of potential explanatory variables. Wood (1969) described the hydrogeology and geochemistry of groundwater in the Saginaw Formation. Meissner and others (1996) reported geochemical characteristics of groundwater from the Saginaw aquifer based on analyses conducted during 1985–87. Wahrer and others (1996) reported geochemical characteristics of groundwater from the Glacial aquifer based on analyses conducted during 1985–87. A report by Holtschlag and others (1996) documents the development of the regional groundwater-flow model and the determination of contributing areas for most production wells in the TriCounty region. Luukkonen (2009) describes the refinement of the original 1996 model, optimization simulations to evaluate alternative groundwater-pumping scenarios under selected management constraints, and a preliminary characterization of groundwater geochemistry.

Description of Study Area

Lansing is located in northwestern Ingham County in the south central part of the Lower Peninsula of Michigan (fig. 1). Groundwater is withdrawn primarily from the Saginaw aquifer, which consists of water bearing sandstones in the Grand River and Saginaw Formations of Pennsylvanian age (fig. 2); however, in Ingham County, erosion has removed most of the Grand River Formation (Vanlier and others, 1973). The Saginaw aquifer can be divided into three units separated by an interbedded series consisting of shale and sandstone lenses and a lowermost shale unit (table 2); however, division into these units also is uncertain in some areas because of incomplete data and heterogeneities within these units (D.B. Westjohn, U.S. Geological Survey, oral commun., 2005). Groundwater from the Glacial aquifer is an important source in some places. Aquifers in the glacial deposits are composed primarily of coarse alluvial and outwash materials. Eskers—buried outwash deposits and thin beds of sand and gravel within the till—are potential sources of water to wells in some areas (Vanlier and others, 1973). The stratigraphic relation between units present in the Lansing area is shown in figure 2; however, these assignments between formations are somewhat uncertain because no lithologic differences or stratigraphic horizons mark a change from one horizon to the next (Westjohn and Weaver, 1996).

Table 2. Approximate ranges in thickness for Saginaw Formation units.

Unit	Range in thickness (feet)
Upper sandstone layer	21–115
Interbedded series unit	1–5
Middle sandstone layer	55–150
Lower shale unit	1–69
Lower sandstone layer	30–119

Methods

Sampling Procedures

All water samples were collected by BWL personnel. USGS standard sampling methods for water samples to be analyzed for the chemicals described in this report are documented in the USGS National Field Manual (NFM; *http://water.usgs.gov/owq/FieldManual/*). Prior to sampling, USGS personnel visited selected well sites with BWL personnel to develop appropriate sample-collection procedures. Among other considerations, the sampling methods for wastewater compounds (Wilde and others, 2004) proscribe the use or wearing of any personal care products that might contain the compounds to be analyzed; document that only sampling and processing equipment made of fluorocarbon polymers, glass, aluminum, or stainless steel should be used; specify the types of bottles (laboratory baked, brown glass) to be used for sample collection; and provide information on the proper cleaning and storing of sampling equipment. In general, raw water samples were collected directly from a tap at the wellhead by BWL personnel following USGS training, and sample collection took place under a protective plastic sheet. Following collection and processing, samples were immediately chilled and shipped overnight to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado.

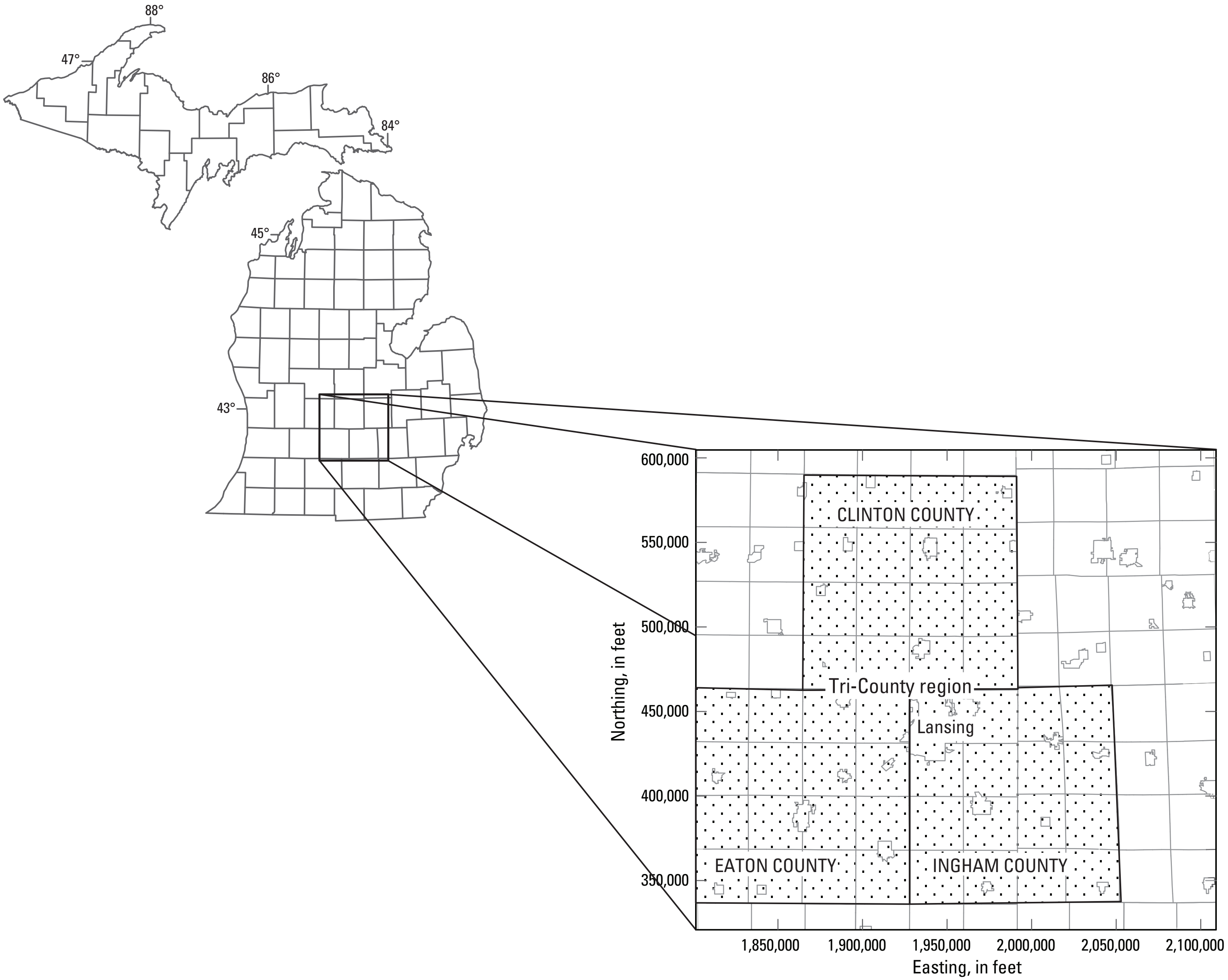


Figure 1. Location of the city of Lansing in the Tri-County region of the Lower Peninsula of Michigan.

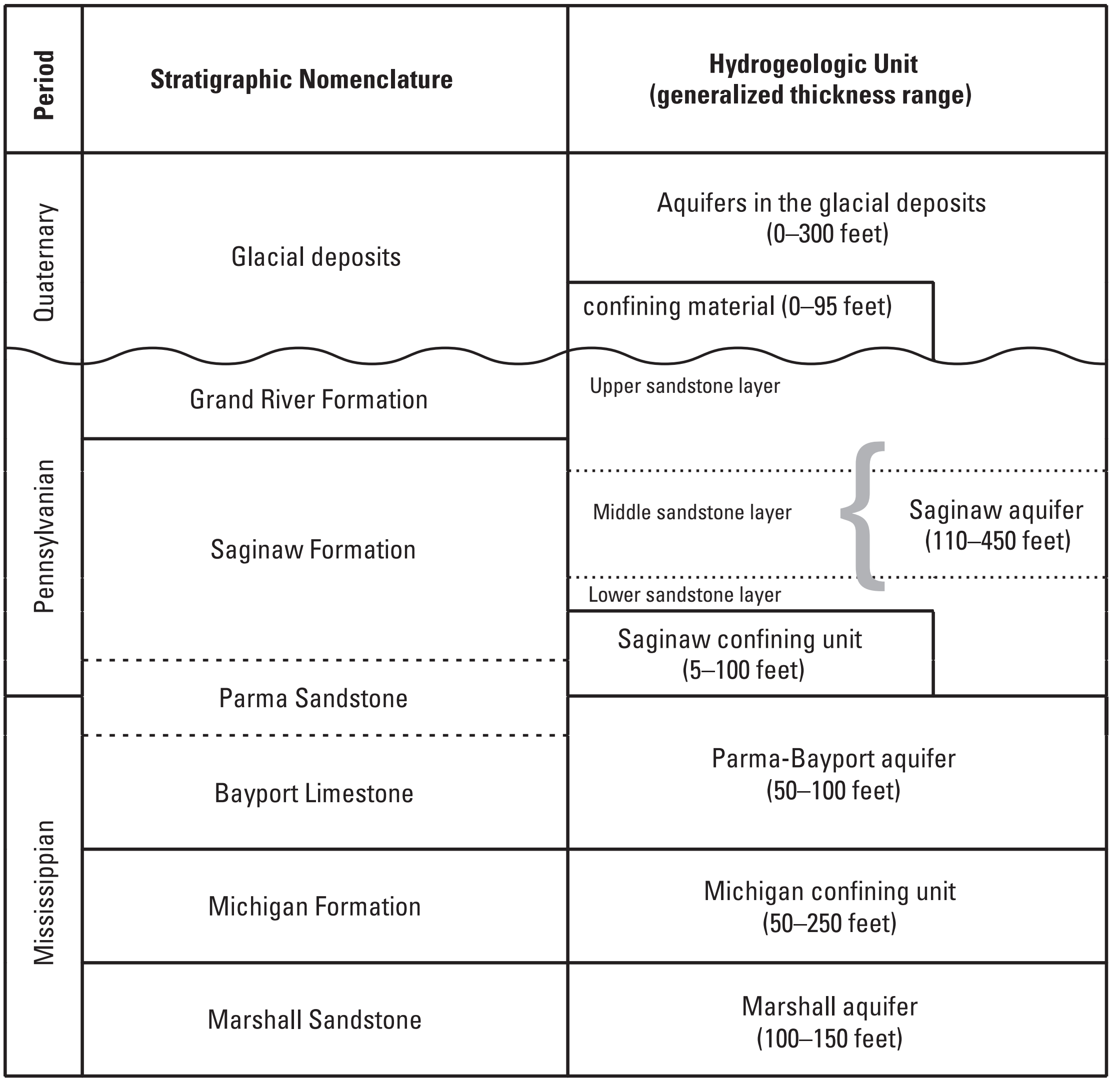


Figure 2. Stratigraphic nomenclature and hydrogeologic units, Lansing, Michigan area. [Note: Figure denotes relation between units present in the Lansing area and not the complete depositional history from the Mississippian through Quaternary periods. The Parma Sandstone is considered by some researchers to form the basal part of the Pennsylvanian Saginaw Formation. Other researchers have assigned the lower part of the Parma Sandstone to the late Mississippian. Dashed line indicates the uncertainty in the placement of the Parma Sandstone into the Pennsylvanian or the Mississippian periods. The Parma Sandstone is hydraulically connected to the Bayport Limestone and these units together form the Parma-Bayport aquifer. Dotted lines represent aquifer layers within the Saginaw aquifer. See table 2 for approximate Saginaw layer thicknesses.]

Analytical Procedures

Wastewater compounds analyzed are identified in table 3. Wastewater compounds were analyzed on unfiltered water samples, using continuous liquid-liquid extraction (CLLE) for sample preparation. Concentrated extracts were analyzed by capillary-column gas chromatography/mass spectrometry (GC/MS). The analytical method used in this report relies on the application of mass-spectrometric techniques, which provide compound-specific fragments that, when coupled with chromatographic-retention characteristics, produce unambiguous identification of each compound. In addition, the specific criteria for the identification of each compound are based upon analysis of authentic standards for all compounds. Further information on the method can be found in Zaugg and others (2006).

Table 3. Wastewater-method compounds and their possible uses or sources.

[RL, reporting limit; µg/L, micrograms per liter; CAS, Chemical Abstracts Service; NA, not applicable; PAH, polycyclic aromatic hydrocarbon]

Name	RL (µg/L)	Synonym	CAS number	Possible uses or sources[1]
1,4-Dichlorobenzene	0.2		106-46-7	Moth repellent, fumigant, deodorant
1-Methylnaphthalene	.2		90-12-0	Gasoline, diesel fuel, or crude oil
2,6-Dimethylnaphthalene	.2		581-42-0	Diesel/kerosene (trace in gasoline)
2-Methylnaphthalene	.2		91-57-6	Gasoline, diesel fuel, or crude oil
3,4-Dichlorophenyl isocyanate	1.6		102-36-3	Dye, chemical manufacture
3-Methyl-1(H)-indole	.2	Skatole	83-34-1	Fragrance, stench in feces and coal tar
3-tert-Butyl-4-hydroxy anisole	.2	BHA	25013-16-5	Antioxidant, general preservative
4-Cumylphenol	.2		599-64-4	Nonionic detergent metabolite
4-n-Octylphenol	.2		1806-26-4	Nonionic detergent metabolite
4-Nonylphenol, total	2	p-Nonylphenol	84852-15-3	Nonionic detergent metabolite
4-Nonylphenol monoethoxylate	1.6	NP1EO	NA	Nonionic detergent metabolite
4-Nonylphenol diethoxylate	3	NP2EO	NA	Nonionic detergent metabolite
4-tert-Octylphenol	.4		140-66-9	Nonionic detergent metabolite
4-tert-Octylphenol diethoxylate	.5	OP2EO	NA	Nonionic detergent metabolite
4-tert-Octylphenol monoethoxylate	1	OP1EO	NA	Nonionic detergent metabolite
5-Methyl-1H-benzotriazole	2		136-85-6	Antioxidant in antifreeze and deicers
Acetophenone	.4		98-86-2	Fragrance in detergent and foods
Acetyl hexamethyl tetrahydronaphthalene	.2	AHTN	21145-77-7	Musk fragrance
Anthracene	.2		120-12-7	Wood preservative, in tar/crude oil
Anthraquinone	.2		84-65-1	Dye/textiles, bird repellent
Atrazine	.2		1912-24-9	Herbicide
BDE conger 47	.3	Polybrominated diphenyl ether	5436-43-1	Flame retardant
Benzo[a]pyrene	.2	Benz[a]pyrene	50-32-8	Regulated PAH
Benzophenone	.2		119-61-9	Fixative for perfumes and soaps
beta-Sitosterol	2		83-46-5	Plant sterol
beta-Stigmastanol	2	Stigmastanol	19466-47-8	Plant sterol
Bis 2-ethylhexyl phthalate	2		117-81-7	Plasticizer
Bisphenol A	.4		80-05-7	Polycarbonate resins, antioxidant
Bromacil	.8		314-40-9	Herbicide, noncrop usage
Bromoform	.2	Tribromomethane	75-25-2	Ozonation byproduct, explosives
Caffeine	.2		58-08-2	Beverages, diuretic
Camphor	.2		76-22-2	Flavor, odorant, ointments
Carbaryl	.2		63-25-2	Insecticide, crop and garden use
Carbazole	.2		86-74-8	Dyes, explosives and lubricants
Chlorpyrifos	.2		2921-88-2	Insecticide, termite and pest control
Cholesterol	2		57-88-5	Fecal indicator, plant sterol
3-*beta*-Coprostanol	2		360-68-9	Carnivore fecal indicator
Cotinine	.8		486-56-6	Primary nicotine metabolite
Diazinon	.2		333-41-5	Insecticide, ants and flies
Dichlorvos	.2		62-73-7	Insecticide, pets and grains
Diethyl phthalate	.2		84-66-2	Plasticizer

Table 3. Wastewater-method compounds and their possible uses or sources.—Continued

[RL, reporting limit; µg/L, micrograms per liter; CAS, Chemical Abstracts Service; NA, not applicable; PAH, polycyclic aromatic hydrocarbon]

Name	RL (µg/L)	Synonym	CAS number	Possible uses or sources[1]
d-Limonene	0.2		5989-27-5	Fungicide, antimicrobial, fragrance
Fluoranthene	.2		206-44-0	Component of coal tar and asphalt
Hexahydrohexamethyl-cyclopentabenzopyran	.2	HHCB	1222-05-5	Musk fragrance
Indole	.2		120-72-9	Pesticide inert, fragrance in coffee
Isoborneol	.2		124-76-5	Fragrance in perfume
Isophorone	.2		78-59-1	Solvent
Isopropylbenzene	.2	Cumene	98-82-8	Phenol/acetone, fuels and paint thinner
Isoquinoline	.2		119-65-3	Flavors and fragrances
Menthol	.2		89-78-1	Flavor in cigarettes, cough drops
Metalaxyl	.2		57837-19-1	Herbicide, fungicide
Methyl salicylate	.2		119-36-8	Liniment, food, beverage, sun block
Metolachlor	.2		51218-45-2	Herbicide
N,N-Diethyl-*meta*-toluamide	.2	DEET	134-62-3	Insect repellent
Naphthalene	.2		91-20-3	Fumigant, moth repellent, gasoline
para-Cresol	.2		106-44-5	Wood preservative
Pentachlorophenol	.8		87-86-5	Wood preservative, fungicide
Phenanthrene	.2		85-01-8	Explosives, tar, diesel and crude oil
Phenol	.2		108-95-2	Disinfectant
Prometon	.2		1610-18-0	Herbicide, noncrop
Pyrene	.2		129-00-0	Component of coal tar and asphalt
Tetrachloroethylene	.4	PCE	127-18-4	Solvent, degreaser
Tributyl phosphate	.2		126-73-8	Antifoaming agent, flame retardant
Triclosan	.2		3380-34-5	Disinfectant, antimicrobial
Triethyl citrate	.2	Ethyl citrate	77-93-0	Cosmetics and pharmaceuticals
Triphenyl phosphate	.2		115-86-6	Plasticizer, resin wax, roofing paper
Tri(2-butoxyethyl) phosphate	.3		78-51-3	Flame retardant
Tri(2-chloroethyl) phosphate	.2		3380-34-5	Plasticizer, flame retardant
Tri(dichlorisopropyl) phosphate	.2		77-93-0	Flame retardant

[1] From Zaugg and others, 2006.

The NWQL uses a statistic called the long-term method detection limit (LT-MDL; Bonn, 2008), which is similar to the current U.S. Environmental Protection Agency (EPA) method detection limit (MDL) (U.S. Environmental Protection Agency, 2005), and is determined on an annual basis for each compound. The LT-MDL is statistically defined as identical to the EPA-MDL: the smallest measured concentration that can be reported with 99-percent confidence that the concentration of the compound is greater than zero, and there is less than a 1-percent chance of a false-positive determination. It is calculated over an extended period of time, and therefore may change over time. In conjunction with the LT-MDL, NWQL uses a laboratory reporting level (LRL) set higher than the LTMDL. LRLs also may change over time if LT-MDLs are revised after annual reviews.

Currently (2013), the NWQL reports without qualification most analytical results greater than the LTMDL (Bonn, 2008). Concentrations of some compounds are always reported as estimated owing to the analytical method used having highly variable performance for that particular compound. Concentrations of some chemicals detected at less than the LRL may be reported if the analytical method includes compound-specific identification—usually a matching spectral signature—such as for the compounds discussed in this report. For these results, there is greater uncertainty as to the actual concentration.

Quality Assurance and Quality Control

Several quality-control sample types are used to interpret ambient environmental concentrations of wastewater compounds in aqueous samples. The quality-control sample types used in this study included field blanks and replicate environmental samples.

Field blanks characterize the likelihood of positive bias or contamination owing to field and laboratory handling. Field blanks consisted of laboratory-grade organic-free water that was processed in the field and laboratory in the same manner as environmental samples. Two field blanks were submitted, and no wastewater constituent was detected in either field blank.

Replicate samples are used to characterize the amount of variability associated with sample collection, processing, and analysis. One field replicate sample was collected for well LN-11. Pyrene was detected at less than the LT-MDL in both samples, but the replicate also had detections of bis (2ethylhexyl) phthalate and phenanthrene (both less than the LT-MDL) although the original sample did not. Discrepancies in results for a primary sample and its replicate may arise when concentrations are near the LT-MDL. Prior studies have indicated that when data are available from more sensitive assays, constituents less than the LT-MDL in the current assay are indeed present in the sample (Haack, 2009). Replicate results indicate two considerations for interpretation of concentrations near the limits of detection for the wastewater method. First, even though a compound is reported as not detected, it may indeed be present. This is particularly true for the analysis used, because the reporting levels are relatively high in comparison to methods that might target individual constituents. Second, when the compound is reported with an estimated concentration, there is confidence that it is indeed present in the sample, but with more uncertainty regarding the actual concentration. Based on these considerations, compounds detected by the wastewater method in either a primary environmental sample or an associated replicate, but not both, should be considered present in the sample.

Statistical Analyses

All statistical tests were evaluated at probabilities (p-values) of obtaining results by chance of less than 0.05 ($p < 0.05$). Spearman Rank Correlation was performed to evaluate correlations among variables. The Wilcoxon-Mann-Whitney test is a nonparametric hypothesis test that was used to determine the probability that the center of the distributions of defined groups of wells were the same. This test, like most nonparametric hypothesis tests, requires no assumptions about the sample population distribution, is resistant to outliers, and is more appropriate for small sample sizes where non-normality is more difficult to detect. Discriminant analysis was used to determine whether one or more quantitative variables could be found to classify the sample data into the two groups (wells with detections and wells without any detections). Canonical discriminant analysis was used to investigate whether there was a linear combination of the quantitative variables that best described the differences between the defined groups of wells.

Well-Water Quality

Organic-Wastewater Compounds Detected

Of the 69 constituents analyzed in samples from 20 wells, 16 were detected. Ten wells had no detections, and 10 had 1 or more compounds detected. The wastewater compounds detected in this study are indicated in bold type in table 4. Three compounds were detected at greater than the LRL: fluoranthene, pyrene, and phenanthrene. Two compounds (isopropylbenzene and phenol) were detected at greater than the LT-MDL but less than the LRL, and estimated concentrations were provided. All remaining compound detections were less than the LT-MDL. Because there were only three results that were at or greater than the LRL, only the presence or absence of a compound or the total number of OWC constituents detected in each well was considered in subsequent evaluations.

All OWCs detected were in the “Industrial chemicals” category. Some of these industrial chemicals are very persistent, such as the polycyclic aromatic hydrocarbons (table 4), whereas the persistence of others varies depending on the environmental setting, such as soil type and condition, and whether or not aerobic. Chemicals in the “Industrial chemicals” category often are detected in groundwater at sites with industrial pollution, but usually at much higher concentrations than those reported in this study. Industrial chemicals also may be found in human wastewater and septic waste, accompanied by pharmaceuticals, chemicals associated with personal care compounds, and human or animal wastes. Chemicals in the “Industrial chemicals” category also are prevalent in urban stormwater (Pitt and others, 1999; Vogel and others, 2009). Polycyclic aromatic hydrocarbons are prevalent in stormwater runoff from pavement treated with sealcoat, which is commonly used in the Midwest of the U.S. (Watts and others, 2010). Vogel and others (2009) applied the same analysis method to stormwater samples in Nebraska as was used for the BWL wells, and did not detect bis (2ethylhexyl) phthalate, isopropylbenzene, or pentachlorophenol, but did detect all remaining constituents detected in BWL wells. Bis (2-ethylhexyl) phthalate and pentachlorophenol are among a list of proposed European stormwater priority pollutants (Eriksson and others, 2007).

Table 4. Wastewater-method compounds grouped by chemical use or typical source.

[Compounds in bold detected in this study]

Industrial chemicals	Human wastewater[1]	Detergent metabolites
1,4-dichlorobenzene	AHTN	4-n octylphenol
1-methylnaphthalene	benzophenone	4-tert-octylphenol
2,6-dimethylnaphthalene	HHCB	4-tert-octylphenol diethoxylate
2-methylnaphthalene	tri(2-chloroethyl)phosphate	4-tert-octylphenol monoethoxylate
3-methyl-1H-indole	tributyl phosphate	nonylphenol diethoxylate
3,4- dichlorophenyl isocyanate	triclosan	octylphenol diethoxylate
4-cumylphenol	tri(dichlorisopropyl)phosphate	*para*-nonylphenol
3-tert-Butyl-4-hydroxy anisole	triethyl citrate (ethyl citrate)	
5-methyl-1H-benzotriazole		**Other**
anthracene	**Human pharmaceutical or metabolite**	acetophenone
anthraquinone	caffeine	camphor
benzo[a]pyrene	cotinine	d-limonene
bisphenol-A	**Sterols**	menthol
bis 2-ethylhexyl phthalate	3-*beta*-Coprostanol (animal)	methyl salicylate
bromoform	*beta*-Sitosterol (plants)	N,N-diethyl-*meta*-toluamide (DEET)
carbazole	*beta*-Stigmastanol (plants)	
diethyl phthalate	Cholesterol (animal)	
fluoranthene		
indole	**Urban herbicides and pesticides**	
isoborneol	bromacil	
isophorone	diazinon	
isopropyl benzene	prometon	
isoquinolone		
naphthalene	**Agricultural herbicides and pesticides**	
para-Cresol	atrazine	
pentachlorophenol	carbaryl	
phenanthrene	chlorpyrifos	
phenol	dichlorvos	
BDE congener 47	metalaxyl	
pyrene	metolachlor	
tetrachloroethylene		
triphenyl phosphate		
tris (2-butoxyethyl) phosphate		

[1] Compounds detected in 100 percent of wastewater-treatment-plant effluents (Glassmeyer and others, 2005).

Although well-water samples were analyzed for an assortment of wastewater-related and potentially human-use compounds, no compound that would most likely be associated with human or animal waste was detected. Table 4 groups all compounds analyzed into typical chemical type and source categories. Constituents detected in 100 percent of wastewater-treatment-plant effluents (Glassmeyer and others, 2005), and human pharmaceuticals or their metabolites were not detected. Likewise, the animal- or plant-derived sterols often found in fecal material from humans or animals were not detected. There were no detections of the nonyl- or octyl-phenols that often derive from detergent breakdown or may be included in a variety of cleaning agents, and therefore are common in human wastewater and septic waste (Glassmeyer and others, 2005). There were no detections of the insect repellent N,N-diethyl-meta-toluamide (DEET) or of the remaining “Other” category of chemicals, many of which are used in personal care products. Using the same or equivalent methods, many of the above categories of chemicals are detectable in surface water in Michigan and elsewhere, especially where wastewater-treatments plants influence surface water (Haack, 2009). Using equivalent methods, the USGS tested 47 groundwater sites in 18 States (Barnes and others, 2008). In that study, coprostanol was detected at 4.3 percent of the tested sites, caffeine at 12.8 percent, 4-octylphenol monoethoxylate at 19.1 percent, triclosan at 14.9 percent, and DEET at 34.8 percent. Additionally, using equivalent methods, the USGS tested 25 groundwater wells that are used as source water for drinking water in 13 States (Focazio and others, 2008). In that study, coprostanol was detected at 4 percent, triclosan at 8 percent, DEET at 12 percent, caffeine was not tested, and 4-octylphenol monoethoxylate was not detected at any site. Analyses were done for three pesticides in the current study, and none of the three were detected. Diazinon, an urban-use pesticide, was not detected by Barnes and others (2008), but was detected at 4 percent of sites by Focazio and others (2008); prometon and bromacil were not tested. Results from these two USGS National surveys indicate that the chemical categories not detected in the current study do occur in groundwater at some locations across the U.S. Overall results show that the tested BWL wells did not contain chemicals typically associated with human wastewater.

Frequency of detection for compounds in the current study is reported in table 5 and is compared to the frequency of detection of the same compounds in the two USGS groundwater studies previously mentioned (Barnes and others, 2008; Focazio and others, 2008). In general, chemicals detected in the BWL wells also have been detected in other groundwater wells across the country.

Well-Water Geochemistry

With the exception of 1985–95, selected BWL wells have been tested each year as part of a routine water-quality monitoring program for concentrations of the major cations calcium, magnesium, and sodium, and for the major anions chloride and sulfate. Bicarbonate concentrations were collected during routine monitoring for 1969–2006 and were estimated using alkalinity and pH for 2007–11 because bicarbonate concentrations were not collected by the BWL for recent years. In addition, pH and specific conductance were measured in most recent years. The number of years of data depends on well age, which ranges from 17 to 86 years in service. Well age was calculated to be 2013 minus the approximate installation date for each well. Thirteen wells had data from 1969 to 1977 and from 2007 to 2011. Two wells had data only from 2000 or later.

Change in Well-Water Geochemistry Over Time

Well-water geochemistry has changed over time (fig. 3). Thirteen wells were tested for major ions at least once from 1969 to 1977 and from 2007 to 2011. For each of the 13 wells, a single year of analysis in each date range (1971 or earliest year for 1969–77 and most recent for 2007–11) was selected. Well LN-28 had a reported sodium concentration of less than 5 milligrams per liter (mg/L) in 2011; this value was replaced by 2.5 mg/L, one-half the detection limit, for subsequent calculations. Table 6 shows the median ion concentrations for each date range for these 13 wells. The Wilcoxon-Mann-Whitney test indicates that the 2007–11 concentration is significantly greater ($p < 0.05$) than the 1969–77 concentration for all ions except bicarbonate, which has significantly decreased (table 6). In 2009, one BWL well exceeded the EPA Secondary Maximum Contaminant level for chloride, which is 250 mg/L.

Because total dissolved solids were not always measured, total dissolved solids were estimated as the sum of the major cations and anions, and the estimated value was compared to available measured values. Estimated total dissolved solids were linearly related to measured dissolved solids with a regression coefficient of determination (R^2) of 0.95, indicating good agreement between the two methods. Total dissolved solids increased from 1969 to 1977 and from 2007 to 2011, as would be expected in the case where ion concentrations were increasing. The median value for the 13 wells with data from both date ranges was 618 mg/L for 1969–77 and 815 mg/L for 2007–11; furthermore, the Wilcoxon-Mann-Whitney test indicated the increase is significant ($p = 0.0403$).

Table 5. Comparison of organic wastewater compound detections in the current study with detections in other studies, and identification of U.S. Environmental Protection Agency drinking water regulated compounds.

[EPA, U.S. Environmental Protection Agency; µg/L, micrograms per liter; nt, not tested]

Chemicals detected	This study (number of samples)	Frequency of detection, in percent			EPA drinking water regulated contaminant	Drinking water maximum contaminant level (µg/L)
		This study	USGS National Groundwater Survey[1] (47 samples)	USGS National Drinking Water Sources Survey[2] (25 samples)		
Polycyclic aromatic hydrocarbons						
Naphthalene	2	10.0	[3]8.5	0.0		
1-Methylnaphthalene	1	5.0	nt	.0		
2-Methylnaphthalene	1	5.0	nt	.0		
Anthracene	1	5.0	2.1	.0		
Fluoranthene	1	5.0	4.3	4.0		
Phenanthrene	2	10.0	2.1	4.0		
Pyrene	6	30.0	2.1	4.0		
9,10-Anthraquinone	1	5.0	nt	4.0		
Plasticizers						
Bis(2-ethylhexyl)phthalate	5	25.0	nt	nt	yes	6
Bisphenol A	1	5.0	29.8	[3]20		
Diethyl phthalate	2	10.0	nt	nt		
Other chemicals						
Carbazole	1	5.0	nt	nt		
Indole	1	5.0	nt	0.0		
Isopropylbenzene	2	10.0	nt	.0		
Pentachlorophenol	1	5.0	nt	4.0	yes	1
Phenol	1	5.0	[3,4]0	[4]32		

[1] Barnes and others (2008).

[2] Focazio and others (2008).

[3] Compound detected in at least one field blank in the indicated study.

[4] Reporting limit 2 µg/L as opposed to 0.2 µg/L in the current study.

Table 6. Median concentrations of major ions and significance levels for 13 wells having data in both date ranges: 1969–77 and 2007–11.

[Concentrations in milligrams per liter]

Ion	Median concentration		Wilcoxon-Mann-Whitney p-value
	1969–77	2007–11	
Calcium	104	140	0.0111
Magnesium	32	46	.0023
Sodium	9	29	.0088
Bicarbonate	386	310	.0004
Chloride	17	68	.0156
Sulfate	47	150	.007

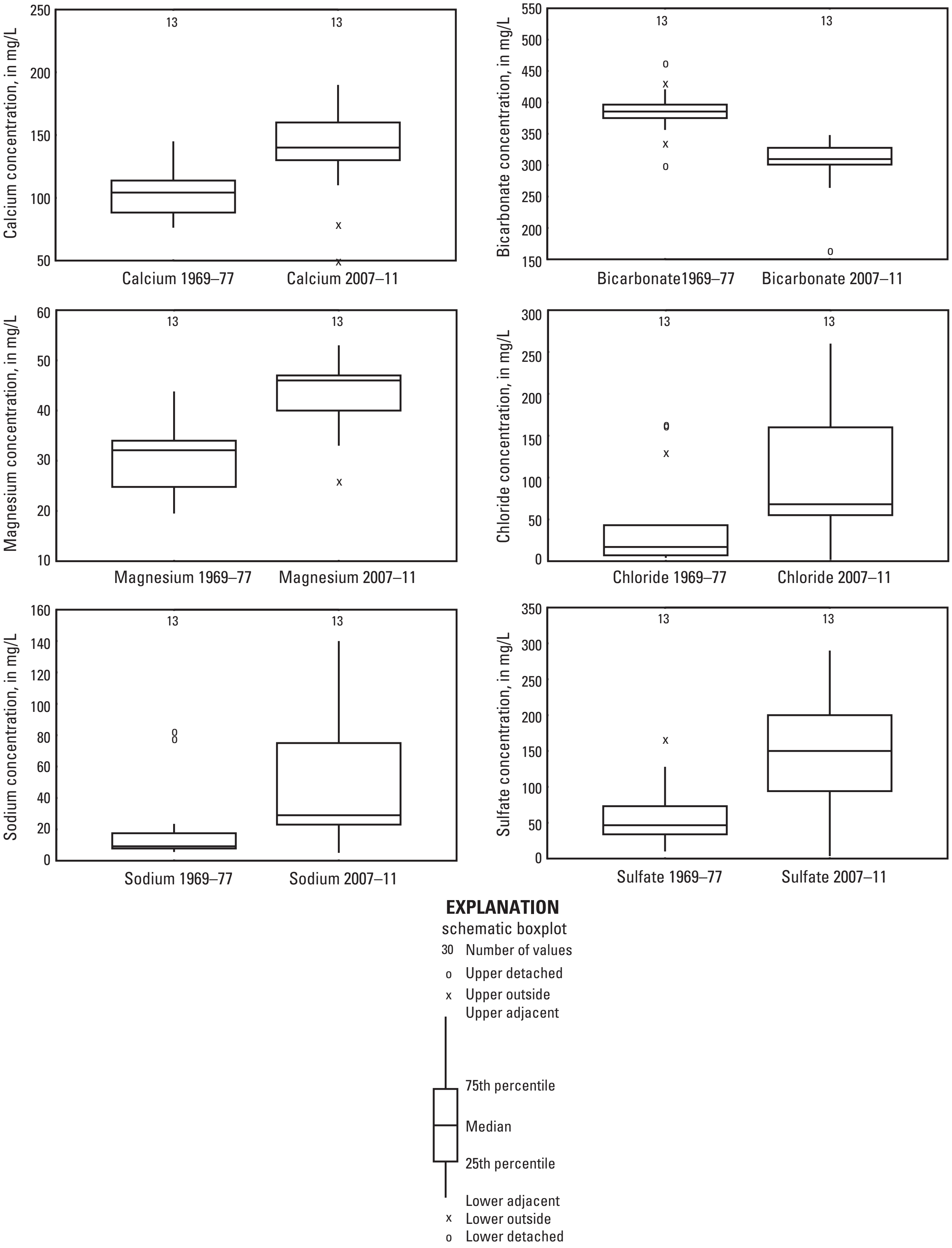


Figure 3. Major ion concentrations, in milligrams per liter (mg/L), for 13 studied Lansing Board of Water and Light wells having data in the years 1969–77 and 2007–11, Lansing area, Michigan.

Wells with and without OWC detections have changed in different ways over time, as indicated in figure 4. Although the eight wells without detections and the five wells with detections both show increases over time in all ions except bicarbonate, the five wells with detections demonstrate a larger increase in sodium and chloride. Median chloride percentage relative to the other anions in wells with detections was 0.10 for 1969–77 and 0.31 for 2007–11; median chloride percentage relative to the other anions in wells without any detections was 0.03 for 1969–77 and 0.14 for 2007–11. In addition, the five wells with OWC detections have shown less increase over time in sulfate. The Wilcoxon-Mann-Whitney test indicates that during 2007–11, the chloride and sodium concentrations are significantly greater in wells with detections, as compared to wells without detections ($p = 0.0123$ and $p = 0.0139$).

The major ion composition of well water also can be evaluated using “Piper plots.” Piper (1944) developed a diagram that enables the classification of water on the basis of the major ions. The Piper plot allows easy visual comparison of the chemistry of water samples, identification of water with similar characteristics, and identification of any change in water chemistry. For the plot, concentrations of the ions are converted to milliequivalents per liter, and then the relative percentages of the cations and anions are determined. For purposes of the plot, cations and anions each sum to 100 percent. If any cation or anion comprises 50 percent or more of the milliequivalents for a water sample, the water is said to be dominated by that ion.

Piper plots for the 13 wells with data from both 1969–77 and 2007–11 are shown in figure 5. During 1969–77, all wells could be characterized as bicarbonate dominated water, since bicarbonate constituted more than 50 percent of the anion composition. All but two wells could be characterized as calcium dominant during 1969–77; the remaining two wells had nearly as much sodium as calcium, and these two wells also had nearly 50 percent chloride composition. By 2007–11, although most wells still were dominated by calcium, two wells had gained significant sodium since 1969–77. In addition, few wells remained bicarbonate-dominated, with chloride and (or) sulfate replacing bicarbonate. Additionally, as indicated by figure 5, wells with and without OWC detections have different geochemistry during 2007–11, with a tendency for a greater proportion of chloride and sodium in four of the five wells with detections. Piper plots show clearly that although the geochemistry of all 13 BWL wells tested has changed over time, wells with OWC detections tended to change in a different manner than those without detections.

Current Well-Water Geochemistry

Piper plots of current well-water geochemistry (most recent analysis from 2007–11) for all 20 BWL wells are presented in figure 6. Comparison of figure 6 with figure 5 indicates that the well-water geochemistry of the seven newer wells (which did not have data for 1969–77) falls into the calcium-bicarbonate dominated category, with one of the seven wells having nearly 50 percent sodium and 50 percent chloride composition. The Wilcoxon-Mann-Whitney test indicates that currently (2013), wells with OWC detections have significantly more sodium and chloride than wells without detections ($p = 0.0235$ and $p = 0.0457$). The total number of detections of OWCs in the BWL wells during 2007–11 was inversely correlated (Spearman Rank Correlation) with the bicarbonate content and the sulfate-to-chloride ratio of those wells. In other words, wells with OWC detections had lower bicarbonate content, more chloride, and less sulfate than wells without detections. These patterns are seen in figures 6 and 7.

Factors That Influence Well-Water Geochemistry and OWC Detections

Role of Basin Brines

The primary natural source of sodium and chloride to wells in the study area would be basin brines. Meissner and others (1996) described water from the Saginaw aquifer in the study area as primarily calcium-bicarbonate dominant and characteristic of water recently recharged to an aquifer. Calcium-sulfate and sodium-chloride dominant water was detected in the Saginaw aquifer, but not typically in the study area. Sodium-chloride dominant water was detected in the Saginaw Bay area, about 70 miles (mi) northeast of the study area (Meissner and others, 1996). That sodium-chloride water was typically much higher in dissolved solids (1,000–5,000 mg/L) and was attributed to mixing with brine from within the aquifer or from underlying aquifers. In addition, Meissner and others (1996) reported that in the southern portion of the aquifer where the study area is located, chloride was typically less than 10 mg/L, but that chloride concentrations in water from the Parma-Bayport aquifer, which lies below the Saginaw aquifer, could reach values greater than 100,000 mg/L. They also reported that higher chloride concentrations were associated with deep wells in the Saginaw aquifer, and that high chloride concentrations in such wells could be due to mixing with underlying waters. Meissner and others (1996) reported that sulfate concentrations in the Saginaw aquifer generally were less than 100 mg/L in the southern portion of the aquifer, encompassing the study area. A natural source of sulfate could be dissolution of gypsum (calcium sulfate) in the Parma-Bayport aquifer, or in portions of the Saginaw aquifer. Because of the interest in the influence of basin brines on BWL well-water quality, several evaluations of the existing well-water geochemistry were conducted.

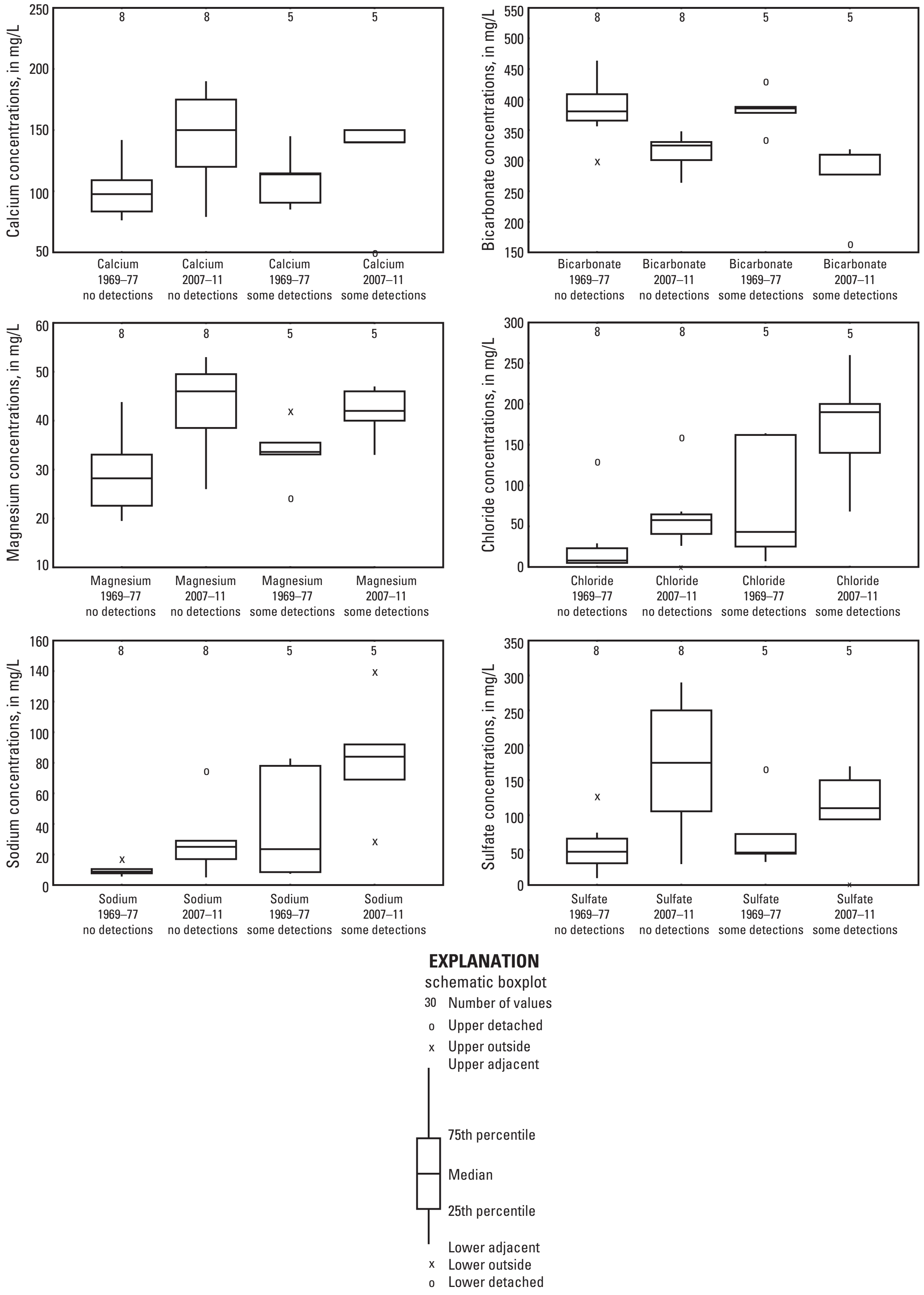
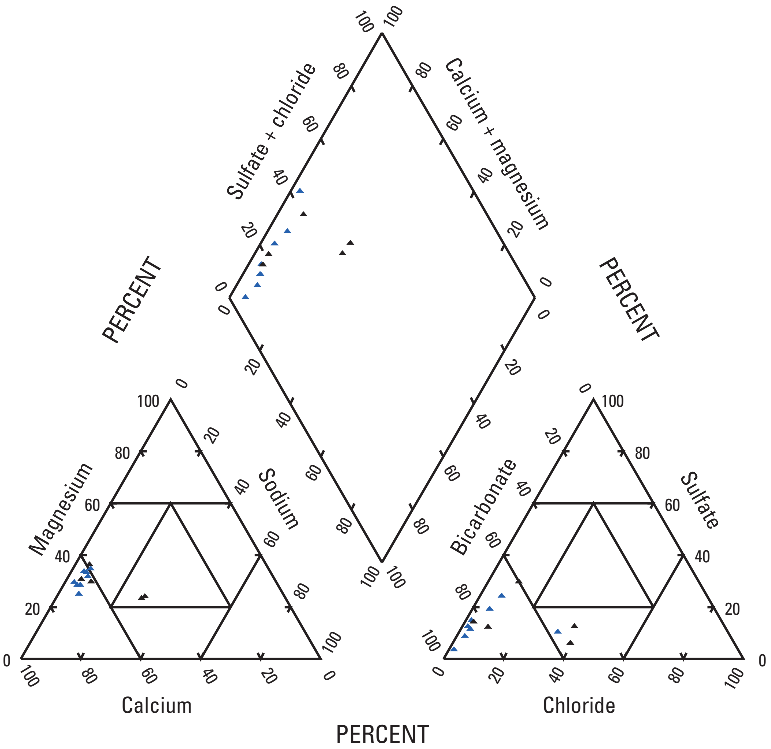


Figure 4. Major ion concentrations, in milligrams per liter (mg/L), for 13 studied Lansing Board of Water and Light wells having data in the years 1969–77 and 2007–11 divided into groups with and without detections of organic-wastewater compounds, Lansing area, Michigan.


Historical data (1969–77)

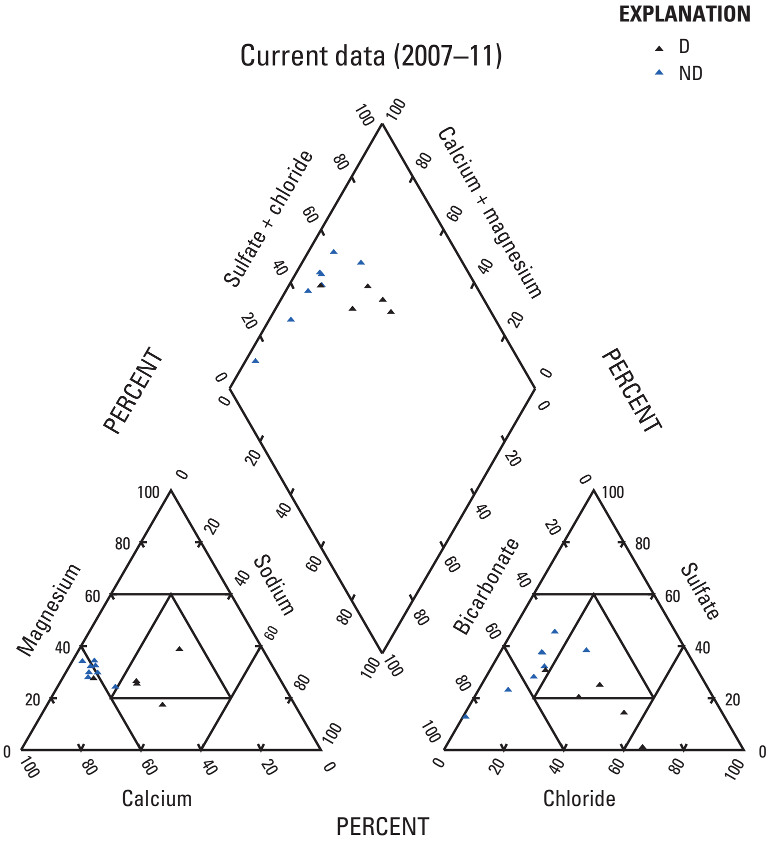

Current data (2007–11)

Figure 5. Historical (1969–77) and current (2007–11) major ion chemistry for 13 Lansing Board of Water and Light production wells shown in figs. 3 and 4, Lansing area, Michigan. (D, organic-wastewater compounds (OWCs) detected; ND, OWCs not detected).

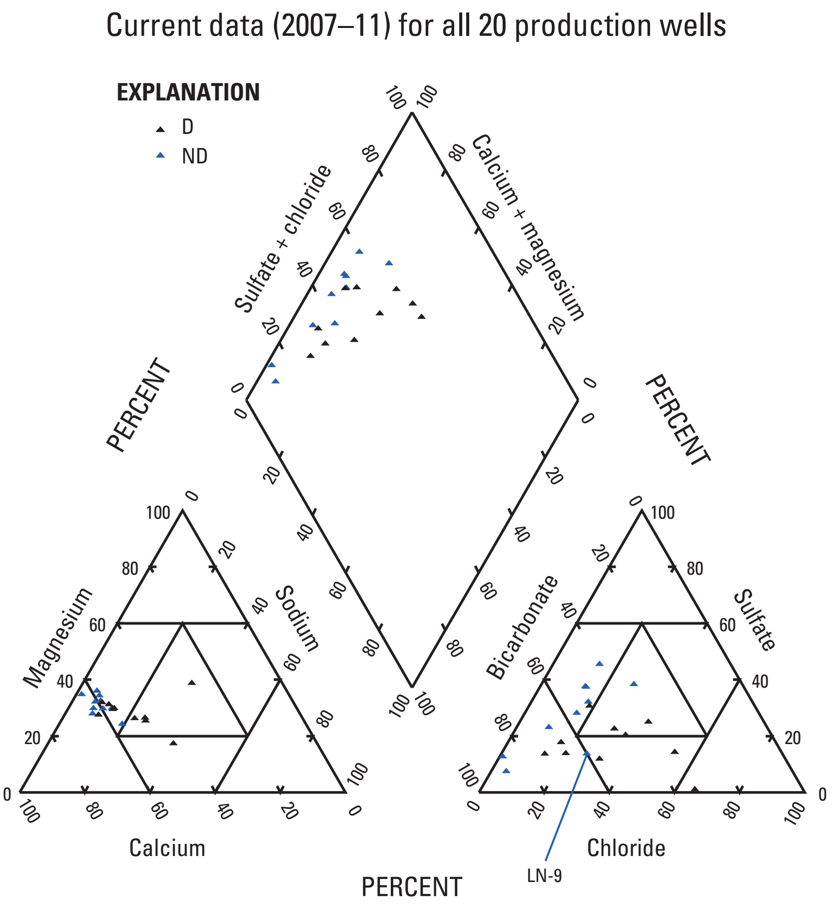


Figure 6. Current (2007–11) major ion chemistry for 20 Lansing Board of Water and Light production wells, Lansing area, Michigan. (D, organic-wastewater compounds (OWCs) detected; ND, OWCs not detected).

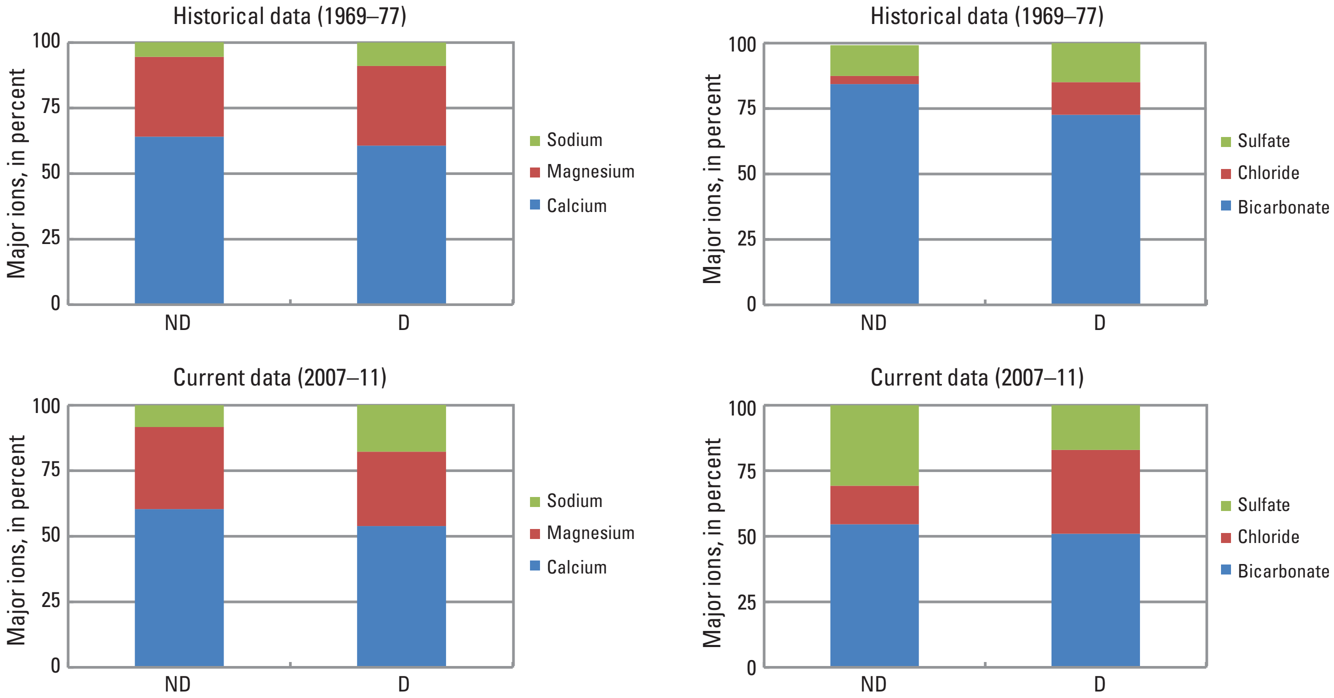


Figure 7. Historical (1969–77, 13 wells) and current (2007–11, 20 wells) major ion percentages in Lansing Board of Water and Light production wells, Lansing area, Michigan. (D, organic-wastewater compounds (OWCs) detected; ND, OWCs not detected).

Well Characteristics Related to Basin Brines

If water from the Parma-Bayport aquifer has been drawn up into the BWL wells over time, then total dissolved solids might be greater in older wells or in wells from which more water has been pumped. Estimated total volume pumped from each well was calculated to be the sum of estimated pumpage used for the 2009 Tri-County regional groundwater model for all modeled time periods representing 1920–2005 conditions. There was no correlation (Spearman Rank Correlation) between well age or the total volume pumped from the well over time and current (2007–11) total dissolved solids concentrations in the BWL wells. The total volume pumped over time for a well is correlated with well age ($p = 0.0003$). Wells were characterized according to whether they were completed above or below the Parma-Bayport aquifer, and the distance in feet above or below this interface was estimated by comparison with the elevation of the bottom of the well calculated as the elevation of the land surface at the well location minus the well depth. The current (2007–11) median total dissolved solids concentration was 644 mg/L in wells completed above the Parma-Bayport interface and 785 mg/L for wells completed below. The Wilcoxon-Mann-Whitney test indicated these values were not statistically different ($p = 0.0626$). Likewise, there was no significant difference in the 2007–11 concentration of calcium, magnesium, sodium, bicarbonate, chloride, or sulfate in wells completed above or below the Parma-Bayport aquifer, and there was no correlation between individual ion concentrations and well age or the total volume pumped from the well over time. Among the 373 estimated total dissolved solids values obtained from the 20 BWL wells, the largest value was 1,382 mg/L. The range of current (2007–11) total dissolved solids was 403 to 1,086 mg/L, which is well within the typical range for the part of the Saginaw aquifer that encompasses the study area (Meissner and others, 1996).

If water from the Parma-Bayport aquifer has influenced well-water geochemistry over time, then the observed increase in total dissolved solids concentration between 1969–77 and 2007–11, and the increase in all ions except bicarbonate, might be related to whether the well was completed above or below the Parma-Bayport aquifer, to well age, or to whether a well was pumped more or less over the period of interest. These physical factors were examined for any correlation with the difference in concentration of total dissolved solids or each individual ion in the 13 wells having data between 1969–77 and 2007–11, as well as the difference in percent composition of each ion over the same time period. Completion of wells above the Parma-Bayport aquifer was significantly and positively correlated only with the increase over time in magnesium concentration. Well age and difference in pumping between 1969–77 and 2007–11 were not correlated with any of these variables.

Total pumping does differentially affect the major ion composition of water from wells with or without OWC detections. Figure 8 shows that, for wells with no OWC detections, wells that have been pumped more over time have lower concentrations of most ions. In contrast, for wells with OWC detections, the pattern is quite different. For wells in which OWCs were detected, there is little decrease in major ions with pumping. In fact, most ions appear to increase, and chloride concentrations are much higher, regardless of pumping, in wells with detections as compared to those without detections.

Completion of wells in the Parma-Bayport aquifer appears to have a slight effect on major ion geochemistry (fig. 9). The deeper into the Parma-Bayport aquifer the greater the concentration of most ions in BWL wells, regardless of whether these had OWC detections. However, sodium and chloride are much greater in wells with detections.

Other variables that were not investigated for this study would potentially help to explain more of the current geochemistry. For example, Wood (1969) reported that a Lansing area well constructed in 1954 was completed near the site of an old brine well and produced water with a chloride concentration of greater than 1,000 mg/L. In addition, nearby wells also had higher than typical chloride concentrations, with a pattern that could be attributed to the variation in pumping rates of the different wells. Notably, this area is near wells LN-4 and LN-23, which exhibited chloride concentrations greater than 250 mg/L intermittently from 1956 to 1963. Neither well has exceeded 250 mg/L of chloride since 1963. In this case, a local source, and pumping effects from adjacent wells, may have contributed to the higher chloride concentrations in these two wells. Well pumping and completion of wells in the Parma-Bayport aquifer appear to at least partially explain aspects of the current geochemistry of BWL wells. However, sodium and chloride concentrations constitute the major geochemical difference between wells with or without OWC detections, and these ion compositions currently are not explained by pumping or by interaction with the Parma-Bayport aquifer.

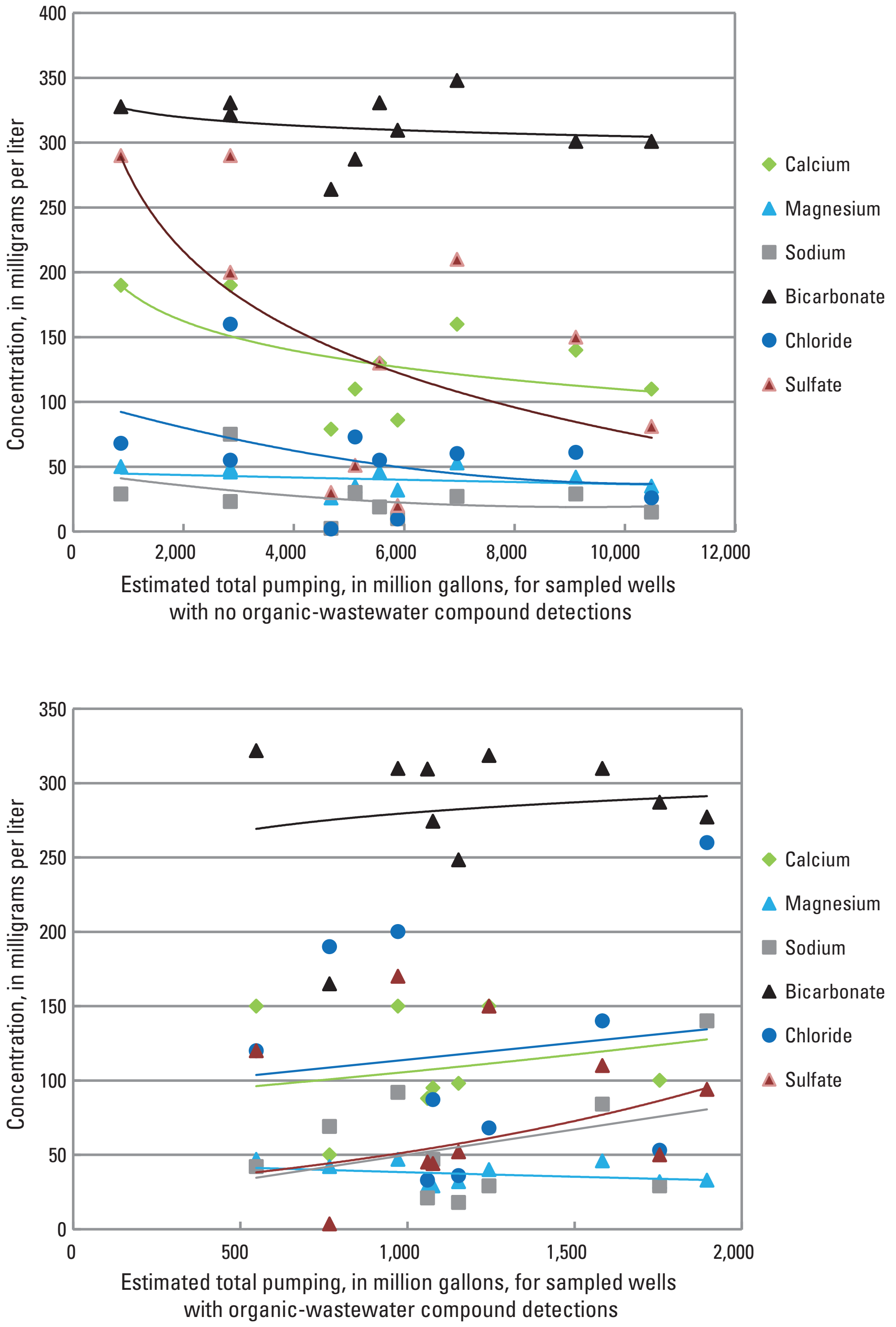
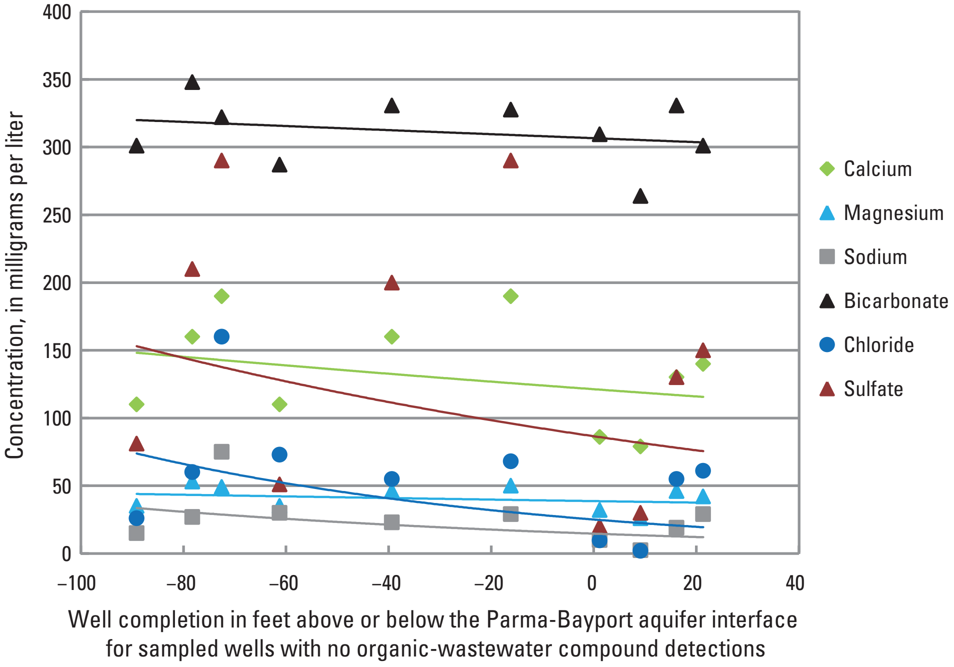


Figure 8. Relation between total pumping and major ion concentrations for wells with and without organic-wastewater compound detections. The lines on each graph are meant to denote general trends in the data.



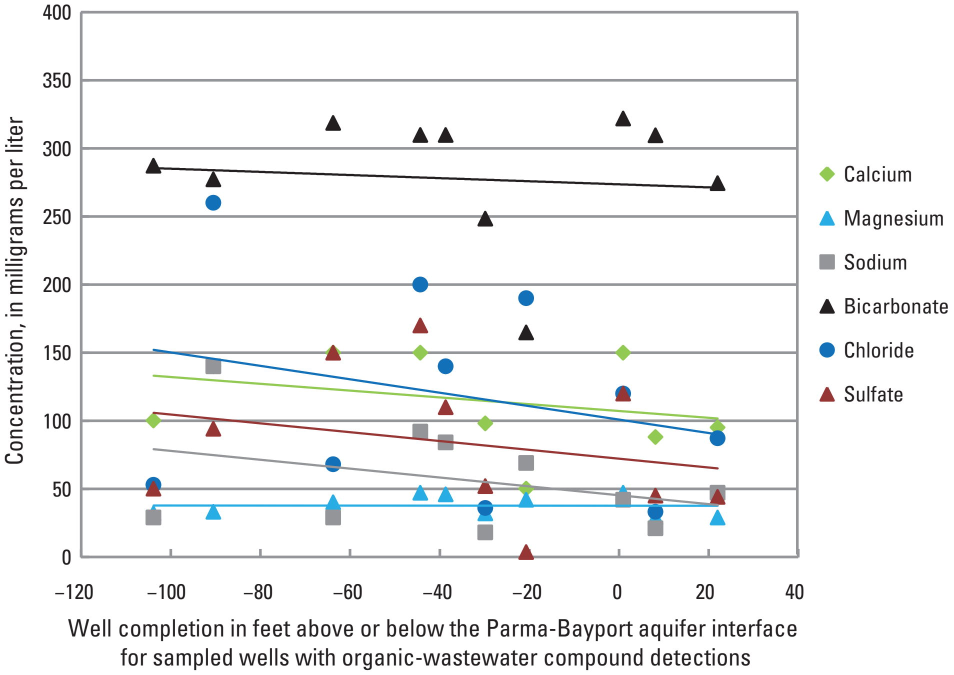


Figure 9. Relation between estimated well completion above or below the Parma-Bayport interface and major ion concentrations for wells with and without organic-wastewater compound detections. The lines on each graph are meant to denote general trends in the data.

Role of Surficial Sources

An alternative explanation for increased sodium and chloride in groundwater is surficial sources. Several studies have shown elevated concentrations of chloride in glacial aquifers related to urban land use. Mullaney and others (2009) reported that water from shallow monitoring wells in urban areas had the largest chloride:bromide ratio, and that urban waters commonly contained chloride:bromide ratios indicating input from sewage or animal waste. In addition, upward trends in chloride loads were apparent in several urban basins for which additional long-term data were available. Likewise, Lindsey and Rupert (2012) evaluated changes in chloride, nitrate, and dissolved solids in networks of wells in urban or agricultural settings across the U.S. They reported that a larger percentage of urban land-use networks had statistically significant increases in chloride, dissolved solids, and nitrate concentrations than agricultural land-use networks. One potential source is the use of salt, primarily for deicing of roads and other impervious surfaces, which has increased in the U.S. since 1950 (Kostick and others, 2007). Other sources of chloride in groundwater in urban areas include wastewater and septic-system discharges, recycling of chloride from drinking water, leachate from landfills and salt storage areas, and stormwater (Eisena and Anderson, 1979; Panno and others, 2006; Mullaney and others, 2009).

Significantly, studies conducted in Michigan have shown a similar influence of surficial land use on sodium and chloride concentrations in wells. Myers and others (2000) reported that recent residential development in suburban areas west of Detroit, Mich., was associated with increased chloride concentration in waters recently recharged (assessed by tritium concentration) to the glacial aquifer. Chloride:bromide ratios have been used to evaluate the sources of chloride in groundwater (Panno and others, 2006). In the study by Myers and others (2000), chloride:bromide ratios indicated that the source of chloride was halite (rock salt) and not brine. Thomas (2000a, b) also reported high chloride concentrations in shallow groundwater in agricultural and residential areas of the western Lake Erie drainage in Michigan and Ohio. Finally, Aichele (2004) reported that chloride concentrations exceeding the secondary maximum contaminant level of 250 mg/L were widely distributed in drinking water wells in Oakland County, Mich. In particular, Thomas (2000b) noted that young waters (as defined by tritium concentration) have significantly higher concentrations of chloride, sodium, calcium, potassium, and sulfate, and higher total dissolved solids, than did older waters. In addition, young waters also had significantly higher concentrations of nitrate, and 97 percent of young waters had one or more detections of volatile organic compounds (VOCs). Older waters were not tested for VOCs or pesticides using equivalent methods as for young waters; therefore, comparisons of these compounds between the two types of waters could not be made. The source of chloride to young waters was inferred to be surficial sources, based on chloride:bromide ratios, and based on the fact that chloride was in higher concentration in shallow wells as opposed to deep wells potentially susceptible to basin brines. These results are very consistent with current findings for the BWL wells.

Well Characteristics Related to Surficial Sources

To address a possible surficial source of sodium and chloride, and because bromide data were not available, a variety of characteristics was compiled (table 7). These well characteristics included potential explanatory variables that might influence whether, or the rate at which, water from the land surface could travel through the glacial deposits to reach the well opening in the Saginaw Formation. Minimum and median traveltimes from the water table to the upper, middle, and lower Saginaw aquifer units were determined using the Tri-County regional groundwater-flow model (Luukkonen, 2009) and the particle tracking program, MODPATH (Pollock, 1989). A total of 300 hypothetical particles were distributed on the sides of each bedrock aquifer cell simulating the sampled Lansing-area wells under 2006–7 pumping conditions. These particles were tracked backward using the steady-state model along flow paths through the groundwater-flow field until they reached a top cell face in the uppermost model layer, which represented the water table. Thus, the position of the particle at the end of the simulation represents the location at the water table where the particle enters the groundwater-flow system. These recharge areas and the 5, 10, and 20 year time-of-travel areas were overlain on urban areas as delineated from 2003 aerial photos of the Lansing area to determine estimates of the percent impervious area in the wellhead-protection area. In this study, time-of-travel areas were defined as areas through which water moves from the wellhead-protection area to the pumping well in the specified amount of time. The wellhead-protection areas consist of the areas (projected up to the land surface) where water enters the groundwater-flow system at the water table and the areas through which water flows from the water table to a simulated pumping well. For example, the 5-year time-of-travel area represents the land-surface area where some of the water entering the groundwater system is estimated to reach the well opening in 5 years or less. Other potential explanatory variables determined from well logs and model estimates included the aquifer and confining material percentages in the glacial and bedrock aquifers, the confining material thickness between the Glacial and Saginaw aquifers, glacial deposit thickness, and bedrock-surface elevation.

Table 7. Well, aquifer, and hydrologic characteristics and groundwater-chemistry variables evaluated in sample analysis.

Well characteristics
Well age
Well depth
Casing depth
Pump capacity
Land elevation
Location
Estimated elevation of Parma-Bayport surface
Estimated completion above or below the Parma-Bayport interface
Potential contamination source nearby
Aquifer characteristics
Till thickness between Glacial and Saginaw aquifers
Shale thickness between Glacial and Saginaw aquifers
Combined confining material thickness between Glacial and Saginaw aquifers
Thickness of glacial deposits
Total sandstone thickness
Total shale thickness
Thickness of uppermost sandstone layer
Thickness of intercepted part of Saginaw aquifer
Estimated percent of Saginaw aquifer intercepted by well
Estimated elevation of top surface of Saginaw aquifer
Bottom elevation of well
Percent aquifer, marginal aquifer, partially confining, or confining material in Saginaw aquifer and Glacial aquifer
Hydraulic properties of Glacial and Saginaw aquifers
Hydrologic characteristics
Typical volumes of use
Total pumping
Median traveltimes in wellhead-protection area
Minimum traveltimes in wellhead-protection area
Groundwater chemistry
Major ion concentrations
Ratios/changes in major ion concentrations

Spearman Rank Correlation indicated that the total number of OWCs in BWL wells, as well as the concentrations of sodium and chloride, were significantly negatively correlated with both the minimum and median time of travel from the upper sandstone layer to the water table in the Glacial aquifer, and also with the minimum time of travel from the middle sandstone layer to the water table in the Glacial aquifer. No other physical characteristic was correlated with total number of OWCs detected, or with sodium and chloride concentrations. Likewise, the Wilcoxon-Mann-Whitney test indicated the same time-of-travel variables were significantly less in the wells with detections as compared to those without. The well with the largest number of detections had one of the lowest median traveltimes. The patterns of sodium, chloride, and OWC detections with respect to the median traveltime from the water table to the upper sandstone aquifer layer are shown in figure 10. A lower traveltime estimate indicates that water from the water table may be drawn into a well more quickly than in the case of a longer traveltime estimate. Lower traveltimes may be related to aquifer characteristics that permit more rapid movement from the water table downward into aquifers below. Pumping may induce water to move from the surface downward into a well, but movement will be constrained by barriers, such as less permeable materials termed confining layers. Figure 11 compares selected well characteristics between wells with and without OWC detections. Other than median traveltime, no characteristic is statistically significantly different ($p < 0.05$) between the two well categories (table 8). However, wells with detections tend to have thicker modeled lower confining material (as simulated in the Tri-County regional model), which is an estimate of the amount of clay or shale between the Glacial and Saginaw aquifers. Areas with little or no clay or shale would have more of a hydraulic connection between the two aquifer units. Thus, wells with OWC detections (and higher sodium and chloride) would be more susceptible to downward movement of water from the overlying glacial materials if this confining material were thin or absent. Figure 12 shows that there is a pattern of lower sodium and chloride concentrations and fewer OWC detections in wells with greater modeled confining material thickness. Specifically, all detections occurred in wells with less than 30 ft of modeled confining material, although some wells in the same category had no detections. Figure 11 also indicates that there are other well characteristics that tend to differ between wells with and without detections, such as the percent of marginal aquifer in the rock (as specified in the Michigan Department of Environmental Quality water-well record database, Wellogic), which was less than 10 for wells with detections, but ranged much higher for wells without detections. The percent marginal aquifer in the rock was nearly a significant variable (table 8). However, it can also be seen in figure 11 that there is wide variation for most well characteristics, and just as for the confining material thickness as simulated in the model, many wells with no detections have similar characteristics to those with detections.

Canonical discriminant analysis using the well characteristics for the 20 recent water samples indicated that the percent marginal aquifer in the rock, the median and minimum traveltimes from the water table to the upper sandstone aquifer layer, the median and minimum traveltimes from the water table to the middle sandstone aquifer, and the sulfate to chloride ratio were significant variables in distinguishing between the two groups. At the 0.1 ($p = 0.1$) significance level, the estimated total pumping and the modeled confining material thickness also would be significant variables. Discriminant analysis with these variables correctly classified all 10 wells with detections into the same group; however, 2 wells with no detections were misclassified into the group of wells with detections. So, as indicated previously in the other analyses, many characteristics are similar for wells in each group.

Comparisons of Specific Wells

To evaluate well characteristics further, three wells were compared (table 9). Well LN-5 had the highest number of OWC detections of any well, and well LN-6 had none. These two wells are very near to each other and have similar well characteristics, with the exception that the driller's log for well LN-5 reports only clay in the overlying glacial materials. Well LN-6 has a value greater than 10 for percent marginal aquifer in the rock, which as described previously is associated with lack of OWC detections. Nevertheless, sodium and chloride concentrations are relatively high for this well. The major difference between wells LN-5 and LN-6 is the fact that well LN-6 has experienced declining pumping since 1971, and the total volume pumped from this well over time is approximately one-half of that pumped from well LN-5.

Well LN-9 (table 9) also was examined for well characteristics that may place this well, which had no OWC detections, within the group of wells with detections in the Piper plots of figures 5 and 6. Well LN-9 is a newer well than LN-5, but its total volume pumped and the volume pumped since 1971 is very similar to that of well LN-5. Sodium and chloride concentrations are much less in well LN-9 than in well LN-5, but well LN-9 falls within the geochemical composition of most wells with detections, which may be related to the relatively aggressive pumping of this well. This well has less than 1 foot (ft) of modeled confining material thickness and only a slightly greater median traveltime from the upper sandstone layer to the water table in the Glacial aquifer. Therefore, well LN-9 may be susceptible to OWC detections.

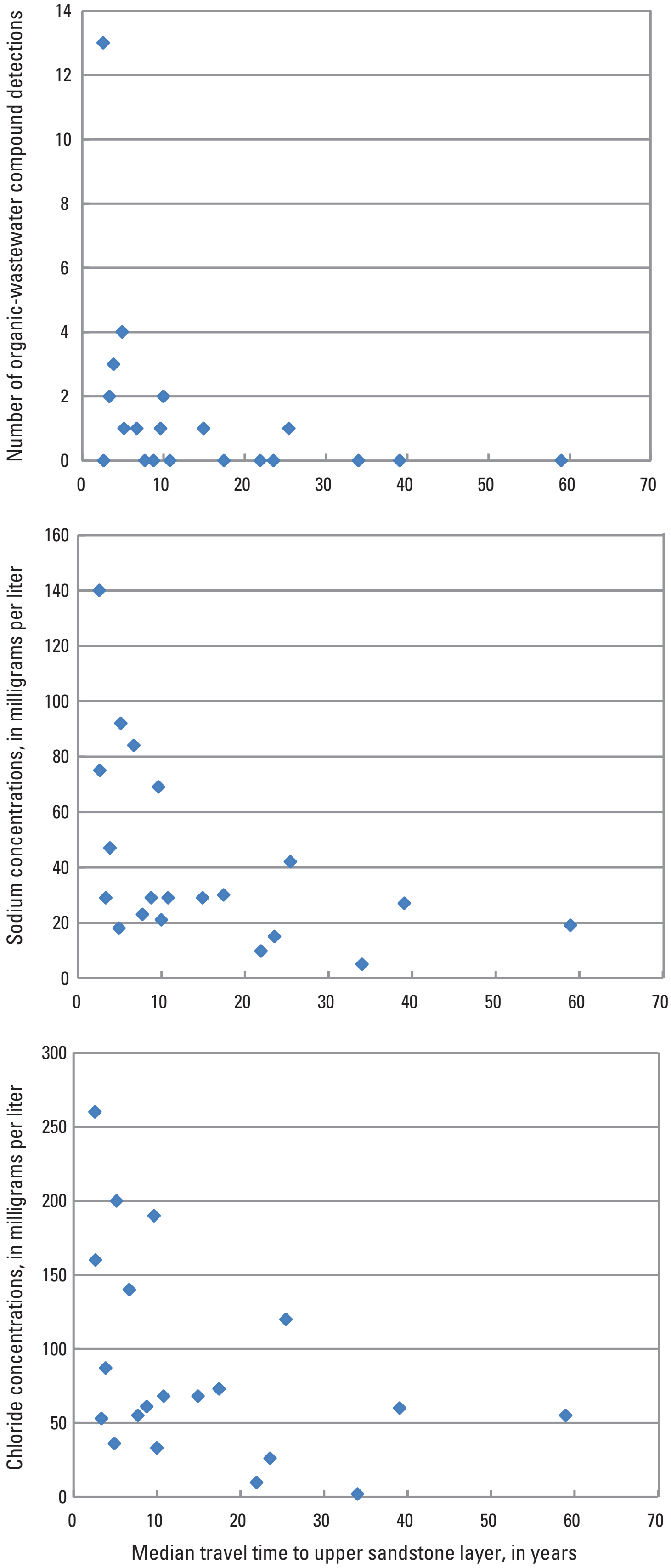


Figure 10. Relation between median traveltime from the water table to the upper sandstone layer and number of organic-wastewater compound detections, sodium concentration, and chloride concentration.

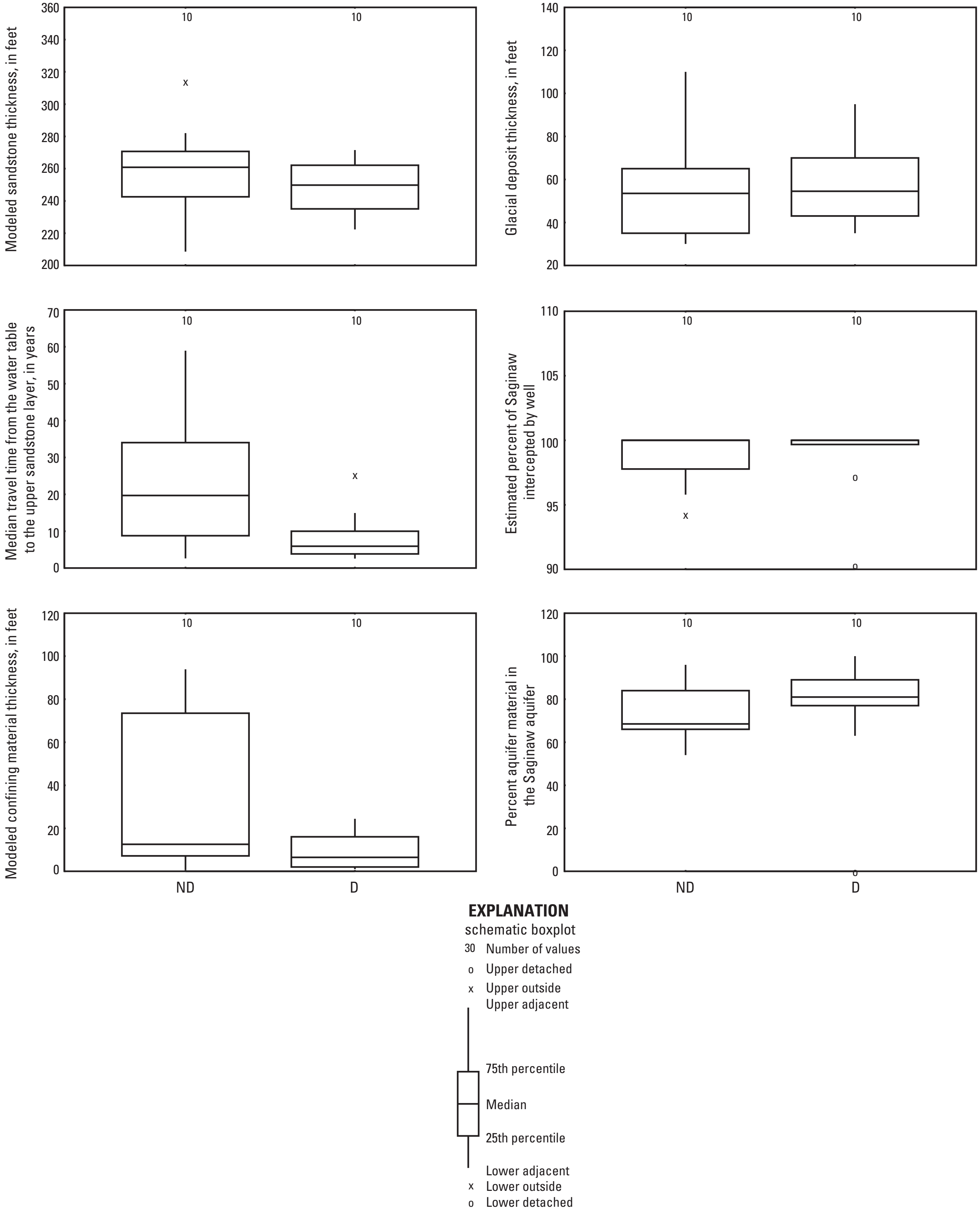


Figure 11. Comparison of selected well characteristics for sampled wells with (D) and without (ND) organic-wastewater compound detections.

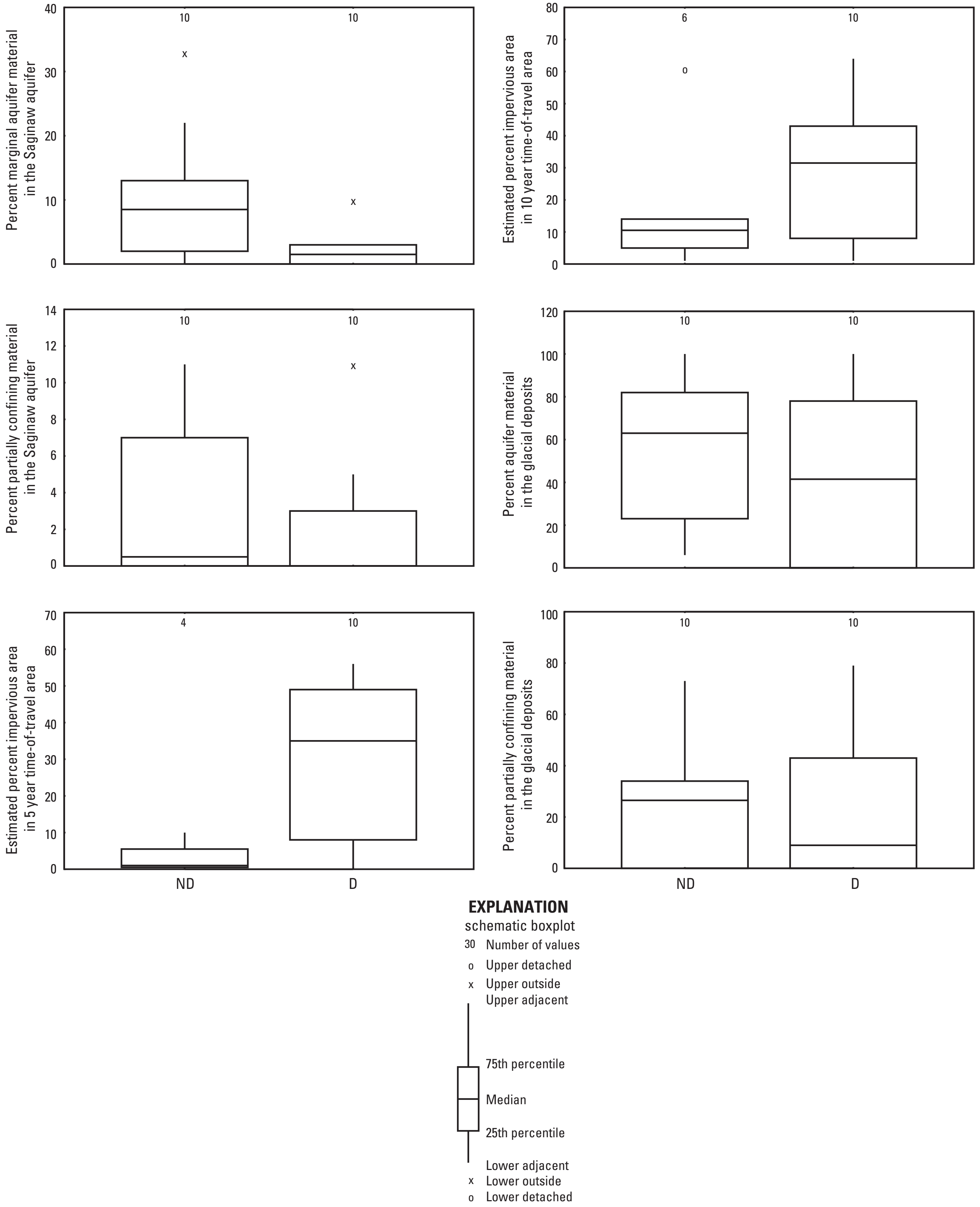


Figure 11. Comparison of selected well characteristics for sampled wells with (D) and without (ND) organic-wastewater compound detections.—Continued

Table 8. Median values for selected characteristics for sampled wells and significance levels.

Well or aquifer characteristic	Median		Wilcoxon-Mann-Whitney p-value
	Sampled wells without detections	Sampled wells with detections	
Median travel time from the water table to upper sandstone layer in Saginaw, in years	19.7	5.9	0.0477
Modeled confining material thickness, in feet	12.5	6.5	.1895
Glacial deposit thickness, in feet	53.5	54.5	.3941
Modeled sandstone thickness, in feet	260.9	249.8	.5525
Estimated percent of Saginaw aquifer intercepted by well	100	100	.9633
Percent aquifer material in the Saginaw aquifer	68.5	81	.2555
Percent marginal aquifer material in the Saginaw aquifer	8.5	1.5	.0573
Percent partially confining material in the Saginaw aquifer	.5	0	.6249
Estimated percent impervious area in 5-year time-of-travel area	1	35	.1113
Estimated percent impervious area in 10-year time-of-travel area	10.5	31.5	.2507
Percent aquifer material in the glacial deposits	63	41.5	.3946
Percent partially confining material in the glacial deposits	26.5	9	.6398

Each BWL well may have a somewhat unique set of characteristics that governs its response to pumping and its susceptibility to water from the Glacial aquifer. Analysis of the available data indicates that the shorter the time of travel between upper layers of the Saginaw aquifer and the water table in the Glacial aquifer, the greater the concentration of sodium and chloride, and the greater probability of OWC detection. In addition, the absence of a confining layer may have an influence on the same constituents. Variability in pumping individual wells over time influences the current geochemistry of the wells. These results, combined with the consistent relation between sodium and chloride concentrations, and OWC detections, are consistent with a surficial and likely anthropogenic source of sodium, chloride, and OWCs. Geochemical models and analysis of additional constituents such as bromide might allow more refined interpretation of the possible sources and processes influencing changes in groundwater geochemistry in BWL wells. Nevertheless, BWL wells demonstrate patterns of geochemical change observed in groundwater in other urban settings.

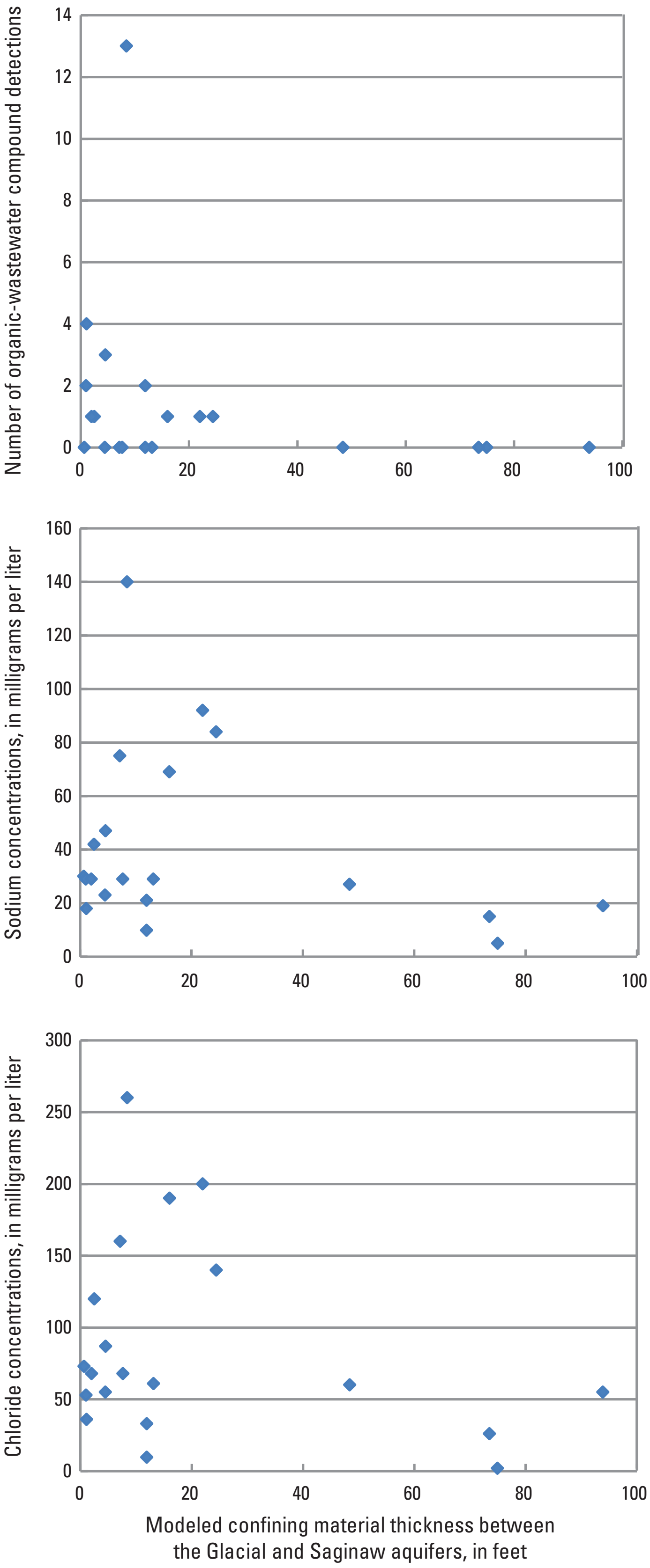


Figure 12. Relation between modeled confining material thickness between the Glacial and Saginaw aquifers and number of organic-wastewater compound detections, sodium concentration, and chloride concentration.

Table 9. Comparison of selected characteristics for wells LN-5, LN-6, and LN-9.

[--, not applicable]

Characteristic	LN-5	LN-6	LN-9
Age, in years	45	45	32
Number of organic wastewater compound detections	13	0	0
Well depth, in feet	436	410	395
Casing depth, in feet	46	43.3	65
Percent aquifer material in the glacial deposits	0	88	21
Percent aquifer material in the Saginaw aquifer	78	66	89
Percent marginal aquifer material in the glacial deposits	0	0	15
Percent marginal aquifer material in the Saginaw aquifer	3	22	2
Percent confining material in the glacial deposits	100	0	5
Percent confining material in the Saginaw aquifer	19	13	2
Percent partially confining material in the glacial deposits	0	0	60
Percent partially confining material in the Saginaw aquifer	0	0	7
Glacial deposit thickness, in feet	45	40	62
Modeled confining material thickness, in feet	8.4	7.1	.6
Modeled sandstone thickness, in feet	260.1	262.1	248.5
Estimated percent of Saginaw aquifer intercepted by well	100	100	100
Estimated completion below the Parma-Bayport interface, in feet	−90.5	−72.5	−61.2
Minimum traveltime from water table to upper sandstone layer, in years	1.2	1.2	8.2
Median traveltime from water table to upper sandstone layer, in years	2.6	2.6	17.4
Minimum traveltime from water table to middle sandstone layer, in years	4.0	4.2	27.0
Median traveltime from water table to middle sandstone layer, in years	10.6	9.8	70.7
Estimated percent impervious area in 5-year time-of-travel area	35	1	--
Estimated percent impervious area in 10-year time-of-travel area	29	1	61
Estimated percent impervious area in 20-year time-of-travel area	41	1	52
Estimated total pumping simulating 1920–2005 conditions in the groundwater model, in million gallons	5,296.0	2,848.0	5,109.4
Estimated total pumping simulating 2000–5 conditions in the groundwater model, in million gallons	1,291.3	100.5	1,142.9

Summary

In 2010, groundwater from 20 Lansing Board of Water and Light (BWL) production wells was tested for 69 organic-wastewater compounds (OWCs). OWCs were detected in one-half of the sampled wells. Three compounds were detected at greater than the laboratory reporting level (LRL): fluoranthene, pyrene, and phenanthrene. Two compounds (isopropylbenzene and phenol) were detected at greater than the long-term method detection limit (LT-MDL) but less than the LRL, and estimated concentrations were provided. All remaining compound detections were less than the LT-MDL. The types of OWCs detected do not indicate contamination with fecal materials or wastewater. No pharmaceuticals were detected, although few were tested. The OWCs detected are common industrial pollutants that may arise from a variety of environmental sources and are common constituents in stormwater. Analysis of the identified chemicals with regard to well characteristics and groundwater-recharge areas may be helpful in identifying factors that contribute to the occurrence of these chemicals in BWL wells. In 2012, the U.S. Geological Survey (USGS) entered into a cooperative agreement with the Tri-County Regional Planning Commission to interpret the results of these analyses and relate detections to local characteristics and groundwater geochemistry.

Analysis of groundwater chemistry data for 1969–2011 indicated that the geochemistry of the BWL wells had changed over time, with the major difference being an increase in sodium and chloride. The concentrations of sodium and chloride were correlated with OWC detections. The BWL wells studied are all completed in the Saginaw aquifer, which consists of water-bearing sandstones of Pennsylvania age. The Saginaw aquifer is underlain by the Parma-Bayport aquifer, and overlain by the Glacial aquifer. Two possible sources of sodium and chloride were evaluated: basin brines by way of the Parma-Bayport aquifer and surficial sources by way of the Glacial aquifer. If water from the underlying Parma-Bayport aquifer had influenced well-water geochemistry over time, then the observed increase in total dissolved solids concentration between 1969–77 and 2007–11, and the increase in all ions except bicarbonate, might be related to whether the well was completed above or below the Parma-Bayport aquifer, to well age, or to whether a well was pumped more or less over the period of interest. There was no correlation (Spearman Rank Correlation) between well age or the total volume pumped from the well over time and total dissolved solids concentrations in the BWL wells for 2007–11. Likewise, there was no significant difference in the 2007–11 concentration of calcium, magnesium, sodium, bicarbonate, chloride, or sulfate in wells completed above or below the Parma-Bayport aquifer, and there was no correlation between individual ion concentrations and well age or the total volume pumped from the well over time. Completion of wells above the Parma-Bayport aquifer was significantly and positively correlated only with the increase over time in magnesium concentration. Well pumping and completion of wells in the Parma-Bayport aquifer appear to at least partially explain aspects of the current geochemistry of BWL wells. However, sodium and chloride concentrations constitute the major geochemical difference between wells with or without OWC detections, and these ion compositions do not appear to be explained by pumping or by interaction with the Parma-Bayport aquifer.

To address a possible surficial source of sodium and chloride, a variety of well characteristics were compiled. These well characteristics included potential explanatory variables that might influence whether, or the rate at which, water from the land surface could reach each well. Spearman Rank Correlation indicated that the total number of detections in BWL wells, as well as the concentrations of sodium and chloride, were significantly negatively correlated with both the minimum and median time of travel from the upper sandstone layer to the water table in the Glacial aquifer, and also with the minimum time of travel from the middle sandstone layer to the water table in the Glacial aquifer. In addition, wells with detections tended to have less modeled confining material thickness (as simulated in the regional groundwater flow model), which is an estimate of the amount of clay or shale between the Glacial and Saginaw aquifers. Based on the potential explanatory variables available for this analysis, the preponderance of the data indicates surficial sources, possibly stormwater runoff.

Each BWL well may have a somewhat unique set of characteristics that governs its response to pumping so it is possible that a relevant explanatory variable was not included in this analysis. For example, pumping from other nearby wells, well-development procedures, or the proximity of potential contaminant sources may be affecting the groundwater geochemistry at each well and the potential for contamination by OWCs. The current analyses indicate that patterns of geochemistry, and the relation between these patterns and volume of pumpage for the BWL wells, indicate other wells may acquire detectable OWCs in the future. Additional analyses and collection of additional data would be needed to more conclusively identify the source and to determine the potential vulnerability of other wells. Nevertheless, BWL wells demonstrate patterns of geochemical change observed in groundwater in other urban settings.

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Publishing support provided by the U.S. Geological Survey
Science Publishing Network,
Columbus Publishing Service Center

For more information concerning the research in this report,
contact the

Director, Michigan Water Science Center
U.S. Geological Survey
6520 Mercantile Way, Suite 5
Lansing, MI 48911–5991
http://mi.water.usgs.gov/

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Haack and Luukkonen—**Organic-Wastewater Compounds, Groundwater Geochemistry, and Well Characteristics, Lansing, Michigan**—Scientific Investigations Report 2013–5139