GROUND-WATER QUALITY

The ground-water quality investigation in Oakland County included field analysis of physical characteristics, as well as laboratory analysis for nutrients, major inorganic ions, and selected trace metals. A brief discussion of the methods and results of each type of analysis will be presented, along with a table of summary statistics. The complete results are provided in table 1C of Appendix 1. More detailed discussions of the geochemistry and the potential health effects of nitrate and arsenic are included to assist Oakland County and local governments in water-resource management issues specific to these chemicals.

Sample collection and analysis

All samples were collected using the clean sampling procedures specified by the USGS National Water-Quality Assessment (NAWQA) program (Shelton, 1994). Unsoftened water samples were collected from domestic wells by connecting to external, garden hose taps. All tubing used in sample collection was Teflon-lined, with high-density poly-ethylene (HDPE) or Teflon fittings and connectors. Physical characteristics (temperature, specific conductance, dissolved oxygen, pH, eH) were measured at the well-site with a Hydrolab H20 connected in-line through a flow-through cell. Before a ground-water sample was collected for laboratory analysis, wells were purged for a period of at least 20 minutes until the above field characteristics had stabilized. Stability was determined on the basis of the following criteria; specific conductance variation less than $2 \mu S/cm$, pH variation less than 0.05 pH units, dissolved oxygen variation less than 0.05 mg/L, and a temperature variation of less than $1^{o}C$. Alkalinity titrations were performed on filtered samples in the field.

All wells were sampled for analysis of major cations, major anions, nutrients, and arsenic. A complete list of laboratory analyses is included in table 2. The USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado performed all analyses listed in table 2.

At 26 sites, replicate samples were collected for analysis by the MDEQ. These samples were collected to examine the comparability of MDEQ analytical results for arsenic, nitrate, and chloride

to results from the USGS NWQL. The MDEQ laboratory uses an inductively coupled plasma mass spectrometry (ICPMS) method for arsenic analyses (MRL = 0.0001 mg/L), and colorimetric methods for nitrate (MRL = 0.4 mg/L) and chloride (MRL = 4 mg/L) analyses.

Five wells were selected to provide information on long-term seasonal variations in ground-water quality. These wells were sampled using methods identical to those described previously for the collection of ground-water-quality samples.

Five wells were sampled to evaluate short-term (0 - 25 minutes) variations in chemical composition of drinking water. Operationally, drinking water is distinguished from ground water by the fact that the well and plumbing system are not purged before sample collection. The sample is thus reflective of what a resident might consume if simply getting a glass of water. Sampling procedures were designed to evaluate potential changes in concentrations of arsenic, manganese, and iron within a domestic plumbing system. Four wells were selected on the basis of detection of arsenic, manganese, and iron in samples analyzed at the NWQL. One well, OAK 41, was added to this sample group because of extensive prior data on record at MDEQ. At wells selected for the short-interval, time-series sample collection, unfiltered samples were collected at intervals ranging from 30 seconds to 2 minutes for the first 20 to 25 minutes of well pumping. Wells were not purged prior to collecting the first sample. These samples were analyzed for total arsenic using a flame atomic absorption method (Brown, 1998). Manganese and iron were analyzed using an ICPMS method (Garbarino and Struzeski, 1998).

Field-Measured Characteristics

Temperature, specific conductance, oxidation-reduction potential (eH), dissolved oxygen (DO), pH, and alkalinity were measured in the field. Results of these analyses are shown in appendix table 1B. No health standards exist for any of these constituents, but the USEPA has issued a Secondary Maximum Contaminant Level for pH based on aesthetic considerations.

Table 2: Water quality characteristics analyzed by the USGS National Water Quality Laboratory
[μS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter]

Parameter name	Units	MRL	Parameter code	Method	Reference
Specific Conductance	μS/cm	1	90095	I278185	Fishman and Friedman, 1989
pH, Laboratory	Standard Units	0.1	403	I258785	Fishman and Friedman, 1989
Total Residue @ 180 °C	mg/L	1	530	I376585	Fishman and Friedman, 1989
Calcium, dissolved	mg/L as Ca	0.02	915	I147287	Fishman and Friedman, 1989
Magnesium, dissolved	mg/L as Mg	0.004	925	I147287	Fishman, 1993
Sodium, dissolved	mg/L as Na	0.06	930	I147287	Fishman, 1993
Potassium, dissolved	mg/L as K	0.1	935	I163085	Fishman and Friedman, 1989
Acid Neutralizing Capacity	mg/L as CaCO$_3$	1.0	90410	I203085	Fishman and Friedman, 1989
Sulfate, dissolved	mg/L as SO$_4$	0.1	945	I205785	Fishman and Friedman, 1989
Chloride, dissolved	mg/L as Cl	0.1	940	I205785	Fishman and Friedman, 1989
Flouride , dissolved	mg/L as F	0.1	950	I232785	Fishman and Friedman, 1989
Bromide, dissolved	mg/L as Br	0.01	71870	I212985	Fishman and Friedman, 1989
Silica , dissolved	mg/L as SiO$_2$	0.1	955	I270085	Fishman and Friedman, 1989
Residue, dissolved 180°C	mg/L	10	70300	I175085	Fishman and Friedman, 1989
Nitrogen, Ammonia, dissolved	mg/L as N	0.02	608	I252290	Fishman, 1993
Nitrogen, Nitrite, dissolved	mg/L as N	0.01	613	I254090	Fishman, 1993
Nitrogen, Ammonia + Organic	mg/L as N	0.1	623	I261091	Patton and Truitt, 1992
Nitrogen, Nitrite + Nitrate, dissolved	mg/L as N	0.05	631	I254590	Fishman, 1993
Phosphorus, total	mg/L as P	0.05	665	I461091	Patton and Truitt, 1992
Phosphorus, dissolved	mg/L as P	0.004	666	EPA 365.1	U.S.EPA, 1993
Phosphorus, Orthophosphate	mg/L as P	0.01	671	I260190	Fishman, 1993
Arsenic, total*	mg/L as As	.001	1002	I406398	Brown, 1998
Arsenic, total, EPA	mg/L as As	.001	1002D	EPA 200.9	U.S.EPA, 1993
Iron, total*	mg/L as Fe	.014	1045	I447197	Garberino and Struzeski, 1998
Iron, dissolved	mg/L as Fe	.01	1046	I147287	Fishman, 1993
Manganese, total*	mg/L as Mn	.003	1055	I447197	Garberino and Struzeski, 1998
Manganese, dissolved	mg/L as Mn	.003	1056	I147287	Fishman, 1993

 * denotes method used for short-interval, time-series sample analysis.

The temperature of water pumped from wells during sampling ranged from 10.4°C to 15.5°C, with a mean of 12°C (approximately 54°F). The annual average daily air temperature for the Pontiac area is between 9 and 10°C (Soil Conservation Service, 1982). Ground-water temperatures are usually 1 to 2°C higher than the mean annual air temperature (Todd, 1980).

The concentration of dissolved solids in water can be approximated in the field by measuring the specific conductance of a sample (Hem, 1985). Fresh water is usually considered to be water containing less than 1,000 mg/L total dissolved solids (Drever, 1988). The USEPA SMCL for dissolved solids is 500 mg/L. On the basis of data collected in this study, the total dissolved solids concentration in ground water in Oakland County [in milligrams per liter (mg/L)] is typically about 58 percent of the specific conductance [measured in microsiemens/centimeter (μS/cm)]. Thus, the threshold between fresh and brackish water in Oakland County would be represented by a specific conductance of approximately 1,800 μS/cm, and the USEPA's SMCL would be represented by a specific conductance of approximately 900 μS/cm. The specific conductance of ground water used for drinking in Oakland County ranged from 395 to 2,950 μS/cm, with a mean value of 925 μS/cm.

Dissolved oxygen concentrations ranged between <0.1 and 7.8 mg/L, with a mean of 0.8 mg/L. In Michigan, the presence of DO in concentrations higher than 1.0 mg/L is typically associated with recently recharged, and usually shallow, ground water. The concentration of dissolved oxygen in the water, along with the oxidation-reduction potential (redox), controls the chemical and microbial reactions that can occur in ground water.

The pH of ground water in Oakland County varies between 6.5 and 7.6, with a mean of 7.1. Most ground water in the United States falls in the range of 6.0 to 8.5 (Hem, 1985). The USEPA SMCL for pH specifies pH should fall between 6.5 and 8.0.

The redox potential of Oakland County ground water ranged from -25mV to 876mV. The redox potential is not directly related to any health effects; rather, it is monitored as an indication of whether the subsurface environment is conducive to removing electrons from materials (high eH) or adding electrons to material (low eH). Higher eH values are often found in recently recharged waters, while lower eH values are found in older waters that have been exposed to more organic matter, carbonates, or bacteria (Drever, 1988). The redox potential of water is an important control on geochemical processes, and the determination of eH can indicate which ions are likely to be mobile in the system. The measurements included in appendix table 1B and elsewhere are approximate, based on results from an electrode measurement, rather than direct measurement of different species of the same ion.

The alkalinity of ground water in Oakland County ranged from 214 to 462 mg/L as $CaCO_3^-$. Alkalinity is a measure of the acid neutralizing ability of a sample, which can be the result of several ions in solution. In the pH ranges described above, the principal ion responsible for alkalinity is bicarbonate, HCO_3^- (Hem, 1985). Like the redox potential, alkalinity is an indicator of the state of the geochemical system, and aids in the interpretation of other chemical constituents.

Inorganic Chemical Constituents

The USEPA has set drinking-water MCLs and SMCLs for several inorganic constituents analyzed in this study. These constituents, the USEPA threshold, and the type of threshold are shown in table 3 (U.S. Environmental Protection Agency, 1996). A complete list of inorganic chemistry analyses can be found in appendix table 1C. A summary of results for each inorganic constituent are shown in table 4.

Table 3. Inorganic constituents analyzed in this study with USEPA Drinking Water Standards [mg/L, milligrams per liter; MCL, Maximum Contaminant Level; SMCL, Secondary Maximum Contaminant Level]

Constituent	Limit	Units	Standard type
Nitrite	1	mg/L as N	MCL
Nitrate	10	mg/L as N	MCL
Chloride	250	mg/L as Cl	SMCL
Sulfate	250	mg/L as SO_4^-	SMCL
Flouride	4	mg/L as F	SMCL
Arsenic	.05	mg/L as As	MCL
Iron	.3	mg/L as Fe	SMCL
Manganese	.05	mg/L as Mn	SMCL
Total Dissolved Solids	500	mg/L	SMCL

Table 4: Summary statistics for selected inorganic constituents detected in water samples from selected wells in Oakland County, Michigan

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ^{o}C, degree Celsius]

Constituent	Maximum	Minimum	Mean	Median
Laboratory pH (Standard Units)	7.9	7.1	7.42	7.43
Nitrogen, Ammonia (mg/L as N)	1.4	<.02	.19	.14
Nitrogen, Nitrite (mg/L as N)	.1	<.01	.01	<.01
Nitrogen, Ammonia + Organic (mg/L as N)	1.52	<.01	.22	.15
Nitrogen, Nitrate + Nitrite, dissolved (mg/L as N)	23.9	<.05	.90	<.05
Phosphorus, dissolved (mg/L as P)	.5	<.004	.02	<.004
Phosphorus, ortho (mg/L as P)	.5	<.01	.02	<.01
Calcium, dissolved (mg/L as Ca)	175	0.15	79.3	76.2
Magnesium, dissolved (mg/L as Mg)	57.7	0.02	29.0	27.5
Sodium, dissolved (mg/L as Na)	431	3.73	66.0	22.8
Potassium, dissolved (mg/L as K)	13	0.1	2.1	1.7
Chloride, dissolved (mg/L as Cl)	661	0.48	103.	23.3
Sulfate, dissolved (mg/L as SO_4^-)	80.7	1.26	29.8	18.5
Flouride, dissolved (mg/L as F)	1.1	<.1	0.4	0.2
Silica, dissolved (mg/L as SiO_2)	23.0	9.25	14.7	14.3
Arsenic, total (mg/L as As)	.176	<.001	.021	.003
Iron, dissolved (mg/L as Fe)	3.58	<.014	1.09	.927
Manganese, dissolved (mg/L as Mn)	.330	<.003	.055	.032
Dissolved Residue of Evaporation, 180 ^{o}C (mg/L)	1620	228	529	387
Bromide, dissolved (mg/L as Br)	5.5	.01	.24	.06
Specific Conductance, (µS/cm at 25°C)	2950	408	913	640

None of the samples contained concentrations of sulfate or fluoride in excess of the SMCL. Samples from two wells exceeded the MCL for nitrate. Samples from more than half of the wells contained concentrations of iron in excess of the SMCL, and samples from nearly half of the wells contained concentrations of manganese in excess of the SMCL. Concentrations of arsenic in samples from five wells exceeded the MCL; although all of those wells were previously identified by MDEQ as having concentrations above the MCL. Samples from seven wells exceeded the SMCL for chloride. Samples from twelve wells exceeded the SMCL for total dissolved solids.

Elevated concentrations of iron, manganese, and arsenic are associated with ground water with lower redox potential at near-neutral pH (Hem, 1985; Kim, 1999; Korte and Fernando, 1991). This association can be observed in wells in Oakland County. However, nitrate and nitrite are readily reduced to nitrogen in low-redox environments. Appropriately, nitrate and nitrite were not present in any well with a concentration of arsenic, manganese, or iron in excess of the USEPA standard. Consumption of water with iron or manganese concentrations above the SMCL is not considered dangerous from a health perspective; however, both materials leave deposits in pipes and on fixtures, impart taste to beverages, and can discolor laundry (Shelton, 1997).

Sulfur is a common element in the Earth's crust, and occurs as sulfate (SO_4^{2-}) in waters with near-neutral pH and redox potential above –100 mV (Hem, 1985). Sulfate can be reduced under certain conditions to hydrogen sulfide, a compound with the smell of rotten eggs. In addition to leaving greenish deposits on plumbing fixtures, sulfate in concentrations above the SMCL can result in diarrhea (Shelton, 1997).

Fluoride is present in many natural waters in concentrations less than 1.0 mg/L. The MCL of 4.0 mg/L has been set to protect public health. Fluoride in excess of 4.0 mg/L can cause skeletal fluorosis, a serious bone disorder (Shelton, 1997). Concentrations in excess of 2.0 mg/L can cause dental fluorosis, a staining and pitting of the teeth (Shelton, 1997)

The SMCL for dissolved solids is based on aesthetic concerns, and is primarily related to the life expectancy of domestic plumbing and appliances. The service life for a hot water heater is reduced by one year for every 200 mg/L of dissolved solids in water above the average 220 mg/L (Shelton, 1997).

Nutrients

Species of nitrogen and phosphorus are frequently referred to as nutrients, because they are essential to plant life and are common in fertilizers, including manure, and in human waste. There are no health restrictions on consumption of phosphorus in drinking water, but the USEPA has set restrictions on nitrate (NO_3^-) and nitrite (NO_2^-).

Sources

Nitrogen and phosphorus are essential to all known forms of life. Consequently, they can be found throughout the environment in varying concentrations, even in rainwater. Typical nitrate concentrations in the precipitation of southwestern Michigan are approximately 0.6 mg/L as N, and typical phosphorus concentrations are 0.05 mg/L (Cummings, 1978)

Human activities have done much to alter the distribution of nutrients in the environment. Application of manure and chemical fertilizers to crops and lawns results in local abundance of nutrients, which is the desired outcome. But over-application can result in local excesses of nutrients, which can reach ground water. Septic tanks are designed to provide a means of containing and treating sewage, which typically contains elevated concentrations of nitrogen and phosphorus. But when environmental conditions, such as a high water table, alter the operation of a septic tank, nitrogen and phosphorus can be released into the ground water. The USEPA considers nitrate concentrations of 3 mg/L as N or higher to be the result of anthropogenic contamination (U.S. Environmental Protection Agency, 1996b).

Occurrence

Concentrations of nitrate and nitrite in Oakland County drinking water ranged from below the reporting limit (0.1 mg/L) to 23.9 mg/L as N, more than twice the MCL. Samples collected from two wells exceeded the MCL, although samples from three more wells contained concentrations greater than 2 mg/L as N. While not above the USEPA threshold for anthropogenic contamination, these concentrations are more than twice the median, and more than three times the atmospheric loading. Nitrite concentrations were consistently less than the MCL of 1.0 mg/L as N, ranging from 0.08 to less than the reporting limit of 0.01 mg/L as N.

The CAER used 6,198 of the 12,942 nitrate analyses performed by MDEQ to generate the map of nitrate occurrence in Oakland County (fig. 8). The majority of the discarded records were removed because of obvious errors in recording the address in the database. In the case of duplicate entries for a well, the highest concentration was retained. Each of the 900 survey sections in Oakland County was then assigned to one of four groups; nitrate present above the MCL, nitrate present below the MCL, nitrate present below 3 mg/L-N, or no observations. Approximately one percent (96) of the 7,814 unique wells identified by the CAER contained concentrations of nitrate greater than the MCL. A more detailed discussion of the mapping methods employed and the comparison between USGS analytical results and MDEQ analytical results is included in Appendix 2.

The map provides a summary of the nitrate data in the MDEQ database. Nitrate concentrations above 3 mg/L-N generally occur along a northeast-southwest axis, coincident with the region previously identified as both the interlobate outwash plains and the region of with the most permeable soils (see figure 5). This pattern of nitrate contamination of ground water through high permeability surface sediments has been widely documented in Michigan (Kittleson, 1987) and elsewhere (Madison and Brunett, 1985).

Nitrate concentrations in ground water change at spatial scales smaller than the square-mile mapping unit used in these maps. The classification applied to any square-mile mapping unit does not necessarily reflect the current status of all wells in that mapping unit. The data archived in the MDEQ database reflect analyses of samples collected between 1983 and 1997, with varying sample collection, handling, and analysis techniques. For example, replicate samples collected in this study, and some samples collected by state and county personnel, employed clean sampling techniques to minimize contamination. Samples in this study (excluding the short-interval samples, discussed later), as well as samples collected by state and county workers, were collected only after the well and plumbing system had been purged. Samples were returned to the state laboratory the same day for analysis within the next two days. The majority of the samples in the MDEQ database, however, were collected by homeowners and shipped by mail to the State laboratory for analysis. Thus there is no standard control on sampling procedures, handling techniques, or the time elapsed between sample collection and analysis.
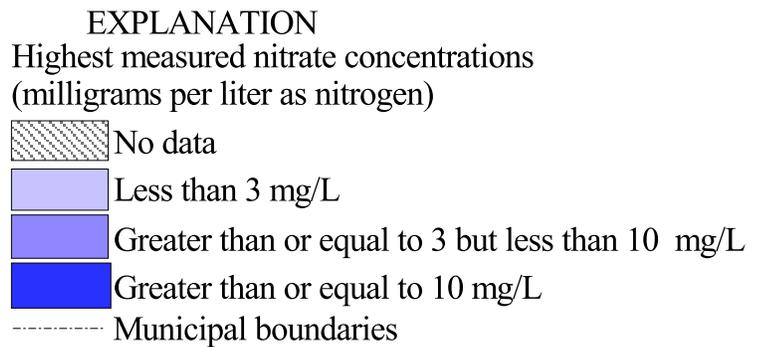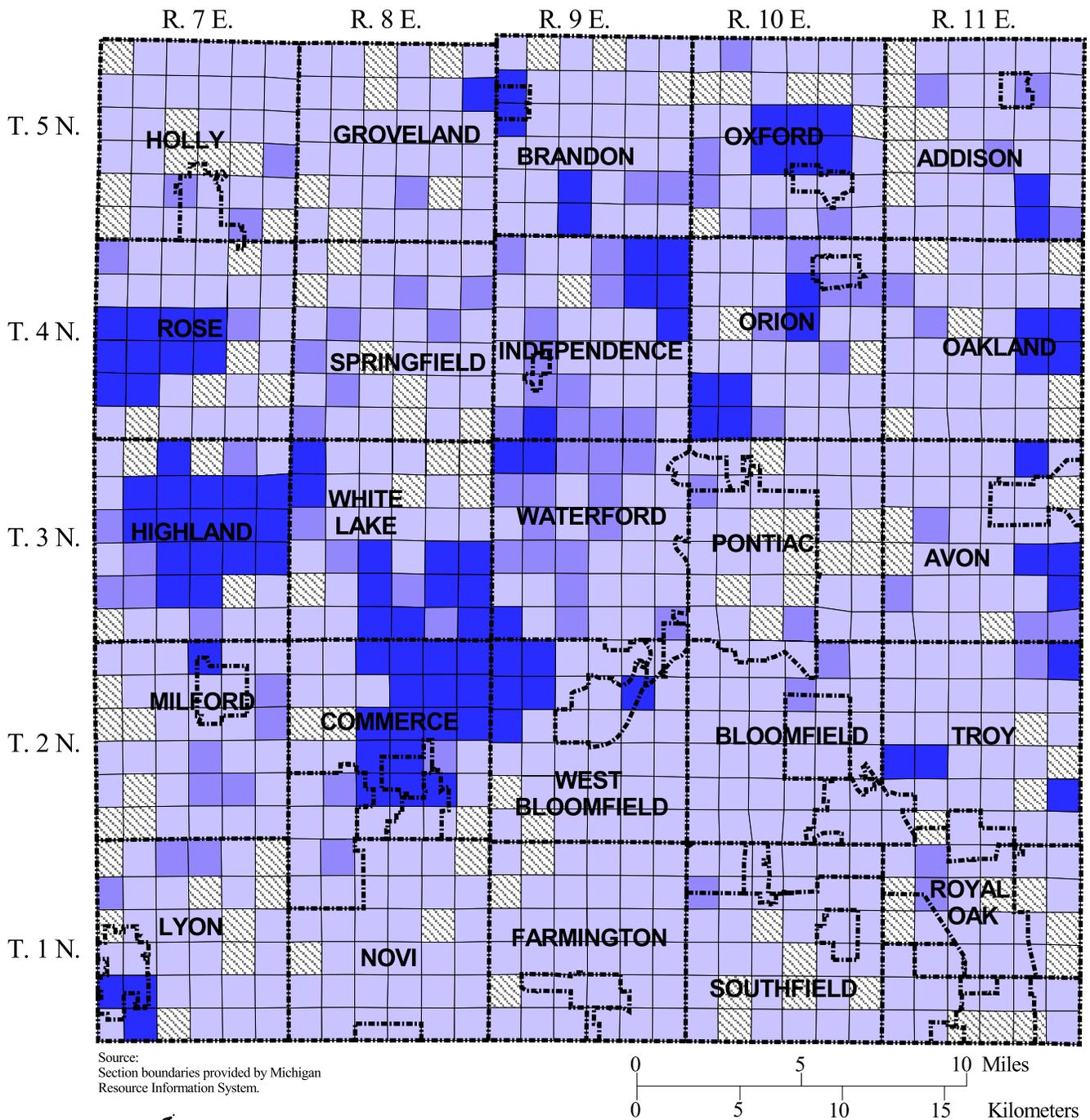
Figure 8. Nitrate distribution in Oakland County, Michigan. Map based on analyses performed at Michigan Department of Environmental Quality Drinking Water Laboratory.

Potential Health Effects

Nitrate has long been linked to methemoglobinemia in infants (Comly, 1945), commonly known as "blue baby syndrome." Methemoglobinemia occurs when nitrite (NO_2^-), a reduced form of nitrate, interacts with red blood cells and impairs their ability to carry oxygen (Mirvish, 1991). This impairment results in anoxia (deficiency of oxygen in the blood) and cyanosis (blue blood). In severe cases, blue-baby syndrome can be fatal (U.S. Environmental Protection Agency, 1996b). Susceptibility varies depending on age, body mass, and diet, but fetuses and infants under 6 months are most at risk. This is because 1) infantile hemoglobin is more susceptible to oxidation by nitrite than adult hemoglobin, 2) infants consume more water per unit body weight than do adults, and 3) the activity of the enzyme system that removes methemoglobin in infants is lower in infants than in adults (Keeney and Follett, 1991). For this reason, the USEPA has set restrictions on nitrate (NO_3^-) and nitrite (NO_2^-) concentrations of 10.0 and 1.0 mg/L as nitrogen, respectively (U.S. Environmental Protection Agency, 1996a). Most laboratories report nitrate and nitrite concentrations in terms of the weight of nitrogen (as above). In terms of the mass of the whole molecule, the MCLs are approximately 45 mg/L as NO_3^- and 3.3 mg/L as NO_2^-.

USGS scientists use clean sampling techniques to collect water for analysis from a residential well, Oakland County, Michigan.

Several authors (Keeney, 1986; Keeney and Follett, 1991; Moller and Forman, 1991; Crespi and Ramazotti, 1991) have accepted the correlation between nitrate consumption and various forms of cancer. Nitrosamines, formed from ingested nitrite and amines, which occur naturally in the digestive tract, also have been identified as carcinogens in laboratory experiments (Crespi and Ramazotti, 1991). Because nitrate and nitrite can be ingested from other sources, such as food and wine, no evidence currently exists for evaluating potential carcinogenic effects of nitrate on human populations (Crespi and Ramazotti, 1991).

Major Ions and Trace Metals

In addition to nutrients, water samples from the wells in Oakland County were analyzed for more than a dozen other characteristics. Summary statistics are provided in table 4. The complete listing of these results is included in appendix tables 1A to 1G. A more detailed description of the sources, occurrence, and health effects of chloride and arsenic has been developed to assist county employees and citizens in making decisions about drinking-water resources.

Collection of water samples for analysis, Oakland County, Michigan.

Chloride

Chloride is found in virtually all ground water. Chloride can occur in ground water naturally, but is also found throughout southeastern Michigan as the result of human activities (Thomas, in press). The principal natural source of chloride in ground water is seawater trapped within the rock matrix (Long and others, 1986). Several anthropogenic sources exist as well, including the salts used on roads for deicing and dust control, and water softeners. Chloride is a conservative ion in solution, and seldom interacts in organic or inorganic reactions in the subsurface (Hem, 1985). As a result, the evidence of anthropogenic additions of chloride may be present for many years.

Occurrence

Samples collected from 7 of the 37 wells exceeded the SMCL for chloride. Samples from every well contained a detectable concentration of chloride, ranging from 0.48 mg/L to 661 mg/L. The mean concentration was 104 mg/L and the median concentration was 23 mg/L.
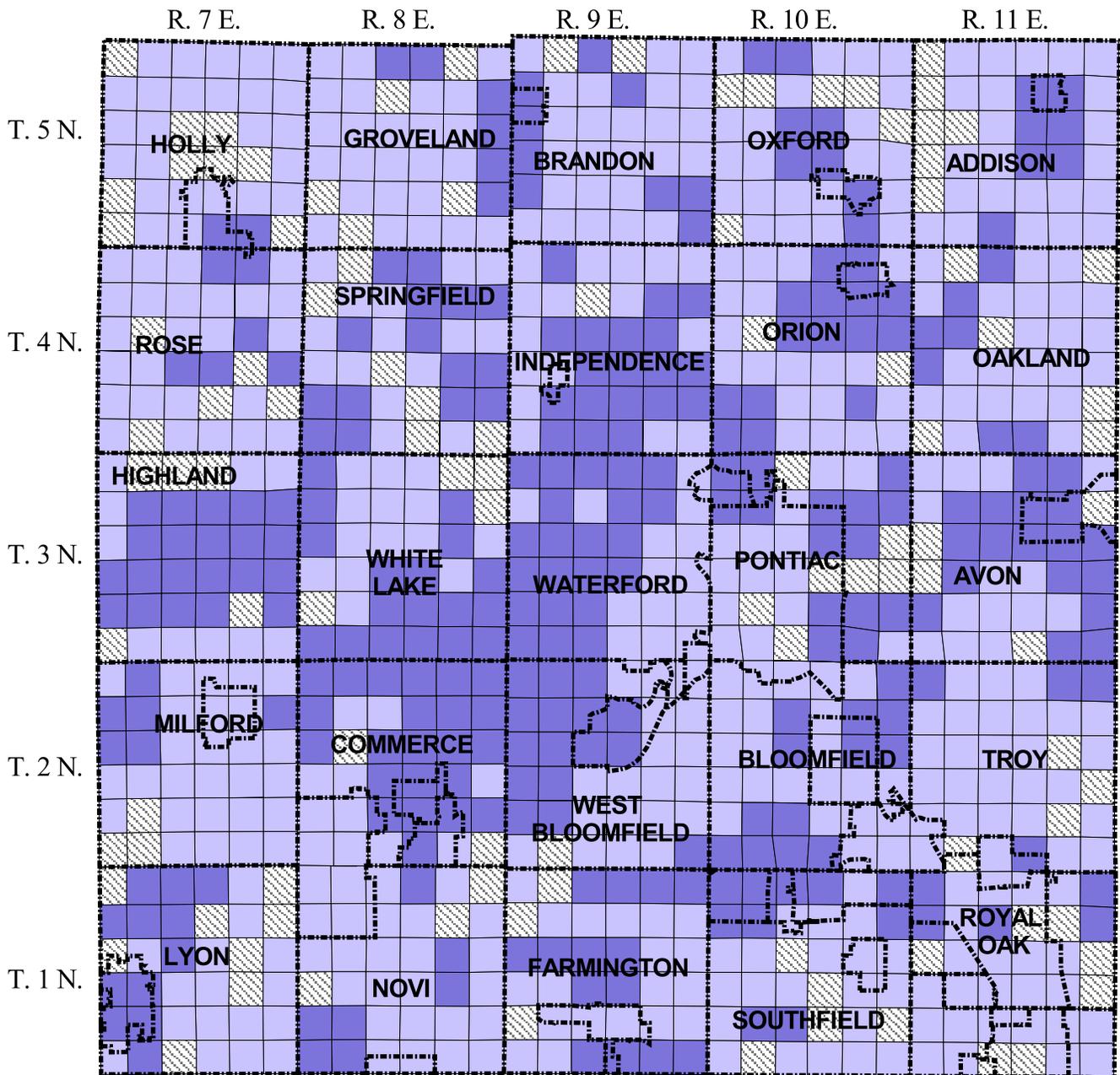
The CAER used 6,228 of the 12,960 chloride analyses performed by MDEQ to generate the map of chloride occurrence in Oakland County (fig. 9). The majority of the discarded records were removed because of obvious errors in the database. In the case of duplicate entries for a well, the highest concentration was retained. Each of the 900 survey sections in Oakland County was then assigned to one of four groups; chloride present above the SMCL, chloride present below the SMCL, chloride present below the MRL, or no observations. Approximately 5 percent (383) of the 7,809 unique wells identified by the CAER contained chloride in concentrations greater than the SMCL of 250 mg/L. Of the unique wells identified from the database, 1,581 did not have sufficient address location data to place them accurately on the map. A more detailed discussion of the mapping methods employed and the comparison between USGS analytical results and MDEQ analytical results is included in Appendix 2.

This map provides a summary of the chloride data in the MDEQ database. Because elevated chloride concentrations in ground water can come from both anthropogenic and natural sources, elevated chloride concentrations can be found throughout the county. Chloride concentrations in ground water can change at spatial scales smaller than the square-mile mapping unit used in these maps. The classification applied to any square-mile mapping unit does not necessarily reflect the current status of all wells in that mapping unit.
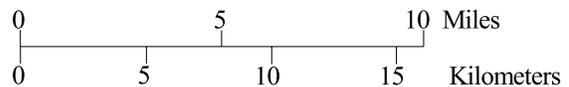
The data archived in the MDEQ database reflect analyses on samples collected between 1983 and 1997, with varying sample collection, handling, and analysis techniques. For example, replicate samples collected in this study, and some samples collected by state and county personnel, employed clean sampling techniques to minimize contamination. Samples in this study (excluding the short-interval samples, discussed later), as well as samples collected by state and county workers, were collected only after the well and plumbing system had been purged. The majority of the samples in the MDEQ database, however, were collected by homeowners and shipped by mail to the State laboratory for analysis. Thus there is no standard control on sampling procedures, handling techniques, or the time elapsed between sample collection and analysis.

Potential Health Effects

Hutchinson (1970) suggested that elevated chloride concentrations could have an effect on persons with pre-existing cardiac (heart) or renal (kidney) problems. The chloride SMCL of 250 mg/L is based on the aesthetic consideration of taste; water with higher concentrations of chloride tastes 'salty' to most people. A greater concern might be the presence of cations with chloride, such as sodium and potassium. Sodium in drinking water can be a concern for those on low sodium diets because of cardiac, circulatory, renal or other problems (Shelton, 1997).

R. 7 E. R. 8 E. R. 9 E. R. 10 E. R. 11 E.

T. 5 N.

HOLLY   GROVELAND   BRANDON   OXFORD   ADDISON

SPRINGFIELD

T. 4 N.   ROSE   INDEPENDENCE   ORION   OAKLAND

HIGHLAND

T. 3 N.   WHITE   WATERFORD   PONTIAC   AVON
         LAKE

MILFORD

T. 2 N.   COMMERCE   BLOOMFIELD   TROY

WEST
BLOOMFIELD

ROYAL
OAK

T. 1 N.   LYON   FARMINGTON
         NOVI   SOUTHFIELD

Source:
Section boundaries provided by Michigan
Resource Information System.

0   5   10 Miles

0   5   10   15 Kilometers

EXPLANATION

Highest measured chloride concentrations
(milligrams per liter)

No data

Less than 250 mg/L

Greater than or equal to 250 mg/L

– · – · – Municipal boundary

Figure 9. Chloride distribution in Oakland County, Michigan. Map based on analyses performed by the Michigan
Department of Environmental Quality Drinking Water Laboratory.

Arsenic

Arsenic is a common element in the Earth's crust, and occurs naturally throughout southeastern Michigan in several forms. In ground water, arsenic has been observed to occur in two forms; the oxidized form, arsenate (As^{+5}), or the reduced form, arsenite (As^{+3}). Kim (1999), working with the USGS Drinking Water Initiative (DWI) project, has shown that most (65-94 percent) of the arsenic in ground water in Oakland County is arsenite. Kim (1999) has also observed that the presence of the bicarbonate ion (HCO_3^-) in solution can enhance the rate of arsenic dissolution into ground water, although the species of arsenic released by this process is arsenate. Arsenate is readily sorbed to metal oxides, such as iron oxide, and rendered immobile (Korte and Fernando, 1996). For arsenic to be released into solution from the mineral form, arsenian pyrite (Kolker and others, 1998), aquifer sediments must first be oxidized, then reduced. The hydrologic mechanism facilitating this process has not yet been determined.
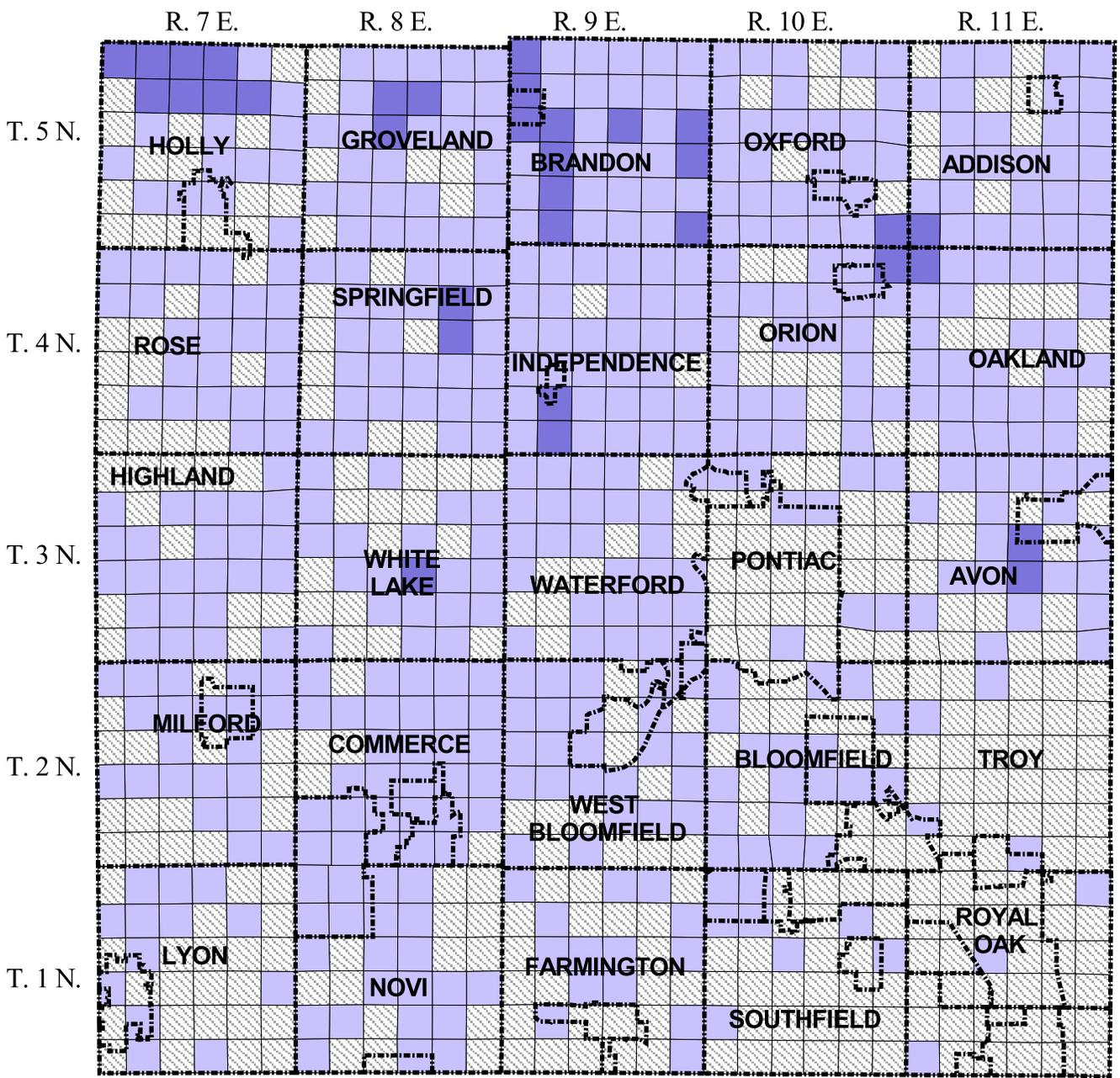
Occurrence

Low concentrations of arsenic are found throughout southeastern Michigan. The largest concentration detected in Oakland County by this study was 0.175 mg/L. Samples from five of the 38 wells exceeded the MCL, 0.05 mg/L, although all had previously been noted to exceed the MCL based on results from the MDEQ laboratory and were sampled to obtain additional supporting chemistry. Of the other wells sampled, 9 contained arsenic in concentrations below the minimum reporting level of 0.001 mg/L. The remaining 24 wells all contained some detectable concentration between 0.001 and 0.050 mg/L.
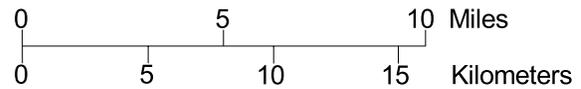
The CAER used 1,988 of the 3,509 arsenic analyses performed by MDEQ to generate the map of arsenic occurrence (fig. 10) using procedures similar to those described for nitrate and chloride. These maps are similar to those released previously in USGS Fact Sheet 135-98 (Aichele and others, 1998). Approximately one percent (24) of the 2,373 unique wells identified by the CAER contained arsenic at concentrations greater than the MCL of 0.05 mg/L. Of the unique wells identified from the database, 385 did not have sufficient address location data to place them accurately on the map. A more detailed discussion of the mapping methods employed and the comparison between USGS analytical results and MDEQ analytical results is included in Appendix 2.

The map provides a summary of the arsenic data in the MDEQ database. Arsenic concentrations in ground water can change at spatial scales smaller than the square-mile mapping unit used in these maps. The classification applied to any square-mile mapping unit does not necessarily reflect the current status of all wells in that mapping unit.

The data archived in the MDEQ database reflect analyses on samples collected between 1983 and 1997, with varying sample collection, handling, and analysis techniques. For example, replicate samples collected in this study, and some samples collected by state and county personnel, employed clean sampling techniques to minimize contamination. Samples in this study (excluding the short-interval samples, discussed later), as well as samples collected by state and county workers, were collected only after the well and plumbing system had been purged. The majority of the samples in the MDEQ database, however, were collected by homeowners and shipped by mail to the State laboratory for analysis. Thus there is no standard control on sampling procedures, handling techniques, or the time elapsed between sample collection and analysis.

Figure 10. Arsenic distribution in Oakland County, Michigan. Map based on analyses performed by the Michigan Department of Environmental Quality Drinking Water Laboratory. The Maximum Contaminant Level (MCL) for arsenic, currently 0.05 mg/L, is being reviewed by the U.S. Environmental Protection Agency.

Potential health effects

The USEPA has set an MCL of 0.05 mg/L for arsenic in drinking water, although no distinction is made between the two arsenic species. In May, 2000 the USEPA proposed revising the MCL to 0.005 mg/L, and is accepting public comment on MCLs of 0.003 mg/L, 0.005 mg/L, 0.010 mg/L, and 0.020 mg/L. A final decision is expected early in 2001.

Several authors have suggested that arsenite may be a more serious health concern than arsenate (Pontius and others, 1994; Kosnett, 1997). The effects of chronic arsenic ingestion are based on the total daily dose and length of exposure, not the concentration specifically. The daily dosage from drinking water can be estimated based on the concentration in the water and the quantity of water consumed. For example:

[As concentration]	* Quantity of water	= Dose
0.050 mg/L	* 2 L	= 0.100 mg
0.025 mg/L	* 2 L	= 0.050 mg

This calculation is only an estimate of total daily arsenic ingestion, because there are other environmental sources of arsenic. Some of these sources include shellfish, meats, dust, soil, and some pigments. The U.S. Food and Drug Administration has estimated that US adults ingest about 0.053 mg As/day from the diet, not including drinking water (Guo and others, 1998). Nearly half of this amount comes from fish and shellfish. Marine shellfish and cod typically contain arsenic concentrations between 10 and 40 mg/kg based on fresh weight (National Academy of Science, 1977). Freshwater fish, other marine fish, pork and beef typically contain less than 1 mg As/kg (National Academy of Science, 1977).

Kosnett (1997) defines three classes of arsenic exposure, and outlines the symptoms and risks associated with each class. For an average adult, low exposure includes inorganic arsenic doses up to 0.5 mg/day. Moderate exposure includes dose of 0.5 to 1.5 mg/day, and high exposures are doses in excess of 1.5 mg/day. These exposure classes are based on the total mass of arsenic ingested from water (described above) and from food. Low doses seldom result in any noticeable symptoms of illness. Moderate exposures for prolonged periods (5 to 15

years) may result in skin discoloration and lesions, anemia, peripheral neuropathy and peripheral vascular disease. In addition to the symptoms of moderate exposure, high doses may result in edema, more pronounced peripheral neuropathy including motor weakness, diminished reflexes, and muscle atrophy. High doses also may result in gastrointestinal disturbances such as nausea and diarrhea, as well as general fatigue and weight loss.

Arsenic has been listed as a Group A human carcinogen by the USEPA on the basis of inhalation and ingestion exposure. The carcinogenic effects of low-level arsenic ingestion in drinking water are widely disputed in the medical literature and are currently under review by the USEPA. Several case studies of groups exposed to arsenic occupationally or medicinally, such as Moselle wine growers (Luchtrath, 1983) and users of the Victorian health tonic 'Fowler's solution,' an alkaline solution of potassium arsenate marketed in the US until 1980, have indicated increased risks of bladder cancers (Cuzick and others, 1992). Several studies in Taiwan (Tsuda and others, 1995; Pontius and others, 1994) have observed increased risk of urinary tract cancers as a result of consuming water containing arsenic. No statistically significant relation was observed between arsenic concentration in drinking water and the occurrence of liver, kidney, bladder, or urinary tract cancer for persons consuming water containing less than 0.33 mg/L in Taiwan (Guo and others, 1998).

Different populations may also have different processes to remove arsenic from the body. Most mammals remove arsenic from their bodies by incorporating the arsenic into organic compounds, a process known as methylation. These organic compounds are easier for the body to remove. Dr. Vasken Aposhian of the University of Arizona has determined that several South American mammals have developed a means of removing arsenic from the body other than methylation (Kaiser, 1998). Several native human populations in the Andes Mountains exhibit a similar trait (Kaiser, 1998). Despite drinking water with levels of arsenic more than twice the USEPA MCL, these populations do not exhibit any increased occurrence of cancer (Kaiser, 1998).

At this point, no comprehensive epidemiological study has been performed on a US population consuming arsenic in drinking water over an

extended period of time. The best information available comes from studies in Taiwan and Bangladesh, whose populations differ sharply from United States populations in lifestyle, diet, and genetic inheritance.

Results of Time-Series Analyses

Analyses of well water samples collected by the Oakland County Health Division and homeowners as part of routine sampling have indicated changes in arsenic concentration of as much as 0.05 mg/L or more over periods of time ranging from days to years. This variation has raised concerns that 1) concentrations of arsenic and other dissolved constituents may be changing in the aquifer, or that 2) some samples may have been collected without an adequate well purge. An inadequate well purge would mean that drinking water (water drawn from a tap immediately) was being compared to ground water (water drawn after the plumbing system and well bore have been purged). As part of this study, ground-water samples were collected from selected wells to attempt to observe long-term variability in the aquifer, while drinking-water samples were collected to evaluate the potential to obtain varying results based on an inadequate purging of the well.

Very little change was observed in any characteristic between ground-water samples collected in June/July 1998 and those collected in December 1998.

All sites exhibited some chemical changes in the short-term drinking-water sampling (Appendix table 1E-1G). Total iron concentrations fluctuated with time in all wells, although the magnitude of the fluctuation was usually less than 10 percent of the concentration. OAK 35 exhibited a marked increase in iron and arsenic concentration over time. Iron concentrations increased from 216 to 1500 μg/L over a span of 10 minutes. Arsenic concentrations increased from 0.001 mg/L to 0.01 mg/L over a time span of four minutes. This sample was collected from a tap at an outbuilding that had not been used for more than two days. This point was sampled because, based on the chemistry data collected earlier, this well was expected to exhibit a short-term change. Improper purging of a well prior to sampling may result in lower concentrations of both arsenic and iron, particularly when the water has been standing in the pipes for a prolonged period.

Results of Replicate Sample Analysis

The analytical results from the USGS NWQL and the MDEQ Drinking Water Laboratory for nitrate, chloride, and arsenic agree closely. Mean differences in concentration measurements for nitrate, chloride, and arsenic were 0.1, 6.8, and 0.0008 mg/L, respectively. The standard deviation of the differences was 0.3, 9.6, and 0.003 mg/L for nitrate, chloride, and arsenic, respectively. Graphs showing the comparative analytical results over a range of concentrations are provided in Appendix 2.

SUMMARY

The quality of ground water in Oakland County is the result of a combination of natural and anthropogenic processes. Many wells produce highly reduced water with high concentrations of iron and manganese. All of the wells sampled during 1998 contained chloride, although most contained concentrations below the U.S. Environmental Protection Agency (USEPA) Secondary Maximum Contaminant Level (SMCL). Twenty-nine of thirty-eight wells contained detectable concentrations of arsenic, although only five contained arsenic concentrations above the USEPA Maximum Contaminant Level (MCL). These five wells are best considered separately, because they were known from previous samplings to contain arsenic, and were sampled to provide additional chemical information. Only two wells contained nitrate in concentrations above the MCL, although three additional wells contained concentrations several times higher than would be expected to be found in precipitation.

Seasonal variations in water-quality were not observed in any of the five wells resampled in December 1998. Some short-term variations during the purging of the wells were observed in all wells. All wells exhibited variation in iron concentration; three of five exhibited fluctuations of approximately 10 percent, while 2 of the five exhibited increasing trends. One well exhibited an increasing trend in arsenic concentration, coincident with an increasing trend in iron concentration. Thus, while in many cases analytical results may not be affected by the length of time a well is purged, in at least one of the five subject wells purge time would have influenced the resulting arsenic concentration.