# Wisconsin Ground Water Association Newsletter

**Inside This Issue:**

## President's Message

It is late summer and time to take stock of the year that is nearly over. Continuing the theme I raised in this column in the Spring newsletter, I want to challenge WGWA members to become involved in this organization. For years I received the WGWA newsletter and attended the WGWA meetings I could fit into my schedule. Then one day, the then President of WGWA, Bruce Hensel called to ask if I would consider running for President-Elect of WGWA. As we were talking it occurred to me that although I had enjoyed being a member of this organization for years, I had not participated in its operation. I felt it was my turn to contribute.

WGWA is your organization. You are a member because you are interested in ground water in Wisconsin and desire to share your interest with others and hear about what is going on in the state related to ground water. WGWA traditionally has met in three different forums; regional meetings, an annual technical meeting and a spring field trip. The regional meeting forum is unique to WGWA. These meetings are a chance to get together with colleagues who work near you for other organizations. Of the five regions, three are currently without area coordinators; Western Area, Southern Area, and Northeast Area.

We need your help. I encourage you to become an area coordinator or assist the current area coordinators. Better yet, contact a colleague at your office or at another firm or agency to co-lead a regional group. The idea is to get people together who have a common interest in ground water. Call a colleague you haven't spoken to in some time and suggest that you share organizing monthly or bi-monthly regional meetings. You can use the *WGWA Notes* e-mail forum to announce the meetings, which

*(Continued on page 2)*

The newsletter is published four times per year. If you have any suggestions or submissions, please contact us, at: Wisconsin Ground Water Association, c/o Ayres Associates, P.O. Box 1590, Eau Claire, WI 54702-1590. Our email address is wgwainfo@wgwa.org; our electronic mailing list is maintained by wgwanotes@wgwa.org; and our web site is at http://www.wgwa.org.

Please contact wgwainfo@wgwa.org if you have submissions for upcoming newsletters.

# President's Message (cont.)

*(Continued from page 1)*

don't have to be formal. Getting together over breakfast or gathering after work is a good start. After a few meetings perhaps someone will think of a person willing to make a brief presentation to the group. Having a formal presentation is not necessary, simply getting together is more important.

The WGWA Board, on your behalf, is involved in several interesting ongoing projects involving ground water in Wisconsin. WGWA co-sponsored the Midwest Ground Water Conference at the Inn on the Park in Madison October 22 to 24. Go to the Water Resources Institute web page for more information (www.wri.wisc.edu). A ground-water summit is being held by the WDNR and other agencies in October to discuss where we have come from since the Ground-Water Law was passed in 1984 and where we are going. The Wisconsin Academy of Science Arts and Letters is organizing Waters of Wisconsin, a discussion of The Future of Our Aquatic Ecosystems and Resources. For more information on the Waters of Wisconsin project go to their web page (www.wisconsinacademy.org/programs/wisconsinidea.html).

Each of the activities listed above provides a forum for exchange of information among people interested in various aspects of ground water. There are many opportunities for you to interact with other ground-water professionals in Wisconsin to share your expertise, gain knowledge, and have fun at the same time.

Please do not hesitate to contact me or any of the board members with your suggestions regarding how to improve the vibrancy and usefulness of WGWA activities to you. This is your organization; working together we can exchange information and enjoy each other's company at the same time.

*Margy Blanchard, WGWA President*

## God Bless America

The members of the WGWA Board and Newsletter Committee extend our sympathies to the many people who have been touched by the tragedy of the terrorist attacks on our country on September 11, 2001. Our thoughts are with you. We are grateful to those of you who are and will be defending our country in the armed forces. We are grateful to the firefighters, police officers, clergy, nurses, doctors, rescue workers and others who have selflessly given of themselves to help in the rescue and recovery efforts. And we join in grieving for the victims and those who gave their lives to save others.

## Fall Technical Conference and Elections

This year, the WGWA fall technical conference meeting will not be held, in lieu of a joint meeting with the Wisconsin Chapter of the American Water Resources Association in March 2002.

WGWA will hold this year's election via mail ballot. The ballots will be mailed to you on December 3, and will be due back two weeks later, by December 17. The results will be announced shortly thereafter.

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# Wayne's Web World (WWW)

## Maps on the Internet -- An Update

In the Winter 2000 issue of the Wisconsin Ground Water Association Newsletter, I described some of the readily available map resources on the Internet. Some of these websites were maintained by governmental agencies, others were endeavors of private enterprise and still others benefited from having the resources of large companies behind them. All of them held the promise of greater things to come.

Well, how have things changed in nearly two years? A little, but a little means so much in some cases. Mapquest (http://www.mapquest.com/), which many of us have used to find the locations of meetings or field sites, has added topographic maps and aerial photographs. Many of the aerial photographs are in color. Unfortunately, when an aerial photograph is available there is only one. The true utility of on-line aerial photographs will not be realized until more than one example of a historical aerial photograph is available for any particular location. A feature on Mapquest that was intended to help travelers find services (for instance, restaurants and lodging) near their destination can be used to help those involved in environmental consulting. For environmental consulting, selecting "gas stations" will display all the locations matching the search criteria within a specified area. Detailed information (name, address and telephone number) for each facility can then be displayed by clicking on the icon.

Omnimap (http://www.omnimap.com) is more of an on-line catalog, but provides an excellent compilation of resources needed by hydrogeologists. For instance, downloadable topographic map indices are available for every State and Territory, as well as on-screen, detailed charts of topographic map symbols. Topographic and geologic maps are available for purchase for every State. Two rare, but valuable publications, offered for sale at this website are the Roadside Geology Guides published by Mountain Press Publishing Company (Missoula, Montana) and the nation-wide set of geologic maps published by the American Association of Petroleum Geologists.

In the previous article on Internet map resources, I noted that Terraserver provides on-screen and downloadable digitized aerial imagery for much of the United States, as well as many other parts of the world. Terraserver has converted to a subscription site. However, the "backdoor" (http://terraserver.homeadvisor.msn.com/) still works the same as always.

I had previously mentioned the availability of free historical maps from the Library of Congress (http://memory.loc.gov/), but didn't describe their characteristics in any detail. These maps are often hand-colored maps showing territorial boundaries for portions of the United States in the 1800s. But there are also more than 1500 perspective (or panoramic) maps from the late 1800s and early 1900s. At first glance the perspective maps would seem to be of little value for determining the locations of features pertinent to a hydrogeologist's work. However, many of the perspective drawings are rich with detail noting the locations of governmental offices, water works facilities, sewage treatment facilities, and local businesses and industries. For instance, on a perspective map of Waukesha, Wisconsin for 1880, a foundry and machine shop is shown on the west bank of the Fox River where it passes under Madison Street. This property is currently an open lot used for parking. On the perspective map for Racine, Wisconsin from 1883, the "Racine Gas Works" on Water Street near the Root River is designated as #66 in map legend.

The USEPA maintains an evolving website they denote as Enviromapper (http:/www.epa.gov/enviro/html/em/index.html/). Enviromapper is divided into seven categories, including Window to My Environment, Envirofacts, Brownfields, Empact, Watersheds, Office of Water, and Superfund. With Enviromapper you can create maps containing various environmental data, including air releases, drinking water, toxic releases, hazardous wastes, water discharge permits, and Superfund sites. Maps can be created on a national, state or county basis.

As the mapping capabilities of the Internet continue to improve and more data is stored in digital form, you can expect the features of the websites noted above to continue to evolve and new websites to be created.

***Wayne Hutchinson***
***Delta Environmental Consultants***

Acrobat Document

# The Ground-Water Source: Notes from the Supply Side

## Aquifer Storage and Recovery (ASR) of Drinking Water Using the Sandstone Aquifer in Wisconsin

Aquifer storage and recovery (ASR) is a technology for storing large volumes of water underground using one or more wells and recovering the water when needed through the same wells. During low demand periods, potable water is recharged and stored in the aquifer and recovered to meet peak, emergency, or long-term demands. The treated water recharged into the aquifer using ASR wells displaces the native ground water around the well, forming a bubble. The recovered water provides suitable water quality to meet demands without re-treatment other than disinfection. As of March 2001, 41 ASR systems are operational in the United States with an additional 50 ASR systems in various stages of development.

By storing water in a natural reservoir underground, aboveground facilities can be designed and operated near average demands instead of peak demands. This reduces both capital and operating costs and improves the usefulness of existing water supply, treatment, and transmission facilities by extending their capacity to meet peak and emergency demands.

### *ASR Applications in Wisconsin and the Midwest*

Since the early 1990s, interest in ASR has been increasing in the Midwest due to increasing water demands. Both historically and currently, many water-supply systems in the Midwest use the deep, Cambrian-Ordovician-aged sandstone aquifer system. However, this aquifer has been excessively overpumped and often yields water containing constituents that exceed one or more drinking water standards (such as, total dissolved solids or combined radium). For these reasons, many communities have converted to other water supplies, reserving their existing deep wells for emergency use. For two of these communities in Wisconsin, the normally dormant wells are being utilized as part of an ASR application for meeting seasonal peak demands while eliminating combined radium standard violations associated with the ground water. Using the existing wells, treated water is recharged and stored in the deep aquifer (Cambrian-Ordovician aquifer) during low-demand periods. The recharge water effectively displaces the native ground water that exceeds the combined radium standard. The recharged water is recovered during higher demand periods allowing the utilities to size their water treatment plant capacity closer to the projected average-day demand instead of the projected maximum-day demand, resulting in significant capital cost savings. Additionally, ASR provides system redundancy and an emergency supply for the communities.

Because of more stringent ground-water standards in Wisconsin, the potable drinking water exceeds state standards during ASR activities for chlorination by-products (trihalomethanes). Thus, even though the treated drinking water meets the proposed stage 2 Enhanced Surface Water Treatment Rule total trihalomethanes (THMs) concentration of 40 micrograms/liter (ug/L), drinking water becomes a “contaminant” when placed in the ground-water environment. For ground water, enforcement standards have been established for individual trihalomethane compounds. In 1996, an American Water Works Association Research Foundation (AWWARF) study showed that THMs naturally degrade during ASR storage. Pilot testing of ASR was performed in Wisconsin to show degradation of THMs during storage as well as to evaluate other water quality concerns.

### Oak Creek, Wisconsin

Oak Creek Water & Sewer Utility, located in southeastern Wisconsin, evaluated ASR as a possible cost-effective alternative to a second water treatment plant expansion. They received co-funding from AWWARF to evaluate the fate of trihalomethanes and radionuclides during ASR operations (Tailored Collaboration Project No. 2539). Using a converted former production well, four recharge and recovery testing cycles were conducted; two small volume, and two full-scale 42 million gallon cycles.

Trihalomethane concentrations in a monitoring well located 180 feet away were observed to degrade over a 6-week storage period. Other constituents of concern in the recovered water, were shown to improve with each testing cycle. The non-potable ground water was effectively displaced by the potable water recharged into the aquifer through the ASR well (see figure). Water quality from the first full-scale cycle (Cycle 3) met all primary drinking standards through 100 percent recovery, but exceeded the secondary drinking water standard for manganese at 85% recovery. Wisconsin DNR allowed Oak Creek to recover the water from the second full-scale cycle into their distribution system.

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Manganese concentrations in the recovered water are expected to decrease with subsequent cycles. The Wisconsin DNR, Oak Creek Water & Sewer Utility, and CH2M HILL are working to develop revisions to policy, administrative rules, or statutes to allow ASR to be used by water utilities statewide. Meanwhile, the Wisconsin DNR has extended the conditional approval to allow Oak Creek Water & Sewer Utility to perform another full-scale cycle in 2001.

The Oak Creek ASR project, funded and performed by the American Water Works Association Foundation, Oak Creek Water & Sewer Utility, CH2M HILL, and Kaempfer & Associates, received state and national level awards in the 2000 Engineering Excellence competition hosted by the American Consulting Engineers Council.

### Green Bay, Wisconsin

The Green Bay Water Utility (GBWU) is also evaluating ASR to assist with their seasonal demands. During 2000, GBWU performed some preliminary testing to identify flow zones and radioactive intervals within the sandstone aquifer within northeastern Wisconsin. Bedrock core data, geophysical logging and packer testing indicated that the Elk Mound formation in the lower portion of the borehole was most permeable contributing up to 65% of the flow. Radioactivity as well as other potential water quality concerns including heavy metals such as arsenic appeared to be related to the deposits in the Trempealeau and Tunnel City Groups. However, packer tests suggested that these water quality concerns could not be isolated without potentially decreasing the yield of the well.

GBWU is in the process of retrofitting one of their dormant deep wells for ASR and plan to begin ASR testing cycles during next fall and winter. During the testing program, radionuclides, arsenic, and other water-quality parameters will be tested and evaluated.

### *Conclusions*

ASR in Wisconsin using the Cambrian-Ordovician-aged sandstone aquifer appears to be a viable technology. During the testing of the aquifer in Wisconsin, the following was concluded:

- The sandstone aquifer allows economically-feasible rates of recharge (1 million gallons per day [MGD]) and recovery (1.5 MGD).
- No evidence of well or aquifer plugging is evident in the data.
- One hundred percent of the water can be recovered without exceeding a primary drinking water standard.
- Trihalomethanes degrade during storage in the sandstone aquifer. After 100 percent of volume recovery, trihalomethane concentrations fall below the ground-water enforcement standards at the ASR well. Therefore, after each seasonal ASR cycle, there is no violation of Wisconsin’s ground-water Enforcement Standards.
- ASR provides utilities with many economic and operational benefits.
- ASR may be a cost-effective solution for other Wisconsin utilities to meet seasonal peak demands, emergency supply, or seasonal water-quality sources.
- Support is needed to resolve the regulatory nconsistencies that limit the application of ASR in Wisconsin.

*Kathi D. Ried, P.G.*
*CH2M HILL*

# The Ground-Water Source (cont.)

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# Model Speak

## A Simple Method to Determine Well Interference Drawdown for Wells Tapping Unconfined Aquifers

By Michael Kasenow, Ph.D., CPG-10324; CGWP-117367 and Paul Pare, M.S.

### Drawdown In A Confined Aquifer

The decline in water level measured from any well during an aquifer pumping test is called drawdown. Drawdown increases over time and decreases with distance from the production well. It should be collected meticulously in the field and recorded with the exact time of measurement. Drawdown and the time of drawdown are the most important field data collected during an aquifer test. The total drawdown (s) is the value recorded in the field, but the total drawdown is often the sum of various drawdown components, some of which can be corrected or neglected under various conditions (Kasenow, 2001). The most accurate drawdown measurements occur under confined flow conditions (s') when observation wells fully penetrate the thickness of homogeneous and isotropic confined aquifer. When this is the case, total drawdown is equal to confined drawdown (s=s').

### Drawdown In An Unconfined Aquifer

Drawdown in wells tapping unconfined aquifers is not as intuitive. Ground water drains under the influence of gravity in this type of aquifer; therefore, the aquifer is dewatered near the vicinity of the production well (Fig. 1). The continuous dewatering of the aquifer reduces the saturated thickness, which reduces the observed or apparent transmissivity as drawdown increases and ground water approaches the well screen. Therefore, total drawdown in a well tapping an unconfined aquifer, can be expressed as the sum of drawdown due to confined flow (s') and drawdown due to dewatering ($s_d$):

$$s = s' + s_d \tag{1}$$

Jacob (1963) developed an expression for that portion of drawdown produced by dewatering (sd) in an unconfined aquifer:

$$s_d = \frac{s^2}{2b} \tag{2}$$

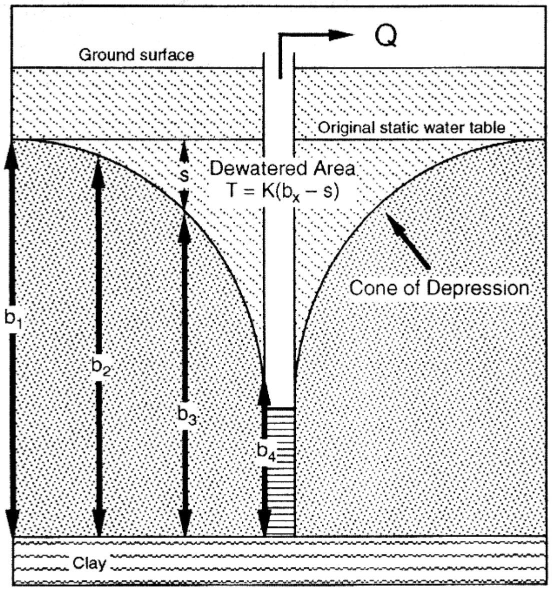

**Figure 1. Drawdown in an unconfined aquifer during a pumping test.**

b = aquifer thickness
s = total drawdown during a pumping period.

Jacob (1963) showed how unconfined drawdown can be corrected to simulate confined drawdown under pumping stress (s=s'). This correction allows for ease of aquifer parameter estimation when using transient solution methods and delayed yield is negligible. This correction is made by using equation (3):

$$s' = s - \left[\frac{s^2}{2b}\right] \tag{3}$$

Unfortunately, equation (3) cannot be easily rearranged to isolate and estimate a field-measured drawdown (s). In order to do so, it must be expressed as a quadratic equation, which has two solutions (Lehr, 1964):

$$s^2 - 2bs + 2bs' = 0 \tag{4}$$

Fortunately, quadratic equations can be expressed as

$$s = \frac{-B \pm \sqrt{B^2 - 4ac}}{2a} \tag{5}$$

where a, B, and c are real numbers. Using this approach, the authors have simplified the solution supplied by

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# Model Speak (Continued)

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equation (4), where s, s', and b are as previously defined:

$$s^2\left[-\frac{1}{2b}\right]+s-s'=0. \quad s=\frac{-1\pm\sqrt{1^2-4\left(-\frac{1}{2b}\right)(-s')}}{2\left(-\frac{1}{2b}\right)} \tag{6),(7}$$

$$s=\frac{-1\pm\sqrt{1-\left(\frac{2s'}{b}\right)}}{-\frac{1}{b}} \quad s=-b\left(-1\pm\sqrt{1-\left(\frac{2s'}{b}\right)}\right) \tag{8),(9}$$

$$s=b\left(1-\sqrt{1-\left(\frac{2s'}{b}\right)}\right) \tag{10}$$

Equation (10) is simply another form of equation (1):

$$s=s'+s_d$$

Although quadratic equations have two solutions, equation (9) has only one reasonable solution, which is equation (10), because the other solution results in a value larger than the aquifer thickness. In order to estimate total unconfined drawdown using equation (10), the theoretical confined drawdown must be known. This is easily completed when the aquifer's transmissivity (T) and storage coefficient (S) have been determined or can be reasonably estimated.

Table 1 compares unconfined field measured drawdowns to total unconfined drawdowns using equation (10). The model drawdowns in Table 1 were determined from the corrected to confined drawdowns in Table 2, which were used to determine T and S. It is clear by these results that equation (10) can be used to estimate total drawdown in an unconfined aquifer, under the stress of a pumping well, when the theoretical confined drawdown is known.

When the theoretical confined drawdown is known, that portion of drawdown due to dewatering can also be determined. For example, the total unconfined drawdowns in Table 1, when corrected using equation (3), are transformed into confined drawdowns. At an observation well distance of 30 feet, and a time of 240 minutes, the corrected or confined drawdown is 3.13 feet. Rearranging equation (1) results in $s_d=s-s'$, which can be used as follows:

$$s_d = 3.35\ ft - 3.13\ ft = 0.22\ ft. \tag{1.1}$$

The predicted drawdown due to dewatering, in this case, is 0.22 ft, and agrees with equation (2).

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**Table 1. Field measured drawdowns for an unconfined aquifer (including dewatering drawdown) compared to model drawdowns (equation 10). Model drawdowns are in bold type. The field measured drawdowns are from U. S. Department of Interior (USDI, 1981).**

| Time (min) | R=30 ft | **30 ft** | 60 ft | **60 ft** | 120 ft | **120 ft** |
|---|---|---|---|---|---|---|
| 4.00 | 0.19 | **0.20** | 0.00 | **0.00** | 0.00 | **0.00** |
| 6.00 | 0.35 | **0.36** | 0.02 | **0.02** | 0.00 | **0.00** |
| 8.00 | 0.51 | **0.50** | 0.04 | **0.04** | 0.00 | **0.00** |
| 10.00 | 0.63 | **0.63** | 0.08 | **0.08** | 0.00 | **0.00** |
| 15.00 | 0.90 | **0.90** | 0.17 | **0.18** | 0.00 | **0.00** |
| 20.00 | 1.11 | **1.11** | 0.27 | **0.28** | 0.01 | **0.01** |
| 25.00 | 1.28 | **1.28** | 0.38 | **0.37** | 0.02 | **0.02** |
| 30.00 | 1.43 | **1.43** | 0.47 | **0.47** | 0.04 | **0.04** |
| 35.00 | 1.56 | **1.56** | 0.55 | **0.55** | 0.05 | **0.06** |
| 40.00 | 1.67 | **1.67** | 0.63 | **0.63** | 0.07 | **0.08** |
| 45.00 | 1.77 | **1.77** | 0.68 | **0.70** | 0.10 | **0.10** |
| 50.00 | 1.86 | **1.86** | 0.76 | **0.77** | 0.12 | **0.12** |
| 55.00 | 1.94 | **1.95** | 0.84 | **0.84** | 0.15 | **0.15** |
| 60.00 | 2.02 | **2.02** | 0.90 | **0.90** | 0.18 | **0.18** |
| 70.00 | 2.16 | **2.16** | 1.00 | **1.01** | 0.21 | **0.23** |
| 80.00 | 2.28 | **2.29** | 1.11 | **1.11** | 0.27 | **0.28** |
| 90.00 | 2.40 | **2.40** | 1.20 | **1.20** | 0.32 | **0.33** |
| 100.00 | 2.50 | **2.50** | 1.28 | **1.28** | 0.37 | **0.37** |
| 110.00 | 2.59 | **2.59** | 1.36 | **1.36** | 0.43 | **0.42** |
| 120.00 | 2.67 | **2.67** | 1.42 | **1.43** | 0.47 | **0.47** |
| 150.00 | 2.88 | **2.88** | 1.61 | **1.61** | 0.60 | **0.59** |
| 180.00 | 3.06 | **3.06** | 1.77 | **1.77** | 0.70 | **0.70** |
| 210.00 | 3.21 | **3.21** | 1.91 | **1.91** | 0.81 | **0.81** |
| 240.00 | 3.35 | **3.35** | 2.02 | **2.02** | 0.90 | **0.90** |

# Model Speak (Continued)

**Table 2. Corrected drawdowns using equation (3). Aquifer thick-ness = 26 ft. T = 151,002 gpd / ft; S = 0.249 (USDI, 1981).**

| Time (min) | r = 30 ft | r = 60 ft | r = 120 ft |
|---|---|---|---|
| 4.00 | 0.19 | 0.00 | 0.00 |
| 6.00 | 0.35 | 0.02 | 0.00 |
| 8.00 | 0.50 | 0.04 | 0.00 |
| 10.00 | 0.62 | 0.08 | 0.00 |
| 15.00 | 0.88 | 0.17 | 0.00 |
| 20.00 | 1.09 | 0.27 | 0.01 |
| 25.00 | 1.25 | 0.38 | 0.02 |
| 30.00 | 1.39 | 0.47 | 0.04 |
| 35.00 | 1.51 | 0.54 | 0.05 |
| 40.00 | 1.62 | 0.62 | 0.07 |
| 45.00 | 1.71 | 0.67 | 0.10 |
| 50.00 | 1.79 | 0.75 | 0.12 |
| 55.00 | 1.87 | 0.83 | 0.15 |
| 60.00 | 1.94 | 0.88 | 0.18 |
| 70.00 | 2.07 | 0.98 | 0.21 |
| 80.00 | 2.18 | 1.09 | 0.27 |
| 90.00 | 2.29 | 1.17 | 0.32 |
| 100.00 | 2.38 | 1.25 | 0.37 |
| 110.00 | 2.46 | 1.32 | 0.43 |
| 120.00 | 2.53 | 1.38 | 0.47 |
| 150.00 | 2.72 | 1.56 | 0.59 |
| 180.00 | 2.88 | 1.71 | 0.69 |
| 210.00 | 3.01 | 1.84 | 0.80 |
| 240.00 | 3.13 | 1.94 | 0.88 |

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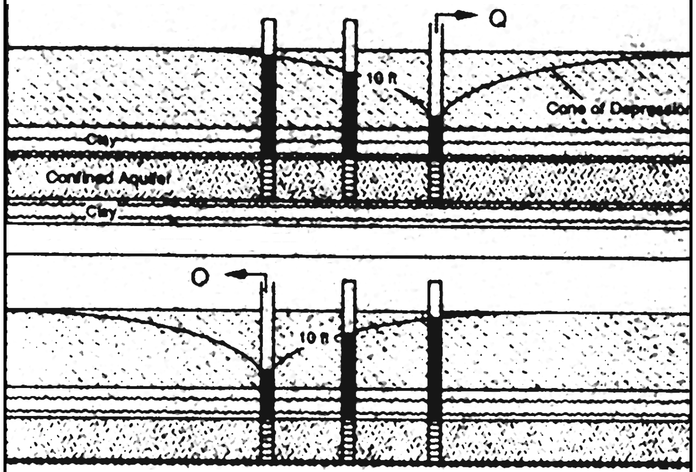
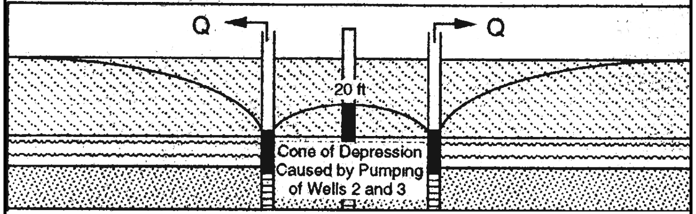
### Predicting Well Interference Drawdown for Wells in Confined Aquifers

Well interference drawdown occurs where cones of depressions from two or more pumping well intersect at some observation point. For wells tapping confined aquifers, well interference drawdown results from an additive process. The drawdowns for each production well, that would have occurred in isolation at some observation point, are added together to determine the well interference drawdown when the same wells are discharging ground

**Figure 2. Well interference drawdown in a confined aquifer.**

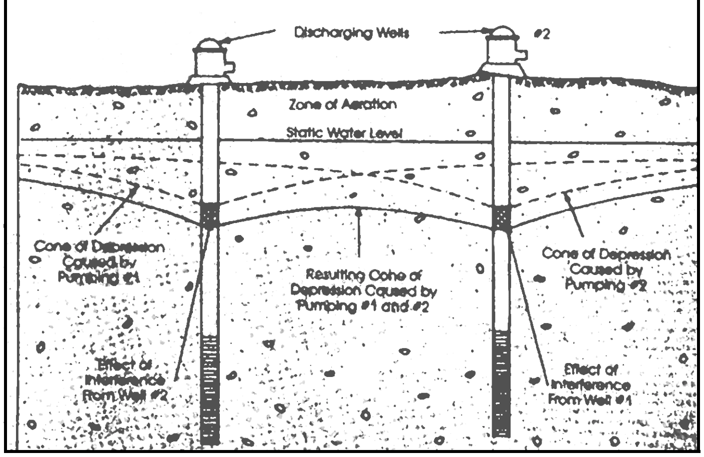


Well 3 pumping and Well 2 remains idle.



Both Wells 2 and 3 pumping at the same time with intersecting cones of depression. Drawdowns within the area of intersecting cones are additive for confined aquifers. Within this area, at required observation points, drawdowns must be added together in order to determine the total drawdown. Notice that the confined aquifer thickness does not change.

**Figure 3. Well interference drawdown in an unconfined aquifer. Although not intuitive, dewatering drawdown must be considered in order to estimate the total drawdown ($s - s' + s_d$). Equation (10) can be used to solve this problem (source: USGS).**



# Model Speak (Continued)

*(Continued from page 11)*

water at the same time (Fig. 2). The following example demonstrates this argument:

1) Production wells 2 and 3 are located at known distances from production well 1. The observed drawdown in production well 1, due to production well 2 pumping at some constant rate, is 10 ft. All other wells are idle. When production well 3 is pumping at some constant rate and all other wells are idle, the observed drawdown in production well 1 is again 10 ft.

2) Well interference drawdown in production well 1, when both production wells 2 and 3 are pumping at the same time, is the sum of drawdown produced by each well, which is 10 ft + 10 ft = 20 ft.

**Predicting Well Interference Drawdown for Wells in Unconfined Aquifers**

Total well interference drawdown for wells tapping unconfined aquifers is not so intuitive, because dewatering reduces the aquifer's saturated thickness. When two or more wells are discharging ground water from an unconfined aquifer, the predicted additive drawdown is always an estimate-in-error of the actual drawdown. The quadratic solution must be completed in order to gain a correct value. The solution is quite simple when using equation (10). Only one additional step is required as follows:

i) Determine the confined drawdown or correct the field drawdown to a confined drawdown using equation (3) for each production well pumping ground water in isolation. In either case, you must determine a confined drawdown produced by each well for an observation point (as before).

ii) Determine a resulting sum for these confined drawdowns (as before).

iii) Use this resulting sum with equation (10) to determine total unconfined well interference drawdown at the observation point ($s = s' + s_d$). The aquifer thickness must be known (Fig. 3).

1) Production wells 2 and 3, constructed in an unconfined aquifer, are located at known distances from production well 1. The corrected confined drawdown measured from production well 1, due to production well 2 pumping at a constant rate, is 9.5 ft. All other wells are idle.

When production well 3 is pumping at a constant rate and all other wells are idle, the corrected confined drawdown measured from production well 1 is 25.5 ft.

2) The total theoretical (corrected to confined) well interference drawdown, in production well 1, when production wells 2 and 3 are pumping ground water at the same time, is the sum of 9.5 and 25.5 ft, which is equal to 35 ft.

3) Now use equation (10) to determine total unconfined well interference drawdown. Aquifer thickness = 100 ft.

$$s = b\left(-1 \pm \sqrt{1-\left(\frac{2s'}{b}\right)}\right) = 100ft\left(1-\sqrt{1-\left(\frac{2(35ft)}{100ft}\right)}\right) = 45.2 \qquad 10$$

This is the same result as reported by Lehr (1964), only completed in a much simpler fashion.

To determine the dewatering component of drawdown use equation (11)

$$s_d = s - s' = 45.2\ ft - 35.0\ ft = 10.2\ ft. \qquad (11)$$

To summarize, total unconfined well interference drawdown in production well 1, when production wells 2 and 3 are pumping ground water at some constant discharge, should be 45.2 ft. The drawdown due to dewatering, when considering this well interference problem, is 10.2 ft. This too is the same result as reported by Lehr (1964) (Table 3). If we would have solved unconfined drawdowns for production wells 2 and 3 on an individual basis and then summed up these drawdowns, the total drawdown in production well 1 would have been underestimated at 40 ft. Therefore it is important to note: the theoretical confined drawdowns for each production well must first be added to determine a sum total, before using equation (10), or a large error may result (in this case over 5 feet of drawdown!).

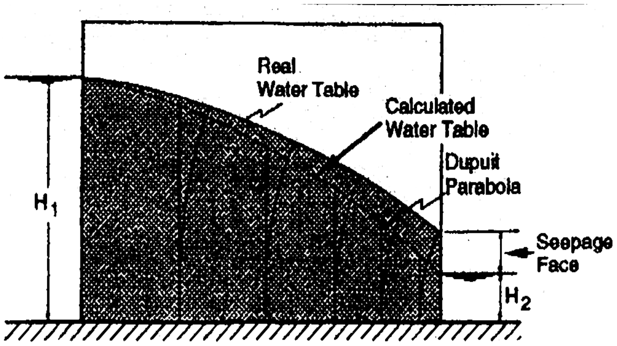
**Table 3. Comparing Lehr's and the authors' quadratic solutions. Aquifer thickness = 100 ft.**

| Well ID: At some distance from PW 1 | Drawdown (ft) |
|---|---|
| PW 2 (corrected using equation (3)) | 9.5 |
| PW 3 (corrected using equation (3)) | 25.5 |
| Total Well Interference Drawdown as if the aquifer were confined (s')——> | 35.0 |
| Lehr's Long Quadratic Solution for (s) | 45.2 |
| Authors' Simplified Quadratic Solution for (s): Equation (10) | 45.2 |

# Model Speak (Continued)

Assumptions: As previously indicated, unconfined delayed yield drainage must have dissipated or be negligible in order to use equation (10). In addition, because equation (10) is based on Jacob's correction for dewatering, which is dependent upon the Theim solution and the Depuit assumptions, this equation should not be used to predict drawdown near a seepage face. If used to predict drawdown near a seepage face, realize that the predicted drawdown is less than the actual value (Fig. 4).

**Figure 4. Unconfined ground-water flow and the Dupuit Parabola (modified from Vukovic and Soro, 1997).**



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* * *

# WGWA Area Meetings and Area Coordinators

## North Central Meeting
## August 14, 2001

The North Central WGWA breakfast meeting was held on August 14, 2001 at the Best Western Midway Hotel in Wausau. Nine people were in attendance. The meeting sponsor was Layne-Northwest, Schofield. Thank you Layne-Northwest!

Mr. Bill Cronk of Layne-Northwest, Pewaukee, gave a presentation on “Drilling Technologies,” specifically those associated with environmental exploration and sampling. Due to most of us being unfamiliar with dual tube drilling technology, Mr. Cronk spent the majority of his presentation describing the benefits of this drilling method – of which there are many. Bill also provide an introduction to some interesting downhole geophysical and video methods capable of providing 3D images of fracture orientation (come to our February 12, 2002 meeting to learn more!). Please feel free to contact Layne-Northwest to help determine the technology that is best suited for your specific project needs.

The North Central Unit has decided to move our meeting schedule from bi-monthly to quarterly meetings. Our next meeting will be on November 13, 2001 at the Best Western Motel in Wausau. Meetings during 2002 are scheduled for February 12, May 14, August 13, and November 12, 2002.

At this time, we have tentatively scheduled speakers for our November 13, 2001 (Earth Tech and Regenesis, "Accelerating Natural Attenuation of Chlorinated and Non-chlorinated Hydrocarbons in Groundwater") and February 12, 2002 (Layne-Northwest, Downhole 3-D logging) meetings. We are requesting volunteers to sponsor our May 14, August 13, and November 12, 2002 meetings. Meeting sponsors typically are responsible for arranging a speaker of their choice to present a topic of interest at our meetings. If interested in sponsoring a future meeting, please contact me at 715-342-3022 or mark_strobel@earthtech.com. Field trip presentations of your facility or project would be especially welcome.

*Mark Strobel, Earth Tech, Inc.*

### WGWA Area Coordinators

Western Area (LaCrosse, Black River Falls, Eau Claire, Chippewa Falls and surrounding area) — Position Open

Southern Area (Madison, and surrounding area) — Position Open

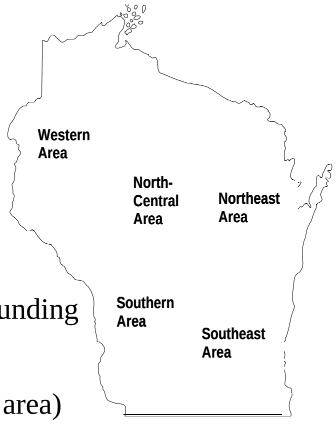
North Central Area (Stevens Point, Wisconsin Rapids, Wausau, Rhinelander and surrounding area)

| | |
|---|---|
| Tod Roush | 715.845.4100; troush@maximusa.com |
| Mark Strobel | 715.342.3022; mark_strobel@earthtech.com |

Northeast Area (Green Bay, Appleton, Oshkosh, Fond du Lac and surrounding area) — Position Open

Southeast Area (Milwaukee, Sheboygan, Racine, Kenosha and surrounding area)

Scott Brockway 262.821.5894, ext. 232; brockws@ttemi.com



# Treasurer's Report

**Account Summary**
**Wisconsin Ground Water Association**
**April 2001 to June 2001**

| | | | |
|---|---|---|---|
| **Beginning Balance** | | | **11786.59** |
| **Ending Balance** | | | **13182.43** |
| **DEPOSITS** | | | |
| 2001 Membership Dues | | 2085.00 | |
| 2001 Field Trip | | 1405.00 | |
| Total Deposits | | 3490.00 | |
| **WITHDRAWALS** | | | |
| Winter 2001 Newsletter | | | |
| | Word Processing | 300.00 | |
| | Printing | Paid in March, $450 | |
| | Postage | 52.60 | |
| Spring 2001 Field Trip | | | |
| | Horicon Marsh Ed. Fund | 200.00 | |
| | Bus Service | 176.25 | |
| | Pontoon Boat | 216.00 | |
| | Reserve Boat | 50.00 | |
| | Food | 414.02 | |
| | Pavilion | 25.00 | |
| | ECCI Printing Services | 135.75 | |
| | (Best Buy color printer cartriges and Kinkos) | | |
| General | | | |
| | Postage- Ayres Associates | 44.54 | |
| | NetStream | 480.00 | |
| Total Withdrawals | | 2094.16 | |

# Board Meeting Minutes

**5:00 PM, Tuesday, August 14, 2001**
**Desert Rose Board Room, Kalahari Resort and Convention Center**
**Wisconsin Dells, Wisconsin**

Persons present: Margy Blanchard, Boyd Possin, Lori Rosemore, Kristen Gunderson (via phone), Kevin Olson, Jeff Hosler, and Bruce Hensel. Shaili Pfeiffer of the Wisconsin Academy of Sciences, Arts and Letters joined at 6:30pm.

1. Call to order about 5:05 pm.
2. Last meeting minutes - E-mailed out to everyone by Kristen after the last meeting. The minutes from the April meeting were approved via e-mail and were included in the last WGWA newsletter. The minutes from this meeting will be approved that same way.
3. Treasurer's Report - $11,786.59 in account as of June 2001. $2,094.16 in total withdrawals from April to June including $400 in payouts for word processing and webpage updates, $52.60 in postage and $450 in printing for the newsletter, and costs associated with the spring field trip. A total of $2,085 was received in 2001 dues and $1,405 in field trip fees. Margy moved to pay $100 to pay for a field trip photo CD collage, Lori seconded, passed 4-0.
4. Membership Report – As of August 1, 2001 - 296 are paid for the current year, including 25 new members.
5. Old Business

a. Newsletter production. Review of duties and responsibilities per the bylaws to maintain timely publishing schedule. Editor reports to the Secretary and the Secretary is responsible for the production of the newsletter. Margy, Wayne, and Deb spoke about why there have been delays in sending the newsletter out. It appears that there are problems in getting reports from the officers (President's Message, meeting minutes, Treasurer's report), getting the mailing list, and getting payment for the ads. We need to better define responsibilities. Secretary will coordinate soliciting ads for the Fall 2001 Newsletter and beyond (consultants and vendors). Please e-mail Kristen the names of the firms you are contacting to avoid multiple solicitations. During the next week, Margy will contact the firms that advertised in the past year to see if they are interested – they can get the rest of 2001 and all of 2002 for the price of 1 year.

b. WGWA Policy on announcing meetings of other organizations – Boyd sent out an e-mail survey. 80-85% would like to receive these notices via *WGWA Notes.* Those who wanted to receive the notifications were evenly split as to whether to send out such notices from for-profit entities only if a decrease is offered in the course fee to WGWA members. The decision: *WGWA Newsletter* notices will be free if WGWA is co-sponsoring, but, if WGWA is not co-sponsoring it must be a paid ad. *WGWA Notes* will be sent out for non-profits and for for-profit groups that offer WGWA member discounts.

c. Midwest Ground Water Conference Update – The Midwest Ground Water Conference meeting will be held October 22 – 24, 2002 at the Inn on the Park in Madison. WGWA is co-sponsoring this event and has agreed to organize vendors. Margy is handling identifying and coordinating the vendors.

d. Regional meetings – how to invigorate them? This issue was discussed while we discussed the mechanism for WGWA to provide input to the Waters of Wisconsin effort. See below

e. Joint spring meeting with AWRA. Margy has been talking with Mike Lemcke, President of AWRA to schedule a joint meeting in March 2002. This will replace what would have been the normal 2001 WGWA Fall Technical Conference.

6. New Business

a. Election of 2002 Officers – WGWA bylaws state that officers serve a calendar year. Normally votes are counted at the Fall Technical conference. This year we will not be holding a fall conference. Therefore, balloting will have to be done separate from a meeting. We discussed having a separate

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mailing of ballots in an attempt to increase the number of ballots that are returned. The President-Elect (Boyd) is responsible for identifying the candidates for 2002. We need to find two candidates for President-Elect. Lori will be completing her second year as treasurer. She is undecided at this point about running for a second two-year term. At least one additional candidate for treasurer will be needed. We determined that candidates must be identified by November 1 and the voting should be completed by November 30, 2001.

b. Ground Water Summit participation by WGWA – The Ground Water Summit will be held October 30 and 31. Boyd is representing WGWA. The Wisconsin Groundwater Coordinating Council (GCC) is organizing the Summit. The purpose of the Summit is to bring together a broad representation of ground-water users and stakeholders to discuss current issues facing ground-water protection and management and to develop ideas and solutions to better protect Wisconsin's ground-water quality and quantity. These solutions could encompass educational efforts, research needs, data management, institutional needs, as well as policy recommendations. It is hoped that the discussion and materials developed as a result of the Summit will assist and guide State agencies, the university system, and the GCC in carrying out ground-water protection programs. More information on the Summit can be found at the GCC's web site: http://www.dnr.state.wi.us/org/water/dwg/gcc/.

c. The Waters of Wisconsin Project participation by WGWA - Shaili Pfeiffer of the Wisconsin Academy of Sciences, Arts and Letters (a private, non-profit organization) joined the group at 6:30 pm to discuss the Waters of Wisconsin Project and how WGWA may contribute to that effort. The project is expected to have the following products: a report (issues of sustainability, ground-water use principles, characterization of Wisconsin's waters, scenario analysis for the future) and October 2002 statewide forum (part of the Academy's Fall Forum). Also holding a series of committee meetings throughout the state (2nd one to be held in LaCrosse in September) with a public form in the evening the day of the meeting. Could incorporate environmental consulting into one of the public forum sessions. Led to an open discussion about various ground-water issues in Wisconsin. Board suggested that WGWA regional groups could each provide an abstract/brief entitled, "The Lost Resource – What to do about Contaminated Ground Water?" The regions each would be able to provide a unique perspective on this question. This will give the regional groups a concrete issue to focus on that hopefully will help reinvigorate the regional meetings. Boyd will contact the WGWA area coordinators to help set up the sessions. The meetings, to be held in September on dates yet to be determined, will be announced via *WGWA Notes*.

The meeting was adjourned at 8:40 p.m.

## New Arsenic Standard

In October 2001, the Bush administration announced that it will accept a new arsenic standard for drinking water. Christie Whitman (United States Environmental Protection Agency Administrator) said the decision will reduce the maximum concentration of arsenic allowed in drinking water from the current 50 parts per billion (ppb) to 10 ppb by 2006.

# Analytical Methods

## Selecting Analytical Methods for the Determination of Oxygenates in Environmental Samples and Gasoline

By I.A.L. Rhodes and A.W. Verstuyft

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### *Demand for analyses is higher, but are the methods reliable?*

Alcohols and ethers are added to gasoline to comply with air emission regulations in certain parts of the country and as octane enhancers. The most widely used oxygenate is methyl t-butyl ether (MTBE), which accounts for more than 85% of oxygenate usage. Oxygenates also include other ethers and alcohols. Oxygenates have significant water solubility, particularly the alcohols which are infinitely soluble in water. When oxygenated fuels are released to the environment they may pose a threat of groundwater contamination. Some oxygenates are relatively refractory to degradation and are difficult to treat once the aquifer has been impacted. There is a growing regulatory concern about oxygenates, and a growing demand for analytical methods to detect these types of compounds in the environment.

Laboratories have expanded existing U.S. Environmental Protection Agency (EPA) methods used for the determination of benzene, toluene, ethylbenzene and xylenes (BTEX) to include oxygenates. These methods rely on purge-and-trap (P&T) or headspace (HS) gas chromatography (GC) using photoionization (PID) or mass spectrometry (MS) detection. The adequacy of EPA methods for the determination of highly water soluble ethers and infinitely soluble alcohols has come under scrutiny because these EPA methods were not developed and their performance has not been formally validated for the determination of these types of compounds. In addition, no formal assessment has been done related to sample preservation and sample preparation issues.

The critical issue is the potential misidentification of oxygenates in environmental samples containing a gasoline-type matrix. Due to a lack of performance data, the reliability of the methods to accurately measure all oxygenates of interest is in question. Because of the widespread misconceptions associated with referring the "EPA methods," and the failure to distinguish between preparation methods and determinative methods, the method discussions should be in terms of the analytical techniques used rather than EPA method numbers. The use of EPA method numbers to refer to determinative methods misleads some to think that the use of the method was somehow sanctioned by EPA for these analytes. Neither the EPA 8000 methods nor the 5000 series prep methods have been validated by EPA for application to oxygenates. The analytical process should not simply refer to "8021" (which does not specify the sample prep method). The quality assurance project plan (QAPP) or report should refer to a "5030 purge-and-trap, 8021 GC-PID method" process or sequence.

This article addresses the current status of oxygenate analysis in environmental samples and fuels, including information about the expected performance when using EPA methods; advantages and disadvantages of different methods, and cost-effective recommendations for meeting data quality objectives.

### *History and Regulations*

A brief summary of the history and use of MTBE, regulations pertaining to MTBE as a gasoline oxygenate and proposed health advisory limits for MTBE in groundwater is useful for the environmental laboratory. The primary source of MTBE in the environment is believed to be transportation, storage and use of oxygenated gasoline. Data on oxygenates other than MTBE is not readily available.

Methyl t-butyl ether, or methyl tert-butyl ether, is a synthetic chemical commonly known as MTBE. MTBE is mixed with gasoline for use in reformulated gasoline (RFG). It is a liquid generally made by combining the chemicals isobutylene and methanol. MTBE was developed in the 1940s; however, it was not commercially produced until the 1970s. MTBE was used

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commercially for the first time in Europe as a gasoline blending component. It was first introduced in the 1980s in the United States as an octane booster to replace alkyl lead additives. In areas in which there is nonattainment of federal Clean Air Act (CAA) standards for air pollutants such as carbon monoxide, the EPA requires the use of oxygenated additives such as MTBE or ethanol as a cleaner burning oxygenating agent during the winter months. The use of other oxygenates is not as well documented.

Gasoline without deposit control additives (typically proprietary to each major oil company) is exchanged or traded among producers to meet contract and demand requirements, as well as to improve transportation logistics. As a result of exchange agreements, a producer may sell a competitor's gasoline that contains different ethers than the producer would add at its own refinery. Thus, an individual oil company's oxygenate use may not be indicative of the oxygenates present in fuel at that company’s station.

MTBE is regulated under the CAA; the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); and the Emergency Planning and Community Right-to-Know Act. It is regulated by the EPA's Offices of Water, Solid Waste, and Emergency and Remedial Response. It is also regulated by the Consumer Product Safety Commission with consumer product limits. In 1990, Congress passed amendments to the CAA that required gasoline to meet a minimum oxygen content requirement, through the addition of oxygenates such as MTBE or ethanol. This minimum oxygen content requirement was designed to lower exhaust pollutants in the worst ozone- and carbon monoxide-contaminated areas. In 1992, gasoline with up to 15% MTBE content by volume was used nationally to meet the first federally mandated wintertime reduction of carbon monoxide. MTBE is blended at 11% in most gasoline sold in California after October 1992.

The state of California has led the way in developing regulations related to MTBE. For example, California's Department of Health Services (DOHS) promulgated, based on taste and odor concerns, an enforceable secondary drinking water maximum contaminant level (MCL) of 5 mg/L for MTBE. DOHS will shortly promulgate a primary human-health-based MCL that will likely be close to the California Office of Environmental Health Hazard Assessment's (OEHHA) public health goal of 13 mg/L MTBE. EPA has suggested, based on taste and odor concerns, a consumer acceptance level of 20-40 mg/L, but has set no MCLs. California is also developing a public health goal for tertiary-butyl alcohol (TBA); however, only one health study exists on which to base this goal. An expedited preliminary assessment by OEHHA in June 1999 suggested that this study would result in a public health goal of 12 mg/L. OEHHA is also charged with performing a health risk assessment of using ethanol in gasoline in 1999.

Most recently, California has established a ban on MTBE, which is slated to begin on December 31, 2002. However, since the state regulators did not get former EPA Administrator Carol Browner's signature on the MTBE waiver, it is not clear from a regulatory standpoint whether there now exists an issue between state and federal regulations for oxygenates. This ban reflects a current drive away from MTBE and toward ethanol, although there are still some concerns about ethanol as an oxygenate.

The other regulatory change in California that directly affects the use of analytical methods is that the state's water boards are now requiring that Method 8260 is run on all samples, which is a significant change from a few years ago. It is also a significant change from the American Petroleum Institute (API) recommendation, which had been to run Method 8260 on one sample per set or per site to confirm presence or absence of MTBE. However, this new requirement by California Los Angeles Regional Water Quality Control Board is driving toward using Method 8260 for all MTBE analyses.

### *What Are MTBE and Other Oxygenates?*

Gasoline and other fuels are derived from petroleum and are primarily composed of compounds containing only carbon and hydrogen atoms. Oxygenates are compounds that contain oxygen atoms in addition to carbon and

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hydrogen. They can be synthesized from petroleum derivatives or plant matter. Oxygenates are added in relatively large concentrations (>5%) and as such are considered to be *blend components* of gasoline. Oxygenates can be added as a high purity chemical, or as a technical grade chemical with traces of other ethers and alcohols. MTBE is the predominant oxygenate in current use; however, other oxygenates are used to meet reformulated gasoline standards.

Since 1995, federal law requires year round addition of oxygenates to gasoline in nine regions of the nation with the worst ozone conditions. The resulting cleaner-burning "reformulated" gasoline (RFG) may not have less than 2% oxygen by weight. MTBE is blended into gasoline in proportions ranging from 11% in RFG to 15% in oxyfuel. MTBE is blended into 31% of all U.S. gasoline and into every gallon of gasoline sold in major California cities. The relative composition of oxygenate is variable and not indicative of any one refiner or distributor.

| Alcohol | CAS No. | Molecular Weight, g/Mole | Water Solubility, mg/L | Henry's Law Constant (Dimension-less) |
|---|---|---|---|---|
| Methanol | 67-56-1 | 32 | Infinitely Soluble | ~1E-4 |
| Ethanol | 64-17-5 | 46 | Infinitely Soluble | ~2E-4 |
| t-Butanol (TBA) | 75-65-0 | 74 | Infinitely Soluble | ~5E-4 |

*Table 1. Alcohols used as blend components.*

Alcohols and ethers are the two classes of oxygenates that may be found in gasoline. Analytical methods for these classes differ because of differences in water solubility and mobility.

Alcohols are a broad class of organic compounds containing a hydroxyl (-OH) functional group. Alcohols can be obtained from plant matter or synthetically from petroleum derivatives. They have many uses, such as in organic synthesis as solvents, and in the manufacturing of detergents, pharmaceuticals, foods, plasticizers and fuels.

| Ether | CAS No. | Molecular Weight, g/Mole | Water Solubility, mg/L | Henry's Law Constant (Dimensionless) |
|---|---|---|---|---|
| Methyl Tertiary-Butyl Ether | 1634-04-4 | 88 | ~40,000-50,000 | ~2E-2 to 12E-2 |
| Diisopropyl Ether (DIPE) | 108-20-3 | 102 | ~2,000-9,000 | ~20E-2 to 40E-2 |
| Ethyl Tertiary-Butyl Ether (ETBE) | 637-92-3 | 102 | ~8,000 | ~11E-2 |
| Tertiary-Amyl Methyl Ether (TAME) | 994-05-8 | 102 | ~20,000 | ~5E-2 |

*Table 2. Ethers used as blend components.*

Alcohols used as blend components are listed in Table 1. These low molecular weight alcohols are highly soluble in water. They cannot be added to gasoline at the refinery because of the potential to be subsequently extracted and phase-separated through water contact in storage tanks and pipelines. Alcohols are typically added at the distribution terminal or truck rack before shipment to the service station by "splash" blending.

Ethers are a class of organic compounds in which an oxygen atom is interposed between two carbon atoms: C-O-C. They can be made from petroleum derivatives and are widely used as industrial solvents. The ethers that have been used as blend components, such as tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE) and diisopropyl ether (DIPE), are listed in Table 2. These ethers are partially soluble in water and are added at the refinery.

**What Are the Commonly Used Analytical Methods for the Determination of Oxygenates in Gasoline?**

Analytical methods for the determination of alcohols and ethers in gasoline include well-established American Society of Testing Materials (ASTM) procedures, as well as adapted EPA methods. While EPA and ASTM methods have not been validated for the determination

(Continued on page 21)

# Analytical Methods (continued)

*(Continued from page 20)*

of oxygenate compounds in environmental samples, the following are methods used to determine oxygenates in gasoline:

- *ASTM D4815.* A multidimensional GC/FID method for the determination of MTBE, ETBE, TAME, DIPE, TBA, and $C_1$ to $C_6$ alcohols in gasoline. The quantification range of this method for individual ethers is 0.1 to 20 mass percent and for individual alcohols is 0.1 to 12 mass percent. This method is the alternative method for oxygenate analysis of federal RFG (40 CFR 80.46), and the designated reference method for California Phase II RFG.

- *ASTM D5599.* A capillary column GC and oxygen flame ionization detection (OFID) method for the determination of MTBE, ETBE, TAME, DIPE, TBA, and $C_1$ to $C_5$ alcohols in gasoline. Only oxygen-containing compounds are detected by OFID. The quantification range of this method for oxygenates is 0.1 to 20 mass percent. Commercial and refinery laboratories commonly use this ASTM version of the federal RFG method (40 CFR 80.46) to analyze RFG.

- *ASTM D5769.* A GC/MS method for benzene, toluene and total aromatics in finished gasoline. This is a detailed, interlaboratory-validated version of the EPA method for reformulated gasoline (40 CFR 80.46). This method has been used by the EPA in the ASTM Reformulated Gasoline Interlaboratory Crosscheck Program for oxygenate analysis although it has not been validated for oxygenates.

- *Detailed Hydrocarbon Analysis by GC/FID-ASTM D 5134.* This method uses 30-meter to 60-meter capillary columns to analyze oxygenates in complex gasoline mixtures or naphthas.

- *EPA SW846 Methods 8240C/8260B.* It is difficult to detect oxygenates directly in a gasoline matrix without dilution. Typically, the best reporting limit is around 0.01 to 1 percent for the ethers and about 0.1 to 20 percent for TBA. This method has not been validated for fuels and its use should be highly discouraged because of the multiple dilutions needed to bring the sample into the calibration range and the complex matrix of the sample.

## *What Are the Commonly Used Analytical Methods for the Determination of Oxygenates in Environmental Samples?*

Oxygenates such as MTBE are primarily regulated by EPA under the Clean Air Act for fuels and modified for specific use by the states. They have not been targets of EPA methods as written, with the exception of MTBE in Method 524.2. However, methods have been expanded to include some of the oxygenates. These include EPA methods using P&T-GC/PID (Methods 8021B/8021A and 602) and EPA methods using P&T-GC/MS (Methods 8260A/8240B, 624, and 524). Although EPA Method 8015 which is based on GC/FID has been used for MTBE analysis, it should be noted that the state of California issued a memorandum on Oct. 21, 1999, which stated that analysts cannot use the method to quantitate individual oxygenate compounds. As such, EPA Methods 8260 and 8021 are the preferred methods. The memo stated that on most chromatographic columns MTBE comes off before the volatile range organics and will not be included in the volatile range result. Other oxygenates, such as TAME and DIPE, will co-elute with the volatile range organics. Certainly, in California, this will change the approach of conducting a combined 8015/8021 for gasoline BTEX, and will likely result in laboratories solely using Method 8260 as total petroleum hydrocarbons (TPH) volatile and BTEX/MTBE as the standard.

| Current Promulgated SW-846 Method | Technology Basis | Other Comparable EPA Methods | Selectivity |
|---|---|---|---|
| 8015 | FID | None | Poor |
| 8021 | PID | 8020, 602, 502.3 | Good |
| 8260 | MS | 8240, 624, 524.2, 1624 | Excellent |

*Table 3. EPA methods.*

Another related issue is that these methods need to be validated for the oxygenates using SW-846 3rd Edition,

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Update III, 1296, Method 3600C, Section 8. This is significant for all of us in the regulated community and the commercial laboratories, because we all use these methods as if they were validated and they are not. As it stands now, EPA's position is that methods are for guidance and that it is the user's responsibility, both the commercial laboratory and the customer, to make sure the method results in technically sound data. As such, it is important to remember that the users need to run multiple samples at multiple concentrations, make sure there aren't matrix effects, and use the Update III criteria for validation of methods.

### *Oxygenates in Environmental Samples: Method Performance*

Limited data have been published by EPA and other researchers indicating that oxygenates are potentially measurable by three SW-846 methods: 8015, 8021 or 8260. This discussion addresses the latter two methods from the most recent promulgated version of SW-846, EPA's methods manual for the RCRA program. Table 3 lists other EPA methods that are technologically comparable to the two discussed here.

These two methods are comparable in terms of sensitivity, accuracy and precision. Method 8021, using GC/PID, tends to be lower in price. Method 8260, a GC/MS method, is generally recognized as more selective, but higher in price. Selectivity or specificity is a term used to describe how well a given technique can provide accurate identification; the ability to unequivocally identify the analyte in the presence of other components that may be also expected to be present. A nonselective method will respond universally to many compounds, and thus is prone to false positive results in the presence of interferences. Method 8021 provides identification based on retention time/elution time, and quantitation is based on signal of standards. The potential problem with the method is that coelutions with hydrocarbons in gasoline may arise. Method 8021 is selective for aromatic compounds but can respond to other compounds, including branched alkanes and olefins. Method 8260 is highly selective, providing a unique identification pattern--the mass spectrum--for virtually any compound (except isomers). It provides identification based on retention time/elution time and qualifying ions. Quantitation is based on a single ion after qualifying criteria are met.

| EPA Method | Matrices | Technology Basis |
|---|---|---|
| 5030 | Water, Methanol Extracts of Soil | Purge-and-Trap |
| 5031 | Water, Aqueous Leachates of Solids | Azeotropic Distillation and Direct Aqueous Injection |
| 5035 | Soil | Closed System Purge-and-Trap |
| 5021 | Soil or Water | Headspace |

*Table 4. Sample preparation methods applicable to oxygenates.*

| | | Accuracy (%) at Spiking Level | | |
|---|---|---|---|---|
| Analyte | MDL, mg/L | 25 mg/L | 100 mg/L | 500 mg/L |
| Methanol | 38 | 50 ± 36 | 46 ± 22 | 49 ± 18 |

*Table 5. Performance of EPA Methods 5031/8260 for oxygenates.*

| Compound | Detection Limit, mg/L | Accuracy, as Recovery, % | Precision, % |
|---|---|---|---|
| MTBE | 0.06 | 97 | 2.5 |
| ETBE | 0.20 | 100 | 1.8 |
| TAME | 0.20 | 97 | 2.1 |

*Table 6. Performance of EPA Methods 5030/8260 for oxygenates.*

With regard to verifying results for these two methods, the analyst's options are reduced if GC/PID is used. The analyst may reanalyze or resample, or using a second column confirmation may help. If the GC/MS method is used, the analyst can check the MS, look at ion ratios and, as a last resort, may reanalyze or resample.

Analyses using any of these three methods must be performed in conjunction with proper sample preparation procedures. Table 4 summarizes the sample preparation methods for measuring oxygenates. To fully describe the method used, both the sample preparation and analytical method must be specified. For example, Methods 5035/8260 would be a closed system purge-

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and-trap with GC/MS detection. Note that the sample preparation methods are not applicable to air samples. EPA has published no validation data except for Method 5031, used in conjunction with Methods 8015 and 8260.

Data for methanol using Methods 5031/8260 are summarized in Table 5. The U.S. Geological Survey (USGS), using Methods 5030/8260, has published the data in Table 6.

### *Emerging Sampling and Analytical Techniques*

There are some newer sampling and analytical methods or newer applications of existing methods that are now coming to the fore with regard to MTBE and other oxygenate analyses. These include solid-phase microextraction (SPME), direct aqueous injection (DAI) into the GC/MS, membrane introduction mass spectrometry (MIMS) and cryofocusing.

*SPME.* While this technique isn't used very often for MTBE analysis in the U.S., the Europeans have used it successfully for such analyses in paint industry wastewater samples. The U.S. Coast Guard published a paper in the *Journal of Microcolumn Separations* in 1998, which described a headspace SPME and two-dimensional GC technique as an approach to MTBE analysis. Although there is a potential of loss of sample when using SPME, the argument for using the technique in oxygenate analysis is that for polar materials in water the analyst can easily do SPME followed by GC.

*DAI.* Directed aqueous injection into the GC/MS is allowed by Method 8015 and has been used to analyze methanol in aqueous samples. DAI is very effective for polar compounds such as the alcohols.

*MIMS.* Information on this highly selective, rapid technique has been published in the literature, and although it has not been validated as a method, it may prove to have some interesting applications with regard to the oxygenates. One published paper stated that although MIMS is a rapid, highly selective, solvent-free method, it might be unusable in the direct collection of analytes from complex samples containing solids such as sludge and soil. Since this capability is clearly desirable for analyzing oxygenates, the paper went on to suggest that purging the sample first, followed by MIMS would be a better overall technique.

*Cryofocusing.* It is a technique that is allowed in Methods 8260 and 624, but other than for air monitoring applications, cryofocusing has not been widely used for many years. However, now that regulators want lower and lower detection limits, the combination of purge-and-trap with cryofocusing will allow a bigger sample to be introduced to the analytical column and detector to drive the detection limits down. Cryofocusing involves freezing the sample in liquid nitrogen, and as the analyst purges, he or she can trap the sample from the typical trapping material and then drive that onto the column by removing the liquid nitrogen cooling. The analyst can heat the entire sample all at once, or either eliminate the trap or add onto the trap and collect all the material in the gas phase in a Thermos bottle that has liquid nitrogen in it. The analyst puts a loop of the column in the container, which allows a further concentration of these molecules into a smaller plug of material thus achieving a higher loading than one can with a purge-and-trap sample preparation. It is a commonly used

| Analyte (ppb) | 8020/21 (5 mL/20C) | 8260/60 (5 mL/20C) | D4815a (5 mL/20C) |
|---|---|---|---|
| TBA | 13.9 | 34.9 | 27.4 |
| MTBE | 0.2 | 1 | 1.1 |

*Table 7. Method detection limits in groundwater samples.*

| Analyte (ppb) | 8020/21 (5 mL/20C) | 8260/60 (10 mL/40C) | D4815a (direct injection-ppm) |
|---|---|---|---|
| TBA | 195.5 | 4.6 | 40.8 |
| MTBE | 0.2 | 1 | 43.6 |
| DIPE | 1.6 | 0.3 | 22.6 |
| ETBE | 5.5 | 0.3 | 10.2 |
| TAME | 1.2 | 0.2 | 16.1 |

*Table 8. Method detection limits in groundwater samples (5 ppm gasoline matrix). The typical reporting limit is 0.1% per oxygenate in the NAPL.*

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# Analytical Methods (continued)

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method in the air methods TO3 and TO14 for volatiles and BTEX, and is currently being applied to water and soils.

### *Method Detection and Reporting Limits*

The issue of method detection limits (MDLs) deserves more attention. The MDL as defined in 40 CFR Part 136, Appendix B, states that it is determined by analyzing a minimum of seven replicates of a single low level lab spike by a single analyst. Multiplication of the standard deviation by the Student's t-value at 99% confidence level (statistically derived parameter from analyses of spiked clean water). The concept of the method detection limit has been challenged by the Inter Industry Analytical Group (IIAG) and will be modified by EPA as part of a Consent Agreement.

Reporting limits for MTBE can differ from .5 ppb up to 5 ppb, depending on the lab's sample treatment (cryofocusing vs. traditional P&T), and the lab's application of the 40 CFR 136, Appendix B MDL protocol.

There are newer method detection limit tables published in a Lawrence Livermore National Lab Global Geochemistry Study which show how selected methods perform and some of the issues with method detection limits and practical quantitation limits for oxygenates in groundwater samples (Tables 7 and 8).

### *Performance-Based Methods*

The key issue for EPA SW-846 methods is that *any* method selected for use be able to produce data of known quality that is consistent with the needs of the project driving its collection. Therefore, whether an SW-846 method (or a non-EPA method) is selected for application, whether the method is used as written in an existing, established laboratory standard operating procedure (SOP), or if the existing SOP is modified, the method should undergo a "demonstration of applicability." This demonstration should address any uncertainties that could arise from the interation of analytes, analytical techniques and matrix effects in the context of the decisions the data are intended to support. The greater the impact of those uncertainties on the ability to make defensible decisions, the more work has to be done to control for those uncertainties as part of the demonstration of applicability. Assumptions should be documented and questioned as necessary.

### *Selecting a Method: Ethers and TBA*

Extensive work by the USGS, Lawrence Livermore and many laboratories indicate that the ethers and TBA are measurable using purge-and-trap GC in conjunction with any of the determinative methods (EPA SW-846 Methods 8015, 8021 or 8260). Based on studies of the most widely used oxygenate, MTBE, potential analytical problems exist with Methods 8015 and 8021. identification of MTBE can be caused when other gasoline components are present, due to coelution of MTBE with these components. This misidentification is most pronounced with Method 8015, but is also apparent with Method 8021, which makes it an unreliable method for TBA. Method 8260 is considered adequate.

Thus, while Method 8021 may be cost-effective, the analyst should verify results by Method 8260. As an

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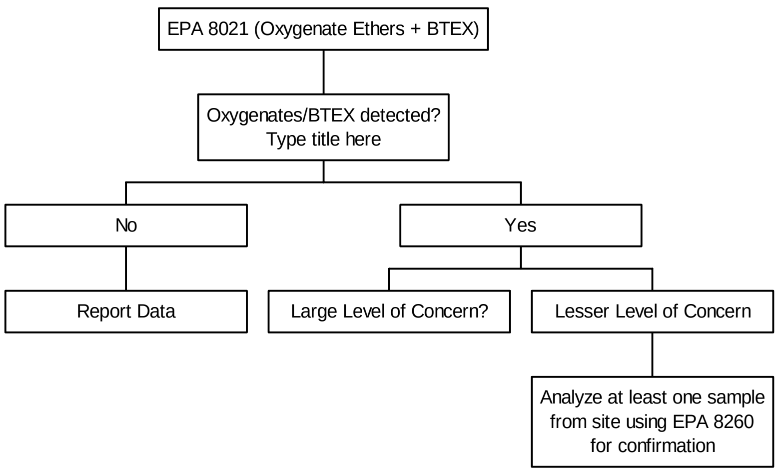
**Figure 1. Choosing an approach to ethers in water samples.**



* This approach may be used for soil and air samples with strict QA/QC.

# Analytical Methods (continued)

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example, the approach shown in the Figure I flow-chart for ethers (MTBE, DIPE, ETBE, TAME) may be used for water samples. This approach may be used for soil and air samples with strict QA/QC.

The conclusions drawn from the Lawrence Livermore National Lab Global Geochemistry Study relative to TBA and ethanol analyses are as follows:

- Method 8021: TBA and ethanol are not recommended as analytes. False positives are common at high TPH concentrations. False positive ether concentrations are typically less than 200 ppb. The method "works" when the ratio of TPH to analyte is less than 15.
- Method 8260 is capable of quantifying all fuel oxygenates tested. TBA sensitivity may be increased by heating purge at 40°C. Ethanol is trickier and thus is best analyzed by direct injection, not P&T. The detection limit for oxygenates in NAPL is approximately 2,000 ppm.
- Modified ASTM 04815/D5599 provide excellent overall analysis of oxygenates, but the drawback is that it is a highly customized method that does not address BTEX or TPH. Only one laboratory is known to provide this analysis for environmental samples. It is the method of choice for NAPL and products with a reporting limit of 0.1%.

The most commonly encountered oxygenates in groundwater appear to be MTBE and TBA. According to a report by Kramer & Douhit (Handex, NJ) presented at the November 2000 Petroleum Hydrocarbons and Organic Chemicals in Groundwater Conference, Anaheim, CA, field experience in New Jersey shows widespread occurrence of TBA with MTBE in groundwater at concentrations that are equal to, or in some cases, exceed the MTBE concentrations. They state that it is not unusual to detect TBA alone in a well (without BTEX or MTBE); however, the opposite is also common.

### *Selecting a Method: Methanol and Ethanol*

Ethanol and methanol, two low-molecular weight, water-soluble alcohols, present even more of an analytical challenge than other oxygenates because they are difficult to analyze at low concentrations. The compounds are not measurable using P&T. Direct aqueous injection by Method 8260, provides ppm-level sensitivity. EPA Method 5031 can be used with Method 8260 to improve sensitivity, but this method shows poor accuracy and is in limited use by laboratories.

In July 2000, the California Regional Water Quality Control Board, Central Valley Region, issued a memo entitled, "Ethanol in Groundwater from Bentonite Pellets," which noted that 21 out of 23 samples taken from newly constructed wells were contaminated with ethanol with a maximum concentration of 1,200,000 ug/L. The contamination was caused by the bentonite pellets used in well construction materials. The pellets are coated with ethanol to slow the rate of hydration when dropped into deep water columns. This problem is a good example of the problems that can be encountered when alcohols, which are present in many types of products, are put in gasoline and their presence in groundwater is automatically (and erroneously in this case) linked to gasoline.

### *Conclusions and Recommendations*

EPA methods have not been validated for the routine measurement of oxygenates in environmental samples. Existing EPA methods are potentially useful for this purpose, and many laboratories have generated internal validation data. Some of the methods in routine use can result in oxygenate misidentification due to interferences from coeluting gasoline components.

The purge-and-trap methods (5030, 5035) can be used for ethers and TBA in soil or water samples. If Method 8015 or 8021 is used, at least one sample per site should be analyzed by Method 8260 to confirm any detectable amounts. Because of the general lack of EPA validation data, laboratories should be requested to provide evidence of their capability to measure oxygenates using any appropriate method. Information on detection limits and recoveries should be provided.

The analysis of environmental samples for methanol and ethanol is more difficult. These compounds cannot be

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# Analytical Methods (continued)

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measured using routine EPA methods. Any analysis requests for these compounds should be carefully considered, and laboratories should provide proof of any stated capabilities.

What should the data user do? First, test the labs from time to time with performance evaluation samples. Then, send at least one or two sets of blind duplicates with each batch. Third, if no historical data exists and you are using Method 8021, confirm at least one MTBE or any other oxygenate hit per site by GC/MS. Finally, for critical data, go straight to GC/MS.

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